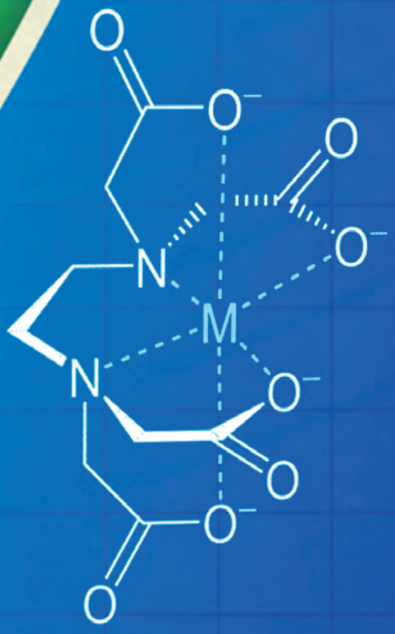
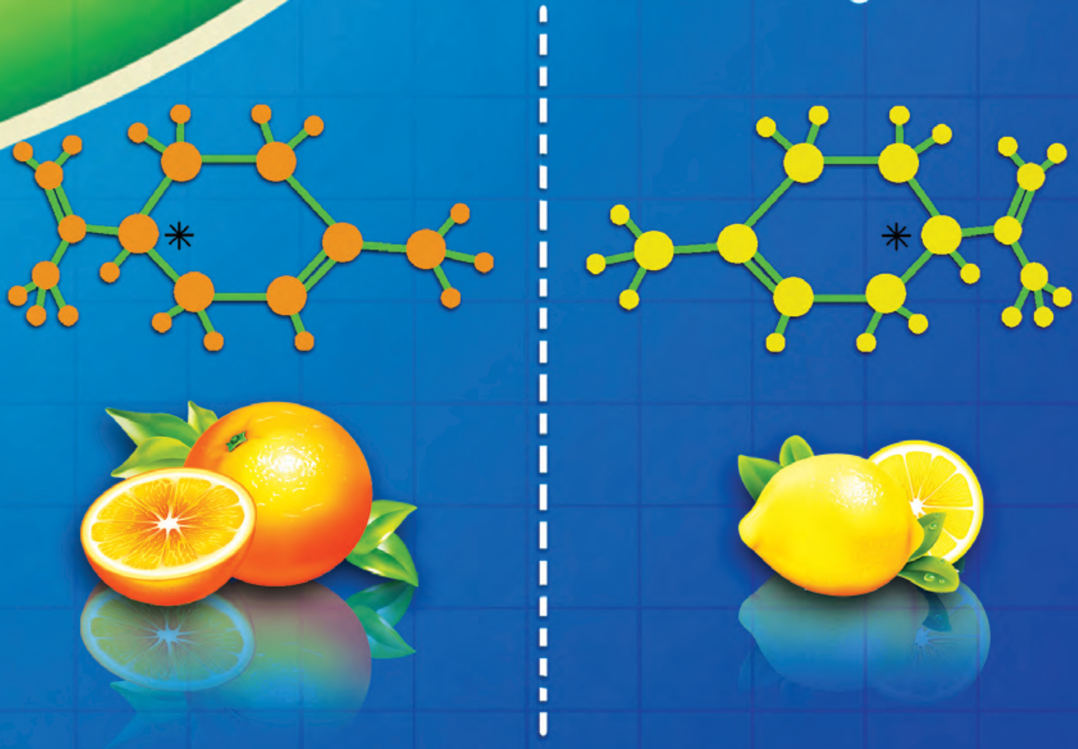
CHEMISTRY

Standard XII





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CHEMISTRY

STANDARD TWELVE

R5W2F5

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2020

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The Constitution of India

Preamble

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

JUSTICE, social, economic and political;

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

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

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

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

NATIONAL ANTHEM

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

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

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

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

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

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

PLEDGE

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

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

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

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

Preface

Dear Students,

We welcome you all to std. XII. For the first time, you were introduced to the subject of chemistry discipline in std XI.

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

Three major branches of chemistry, namely organic chemistry, inorganic chemistry and physical chemistry are presented in separate units in this book. Care is taken to have an integrated approach in deliberation of their contents. Chemistry is highly applied subject. In the unit "applied chemistry" along with the application of chemistry in life science and materials in everyday life, the upcoming applied branches, namely nanochemistry and green chemistry are also introduced. You can learn basic principles, understand facts and put them into practice by learning in the classroom and laboratory. The textbook is presented in a simple language with relevant diagrams, graphs, tables, photographs. This will help you to understand various terminology, concepts with more clarity. All the illustrations are in colour form. The new syllabus focuses on the basic principles, concepts, laws based on precise observations, their applications in everyday life and ability to solve different types of problems. The general teaching - learing objectives of the revised syllabus are further determined on the basis of the 'Principle of constructivism' i.e. self learning.

The curriculum and syllabus is designed to make the students to think independently. The students are encouraged to read, study more through the additional information given in the colored boxes. Activities have been introduced in each chapter. These activities will help to understand the content knowledge on your own efforts. QR code has been introduced for gaining the additional information, abstracts of chapters and practice questions/ activities.

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

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

Our best wishes to all !

(Vivek Gosavi)
Director
Maharashtra State Bureau of Textbook
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Pune
Date : 21 February 2020
Bharatiya Saur : 2 Phalguna 1941

- For Teachers -

Dear Teachers,

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

- To begin with, get familiar with the textbook yourself.
- The present book has been prepared for constructivism and activity based learning.
- Teachers must skilfully plan and organize the activities provided in each chapter to develop interest as well as to stimulate the thought process among the students.
- Always teach with proper planning.
- Use teaching aids as required for the proper understanding of the subject.
- Do not finish the chapter in short.
- Follow the order of the chapters strictly as listed in the contents because the units are introduced in a graded manner to facilitate knowledge building.
- Each unit is structured in a definite manner. It starts from the basic concepts of general chemistry required for each branch of chemistry. Application of this knowledge will help students to understand further chapters in each unit.
- Each chapter provides solved problems on each and every concept and various laws. The solved problems are put into boxes. Teachers should explain each step of the problems to the student and give them practice.
- Invite students' participation by making use of the boxes like 'Can You Recall', 'Do you know?'
- Encourage the students to collect related information by providing them the websites.
- Teaching- learning interactions, processes and participation of all students are necessary and so is your active guidance.
- Do not use the content of the boxes titled 'Do you know'? for evaluation.
- Exercises include parameters such as co-relation, critical thinking, analytical reasoning etc. Evaluation pattern should be based on the given parameters. Equal weightage should be assigned to all the topics. Use different combinations of questions.
- Illustrative figures are included to help assimilation of new concepts. Teachers should note that students are not expected to draw all the figures included in this book. As a part of evaluation students can be asked to draw schematic diagrams/structures and interpret or label other complicated figures.

Can you recall ?

Remember...

Do you know ?

Observe and discuss...

Use your brain power

Can you tell ?

Internet my friend

Try this...

Activity :

Can you think ?

Cover page :

- **(+) - Limonene and (-) Limonene :** major contributors to the characteristic flavours of peelings of oranges and lemons respectively.
- **Image of gold surface :** Au (111), obtained by Scanning Tunneling Microscope (STM).
- **Structures of coordination complexes :** haemoglobin, chlorophyll and metal -EDTA complex.

Competency Statements - Standard XII

Area/ Unit/ Lesson	After studying the contents in Textbook students.....
Physical Chemistry	• Distinguish crystal structures illustrating unit cell and packing efficiency in cubic systems. • Gain information on point defects and band theory in relation to electric and magnetic behavior. • Define solubility and rationalise its dependence on various factors. • Explain Henry and Raoult's laws. • Derive expressions for colligative properties. • Learn van’t Hoff factor and its correlation with dissociation constant. • Catagorize strong and weak acid bases. • Learn Ostwald’s dilution law. • Derive Henderson Balch Hassel equation. • Explain the role of buffer solutions in controlling of pH. • Understand spontaneity of reactions. • Know reversible/irreversible processes and PV work. • Understand first and second laws of thermodynamics. • Work out change in enthalpy, entropy and Gibbs' functions in physical and chemical transformations. • Apply Hess’s Law in thermochemical equations. • State what are strong and weak electrolytes. • Define Kohlrausch law and state its importance. • Understand functioning of electrolytic and galvanic cells. Write half cell reactions there in. • Describe type of electrodes. • Derive Nernst equation and understand its importance. • Know what are dry cell, lead strong batteries and fuel cells. • Describe the electrochemical series and its implications. • Define average and instantaneous rate, order and molecularity in kinetics • Formulate differential and integral rate laws for zero and first order reactions. • Understand basis of collision theory of reaction rates • Sketch qualitatively potential energy curve. Understand acceleration of reactions in the presence of catalyst. • Solve relevant numerical problems.
Inorganic chemistry	• Write electronic configuration of groups 16, 17, 18 and those of d and f blocks. • Correlate atomic properties of elements with electron configuration. • Explain the anomalous behaviour of ‘O’ and ‘F’. • Understand allotropy in ‘O’ and ‘S’. • Draw structures of oxyacids of ‘sulfur’ and ‘halogens’. • Write reactions for preparation, chemical properties of O_2, O_3, SO_2, H_2SO_4, Cl_2, HCl, $KMnO_4$, $K_2Cr_2O_7$. • Draw structures of interhalogen and xenon compounds and illustrate their properties. State the methods of preparation with reaction. • Know chemistry of the elements belonging to groups 16, 17, 18. • Understand the principles of metallurgy in extraction of iron. • Compare lanthanoides and actinoides. • Enlist properties of the manmade post actinoide elements. • Understand Werner theory of coordination compounds. • Understand and apply EAN rule for stability of coordination compounds. • Understand diverse isomerism in coordination compounds. • Use the concept of hybridization for predicting structures and magnetic behaviour of complexes based on the V.B.T. • Understand C.F.T. Sketch qualitatively d-orbital splitting diagrams in octahedral and tetrahedral ligand field environments. • Distinguish between high spin and low spin complexes. • Predict structure, colour and magnetic properties of the complexes based on the C.F.T.

Organic Chemistry	• State common and IUPAC names of compounds and methods of preparation of halogen derivatives, alcohols, phenols, ethers, aldehydes, ketones, carboxylic acid and amines. • Understand structure, chemical properties, laboratory tests and reactions of the above functional groups. • Explain acid or base strength of alcohols, phenols, carboxylic acids and amines. • Explain trends in boiling point and solubility of compounds of above functional groups in terms of intermolecular forces. • Understand optical activity, recognize chiral molecules and represent with Fischer projection and wedge formulae. • Understand mechanism of nucleophilic substitution reactions and influencing factors.
Applied Chemistry	• Classify carbohydrates, amino acids, nucleic acids. • Represent monosaccharides using the Fischer projection formula. • Represent monosaccharides, disaccharides and polysaccharides using the Haworth formula. • Correlate properties of carbohydrates to the presence or absence of potential aldehyde group. • Learn four level structure of proteins and primary structures nucleic acid. • Represent primary structure of dipeptide and tripeptide from data on the terminals. • Understand enzyme catalysis and double strand DNA structure. • Understand classification of polymers on the basis of source, structure, intermolecular forces, polymerization, number of monomers and biodegradability. • Understand addition and condensation polymerization. • Know properties, structure and preparation of natural rubber, vulcanized rubber, Buna-S, viscose, LDP, HDP, teflon, polyacrylo nitrile, polyamide, polyesters, phenol-formaldehyde resin and PHBV. • Understand scope of green chemistry with reference to sustainable development. • Recognize twelve principles of green chemistry and their implementation. • Correlate the Chemistry knowledge gained so far as pro or counter to the principles of green chemistry. • Understand scope and applications of nanochemistry. • Gain knowledge of a synthetic method and properties of nanoparticles. • Know instrumental techniques for characterization of nanomaterials.

CONTENTS

1. SOLID STATE

Can you recall ?

- What are the three most common states of matter?
- How does solid state differ from the other two states ? (Answer with reference to volume, shape, effect of temperature and pressure on these and the motion of constituent particles and interparticle forces.)

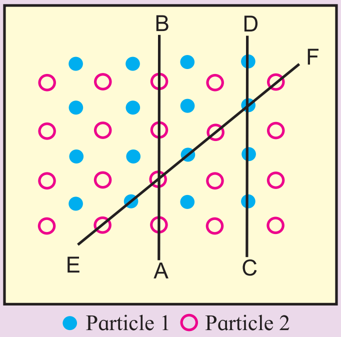
1.1 Introduction : As studied earlier, the solid state of matter is characterised by strong interparticle forces of attraction. As a result most solids have definite shape and volume, which change only slightly with change in temperature and pressure. The smallest constituent particles of various solids are **atoms**, **ions** or **molecules**. All such smallest constituent particles of solids will be referred to as '**particles**' in this chapter.

1.2 Types of solids : There are two types of solids, namely crystalline solids and amorphous solids.

Observe and discuss...

- Collect the following solids : grannular sugar, common salt, blue vitriol.
- Observe a few grannules of these solids under a magnifying lens or microscope.
- Discuss your observations with reference to the following points : (i) Shape of the grannules, (ii) Smoothness of faces of the grannules and (iii) Angles between various edges of the grannules.
- All the above solids are crystalline solids. Name the properties of crystals that you observed in this activity.

Try this...



Observe the above figure carefully. The two types of circles in this figure represent two types of constituent particles of a solid.

- Will you call the arrangement of particles in this solid regular or irregular ?
- Is the arrangement of constituent particles same or different in directions $\overrightarrow{AB}$, $\overrightarrow{CD}$, and $\overrightarrow{EF}$?

1.2.1 Crystalline solids : Study of many crystalline solids indicates that they possess the following characteristic properties.

i. There is a **regularity** and **periodicity** in the arrangement of constituent particles in crystalline solids. The ordered arrangement of particles extends over a long range.

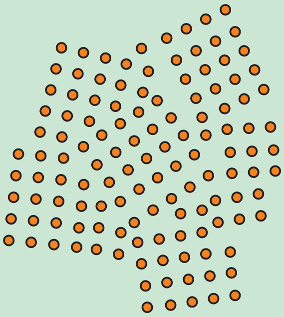
ii. Crystalline solids have **sharp melting points**, that is, they melt at a definite temperature.

iii. All crystalline substances except those having cubic structure are **anisotropic**. In other words their properties like refractive index, thermal and electrical conductivity, etc, are different in different directions.

Ice, salts such as NaCl, metals such as sodium, gold, copper and materials such as diamond, graphite, ceramics are examples of crystalline solids.

Do you know ?

- A single crystal has ordered (regular and periodic) arrangement of constituent particles throughout its bulk.
- Majority of crystalline solids, including metals, are polycrystalline in nature. Single grannule of a polycrystalline solid is made of many single crystals or crystallites packed together with different orientations.
- Single crystals are difficult to obtain. Diamond is an example of naturally formed single crystal.



1.2.2 Amorphous solids : The particles of a liquid are in constant motion. The stop action photograph of a liquid describes the amorphous state. In fact, they are supercooled liquids. Amorphous solids have the following characteristics.

i. The constituent particles in amorphous solids are **randomly arranged**. The particles do not have long range ordered structure, but they do have a short range order.

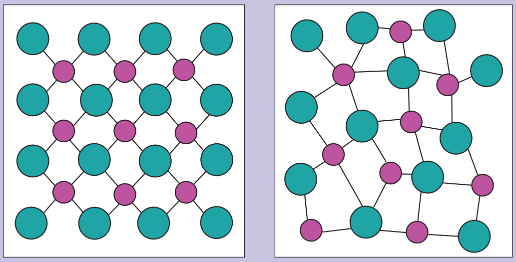
ii. Amorphous solids do not have sharp melting points. They melt gradually over a **temperature interval**. On heating, amorphous solids gradually and continuously soften and start to flow.

iii. These solids are **isotropic**. In other words, their properties such as refractive index, conductivity are all independent of direction of measurement. They exhibit the same magnitude for any property in every direction.

Glass, plastic, rubber, tar, and metallic glass (metal-metalloid alloy) are a few examples of amorphous solids.

Use your brain power

Identify the arrangements A and B as crystalline or amorphous.



1.2.3 Isomorphism and polymorphism

Similarity or dissimilarity in crystal structure of different solids is described as isomorphism and polymorphism.

i. Isomorphism : Two or more substances having the same crystal structure are said to be isomorphous. In these substances the chemical composition has the same atomic ratio. For example (i) NaF and MgO (ii) $NaNO_3$ and $CaCO_3$ are isomorphous pairs, and have the same atomic ratios, 1:1 and 1:1:3, respectively, of the constituent atoms.

ii. Polymorphism : A single substance that exists in two or more forms or crystalline structures is said to be polymorphous. Polymorphs of a substance are formed under different conditions. For example : Calcite and aragonite are two forms of calcium carbonate; α-quartz, β-quartz and cristobalite are three of the several forms of silica. Polymorphism occuring in elements is called **allotropy**. For example: three polymorphic (allotropic) forms of carbon are diamond, graphite and fullerene.

Do you know ?

Many crystalline forms of silica (SiO_2) are found in nature. Three of them are α-quartz, β-quartz and cristobalite


cristobalite


α-quartz


β-quartz

1.3 Classification of crystalline solids :

Crystalline solids are further classified into four categories : ionic solids, covalent network solids, molecular solids and metallic solids.

1.3.1 Ionic crystals : Ionic crystals have the following characteristics :

i. The constituent particles of ionic crystals are **charged ions**. The cations and anions may differ in size.

ii. Each ion of a given sign of charge is bonded to ions of opposite charge around it by coulomb force. In other words, the particles of ionic crystals are held by **electrostatic force of attraction** between oppositely charged ions.

iii. Ionic crystals are **hard** and **brittle**. They have **high melting points**.

iv. These are **nonconductors of electricity** in solid state. However, they are good conductors when melted or dissolved in water.

For example : NaCl, K_2SO_4, CaF_2, KCl are ionic crystals.

1.3.2 Covalent network crystals

Characteristics of covalent network crystals are as follows :

i. The constituent particles in covalent network solids are **atoms**.

ii. The atoms in these crystals are linked by a continous system of **covalent bonds**. The result is a rigid three dimensional network that forms a giant molecule. The entire crystal is a single molecule.

iii. As a result of rigid and strongly bonded structure, covalent network crystals are **very hard**. In fact they are the hardest and most **incompressible** of all the materials. These crystals have **high melting and boiling points**.

iv. The electrons are localised in covalent bonds and hence are not mobile. As a result, covalent solids are **poor conductors** of heat and electricity.

For example : diamond, quartz (SiO_2), boron nitride, carborandum are covalent network solids.

Do you know ?

Diamond is the hardest known material.

Try this...

Graphite is a covalent solid yet soft and good conductor of electricity. Explain.

Can you recall ?

- What are structures of diamond and graphite ?
- What are the types of covalent bonds those link carbon atoms in diamond and graphite ?
- Are all the valence electrons of carbon atoms in graphite localized to specific covalent bonds ?

Remember...

Both ionic and covalent crystals are hard and have high melting and boiling points. We can use electrical properties to distinguish between them. Both are insulators at low temperature.

Ionic solids become good conductors only at high temperature, above their melting points.

The conductivity of covalent solids is in general low and increases with temperature. However, there is no abrupt rise in conductivity when substance is melted.

1.3.3 Molecular crystals : Substances such as Cl_2, CH_4, H_2, CO_2, O_2 on solidfication give molecular crystals. Crystalline organic compounds are also molecular solids.

i. The constituent particles of molecular solids are **molecules** (or unbonded single atoms) of the same substance.

Can you recall ?

What is a hydrogen bond ?

ii. The bonds within the molecules are covalent. The molecules are held together by various intermolecular forces of **attraction**. (Refer to XI Std. Chemistry Textbook, Chapter 10). For example :

   a. **Weak dipole-dipole interactions** in polar molecules such as solid HCl, H_2O, SO_2, which possess permanent dipole moment.

   b. **Very weak dispersion or London forces** in nonpolar molecules such as solid CH_4, H_2. These forces are also involved in monoatomic solids like argon, neon. (These substances are usually gases at room temperature.)

   c. **Intermolecular hydrogen bonds** in solids such as H_2O (ice), NH_3, HF and so forth.

iii. Because of weak intermolecular attractive forces, molecular solids are usually soft substances with **low melting points**.

iv. These solids are **poor electrical conductors** and are good insulators.

1.3.4 Metallic crystals : These are crystalline solids formed by atoms of the same metallic element, held together by a metallic bond.

Metallic bond : In a solid metal, the valence electrons are delocalised over the entire crystal leaving behind positively charged metal ions. Therefore, metallic crystals are often described as an array of positive ions immersed in a sea of mobile electrons. The attractive interactions between cations and mobile electrons constitute the metallic bonds. (For more details refer to section 1.9.2)

Metallic crystals have the following properties:

i. Metals are **malleable**, that is, they can be hammered into thin sheets.

ii. Metals are **ductile**, that is, they can be drawn into wires.

iii. Metals have **good electrical and thermal conductivity**.

Examples : metals such as Na, K, Ca, Li, Fe, Au, Ag, Co, etc.

The properties of different types of crystalline solids are summarized in Table 1.1.

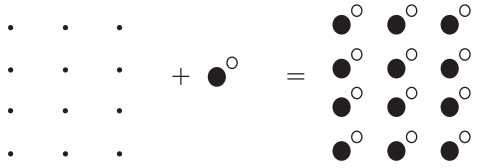
1.4 Crystal structure : The ordered three dimensional arrangement of particles in a crystal is described using two terms, namely, lattice and basis.

1.4.1 Crystal, lattice and basis : Lattice is a geometrical arrangement of points in a three dimensional periodic array. A crystal structure is obtained by attaching a constituent particle to each of the lattice points. Such constituent particles that are attached to the lattice points form the basis of the crystal lattice. Crystal

Table 1.1 : Properties of four types of crystalline solids

Type Property	Ionic solids	Covalent network solids	Molecular solids	Metallic solids
1. Particles of unit cell	Cations and anions	Covalently bonded atoms	Monoatomic or polyatomic molecules	Metallic ions in a sea of electrons
2. Interparticle forces	Electrostatic	Covalent bonds	London, dipole-dipole forces and/or hydrogen bonds	Metallic bonds (attraction between cations and mobile valence electrons)
3. Hardness	Hard and brittle	Very hard	Soft	Variable from soft to very hard
4. Melting points	High 600^{0}C to 3000^{0}C	High 1200^{0}C to 4000^{0}C	Low (-272^{0}C to 400^{0}C)	Wide range (-39^{0}C to 3400^{0}C)
5. Thermal and electrical conductivity	Poor electrical conductors in solid state. Good conductors when melted or dissolved in water	Poor conductors Exceptions : i. Graphite : good conductor of electricity. ii. Diamond : good conductor of heat	poor conductor of heat and electricity	good conductor of heat and electricity
6. Examples	NaCl, CaF_2	diamond, silica	ice, benzoic acid	Na, Mg, Cu, Au

lattice is also called space lattice of crystal. Thus, crystal is the structure that results by attaching a basis to each of the lattice points. It is represented by the following equation.



Lattice + Basis = Crystal

1.4.2 Unit Cell : The space lattice of a crystal is built up of a three dimensional basic pattern. This basic pattern is repeated in three dimensions to generate the entire crystal. **The smallest repeating structural unit of a crystalline solid is called unit cell.**

When the unit cells are stacked together to generate the crystal, each unit cell shares its faces, edges and corners with neighbouring unit cells. It is important to understand that the geometric shape of a unit cell is same as that of the macroscopic crystal. For example, if the crystal has cubic shape the unit cell will also have its constituent particles arranged to form a tiny cube.

The dimensions of unit cell along the three axes are denoted by the symbols a, b and c. The angles between these axes are represented by the symbols ∝, β and γ as shown in Fig 1.1.

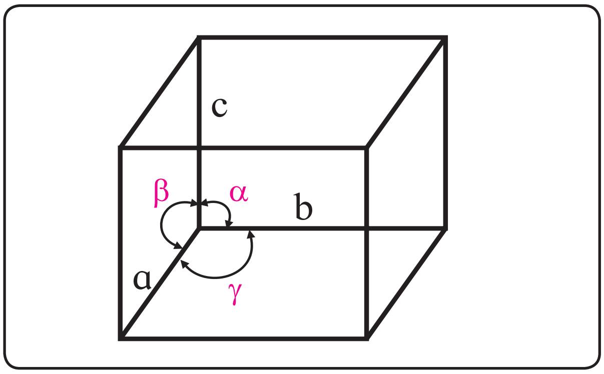


Fig. 1.1 : Unit cell parameters

1.4.3 Types of unit cell : There are four types of unit cells.

i. Primitive or simple unit cell : In primitive unit cell, the constituent particles are present at its corners only.

ii. Body-centred unit cell : In this type of unit cell, one constituent particle is present at the centre of its body in addition to the corner particles.

iii. Face-centred unit cell : This unit cell consists of particles at the centre of each of the faces in addition to the corner particles.

iv. Base-centred unit cell : This unit cell consists of particles at the centre of any two of its opposite faces in addition to the corner particles.

1.4.4 Crystal systems :
By mathematical analysis, it has been proved that only fourteen different kinds of space lattices are possible. In other words, there are only 14 ways in which similar points can be arranged in a three dimensional order. These 14 lattices, which describe the crystal structure, are called **Bravais lattices**.

Fourteen Bravais lattices are divided into seven crystal systems. The possible combinations of lattice point spacings (a, b and c) along three axes and the angles ($\propto$, β and γ) between these axes give rise to seven crystal systems. In other words, seven crystal systems are associated with 14 Bravais lattices also called 14 unit cells.

The seven crystal systems are named as cubic, tetragonal, orthorhombic, rhombohedral, monoclinic, triclinic and hexagonal system. Cubic system will be discussed in the following section.

1.5 Cubic system :
There are three kinds of unit cells in cubic system : primitive or simple cubic (sc), body-centred cubic (bcc) and face-centred cubic (fcc) (Fig. 1.2).

i. Simple cubic unit cell (sc) has a particle at each of the eight corners of a cube.

ii. Body-centred cubic unit cell (bcc) has particles at its eight corners and an additional particle in the center of the cube.

iii. Face-centred cubic unit cell (fcc) has particle at the centre of each of six faces in addition to the particles at eight corners of the cube.

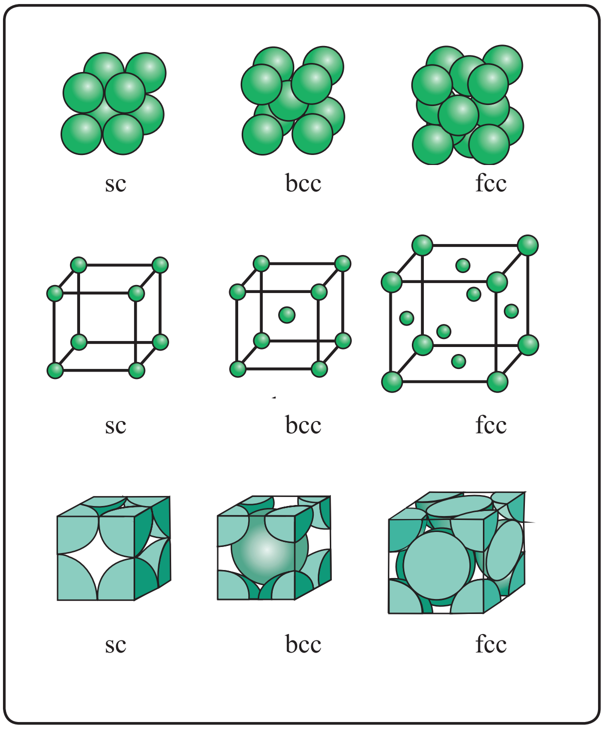


Fig. 1.2 : Cubic unit cell

1.5.1 Number of particles in cubic unit cells

i. Primitive or simple cubic unit cell (sc) : A simple cubic cell has particles at its eight corners. When these unit cells are stacked together, particle at each corner of a given unit cell is shared with seven other neighbouring cubes that come together at that corner. As a result the corner particle contributes its 1/8th part to the given unit cell. Thus, a **simple cubic cell has** $1/8 \times 8 = 1$ **particle per unit cell**.

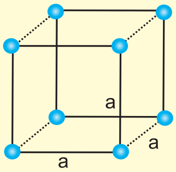
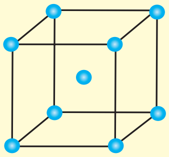
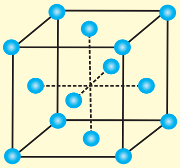
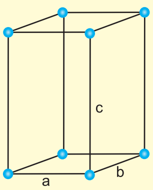
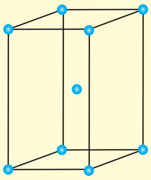
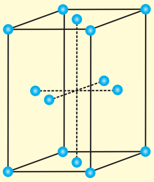
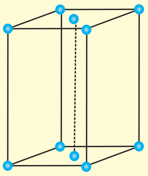
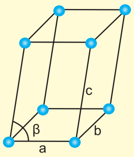
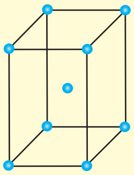
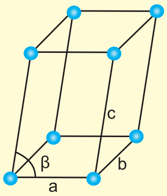
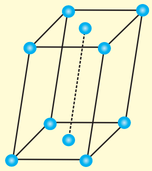
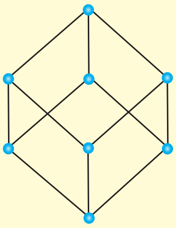
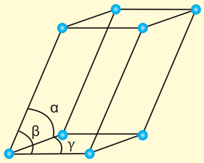
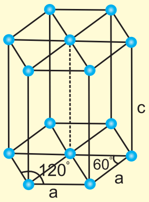
ii. Body-centred cubic unit cell (bcc) : A bcc unit cell has eight corner particles and an additional particle at the centre of the cube. One eighth of each particle from eight corners belongs to the given unit cell as mentioned in simple cubic unit cell.

The particle at the centre of a given cube is not shared by any other cube. Hence, it belongs entirely to the given unit cell. Thus bcc unit cell has one particle from eight corners plus one particle in the centre of the cube, making total of **2 particles per bcc unit cell**.

iii. Face-centred cubic unit cell (fcc) : A fcc unit cell has particles at the eight corners plus particles at the centre of its six faces. As described in simple cubic unit cell, one particle

Do you know ?

The names of fourteen Bravais lattices (unit cells) for each of the seven crystal system are shown below.

Crystal system	Bravais lattices	
	Name	**unit cell structure**
1. Cubic	i. simple or primitive ii. body-centred iii. face-centred	 i.  ii.  iii.
2. Orthorhombic	i. simple or primitive ii. body-centred iii. face-centred iv. base-centred	 i.  ii.  iii.  iv.
3. Tetragonal	i. simple or primitive ii. body-centred	 i.  ii.
4. Monoclinic	i. simple or primitive ii. base centred	 i.  ii.
5. Rhombohedral	i. simple or primitive	
6. Triclinic	i. simple or primitive	
7. Hexagonal	i. simple or primitive	

from eight corners belongs to the given unit cell.

Each particle at the centre of the six faces is shared with one neighbouring cube. Thus,1/2 of each face particle belongs to the given unit cell. From six faces, 1/2 × 6 = 3 particles belong to the given unit cell.

Therefore, **fcc unit cell has** one corner particle plus 3 face particles, **total 4 particles per unit cell**.

Remember...

Each corner particle of a cube is shared by 8 cubes, each face particle is shared by 2 cubes and each edge particle is shared by 4 cubes.

1.5.2 Relationship between molar mass, density of the substance and unit cell edge length, is deduced in the following steps

i. If edge length of cubic unit cell is ***a***, the volume of unit cell is a^3.

ii. Suppose that mass of one particle is ***m*** and that there are ***n*** particles per unit cell.

$$\text{Mass of unit cell} = m \times n \qquad \text{.............(1.1)}$$

iii. The density of unit cell (ρ), which is same as density of the sub-substance is given by

$$\rho = \frac{\text{mass of unit cell}}{\text{volume of unit cell}} = \frac{m \times n}{a^3} = \text{density of substance} \qquad \text{............. (1.2)}$$

iv. Molar mass (M) of the substance is given by

M = mass of one particle × number of particles per mole

$= m \times N_A$ (N_A is Avogadro number)

Therefore, $m = M/N_A$ .... (1.3)

v. Combining Eq. (1.1) and (1.3), gives

$$\rho = \frac{n\,M}{a^3\,N_A} \qquad \text{............. (1.4)}$$

By knowing any four parameters of Eq. (1.4), the fifth can be calculated

Problem 1.1 : When gold crystallizes, it forms face-centred cubic cells. The unit cell edge length is 408 pm. Calculate the density of gold. Molar mass of gold is 197 g/mol.

Solution :

$$\rho = \frac{M\,n}{a^3 N_A}$$

M = 197 g mol^{-1}, n = 4 atoms for fcc,
$N_A = 6.022 \times 10^{23}$ atoms mol^{-1},
$a = 408$ pm $= 408 \times 10^{-12}$m $= 4.08 \times 10^{-8}$ cm

Substitution of these quantities in the equation gives

$$\rho = \frac{197\ \text{g}\ \cancel{\text{mol}^{-1}} \times 4\ \cancel{\text{atom}}}{(4.08\times10^{-8})^3\ \text{cm}^3 \times 6.022\times10^{23}\ \cancel{\text{atom}\ \text{mol}^{-1}}}$$

$= 19.27\ \text{g/cm}^3,\ 19.27 \times 10^3\ \text{kg/m}^3.$

1.6 Packing of particles in crystal lattice

Constituent particles of a crystalline solid are close packed. While describing the packing of particles in a crystal, the individual particles are treated as hard spheres. The closeness of particles maximize the interparticle attractions.

The number of **neighbouring spheres that touch any given sphere is its coordination number**. Magnitude of the coordination number is a measure of compactness of spheres in close-packed structures. The larger the coordination number, the closer are the spheres to each other.

1.6.1 Close packed structures : The three dimensional close packed structure can be understood conveniently by looking at the close packing in one and two dimensions.

a. Close packing in one dimension : A close packed one dimensional structure results by arranging the spheres to touch each other in a row (Fig. 1.3 (a)).

b. Close packing in two dimensions : A close packed two dimensional (planar) structure results by stacking the rows together such that they are in contact with each other. There are two ways to obtain close packing in two dimensions.

i. Square close packing : One dimensional rows of close packed spheres are stacked over each other such that the spheres align vertically and horizontally (Fig. 1.3 (b)). If the first row is labelled as 'A' type, being exactly same as the first row, the second row is also labelled as 'A' type. Hence this arrangement is called A, A, A..... type two dimensional arrangement. In this arrangement, every sphere touches four neighbouring spheres. Hence, two dimensional coordination number, here, is 4. A square is obtained by joining the centres of these four closest neighbours (Fig. 1.3(b)). Therefore, this two dimensional close packing is called **square close packing in two dimension**.

ii. Hexagonal close packing : Close packed one dimensional row (Fig. 1.3 (a)) shows that there are depressions between the neighbouring spheres. If the second row is arranged in such a way that its spheres fit in the depressions of the first row, a staggered arrangement results. If the first row is called 'A' type row, the second row, being different, is called 'B' type. Placing the third row in staggered manner in contact with the second row gives rise to an arrangement in which the spheres in the third row are aligned with the spheres in the first row. Hence the third row is 'A' type. Similarly spheres in the fourth row will be alligned with the spheres in the second row and hence the fourth row would be 'B' type. The resulting two dimensional arrangement is 'ABAB...' type (Fig. 1.3 (c)). In this arrangement each sphere touches six closest neighbours. Thus, the two dimensional coordination number in this packing is 6. A regular hexagon is obtained by joining the centres of these six closest spheres (Fig. 1.3 (c)). Hence, this type of two dimensional close packing is called hexagonal close packing in two dimensions. Compared to the square close packing in two dimensions, the coordination number in hexagonal close packing in two dimensions is higher. Moreover the free space in this arrangement is less than in square packing, making it more effecient packing than square packing. From Fig.1.3(c) it is evident that the free spaces (voids) are triangular in shape. These triangular voids are of two types. Apex of the triangular voids in alternate rows points upwards and downwards.

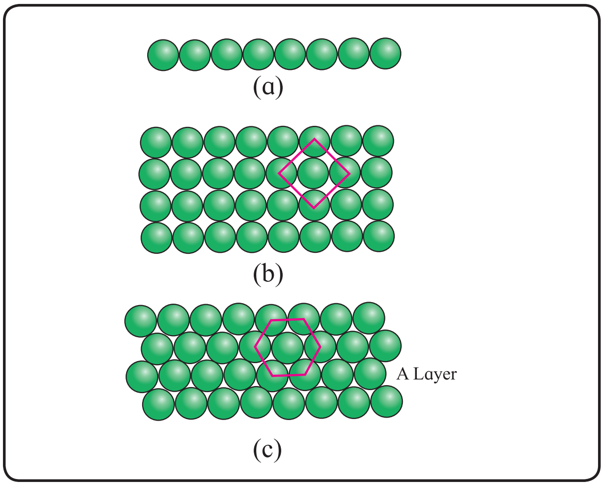


Fig. 1.3 : (a) Close packing in one dimension (b) square close packing (c) Hexagonal close packing in two dimension

c. Close packing in three dimensions : Stacking of two dimensional layers gives rise to three dimensional crystal structures. Two dimensional square close packed layers are found to stack only in one way to give simple cubic lattice. Two dimensional hexagonal close packed layers are found to stack in two distinct ways. Accordingly two crystal structures, namely, hexagonal close packed (hcp) structure and face centred cubic (fcc) structure are formed.

i. Stacking of square close packed layers: Stacking of square close packed layers generates a three dimensional simple cubic structure. Here, the second layer is placed over the first layer so as to have its spheres exactly above those of the first layer (Fig. 1.4). Subsequent square close packed layers are placed one above the other in the same manner. In this arrangement, spheres of all the layers are perfectly aligned horizontally as well as vertically. Hence, all the layers are alike, and are labelled as 'A' layers. This arrangement of layers is described as 'AAAA... ' type. The structure that results on stacking square close packed layers is **simple cubic**. Its unit cell is the **primitive cubic unit cell** (Fig. 1.4).

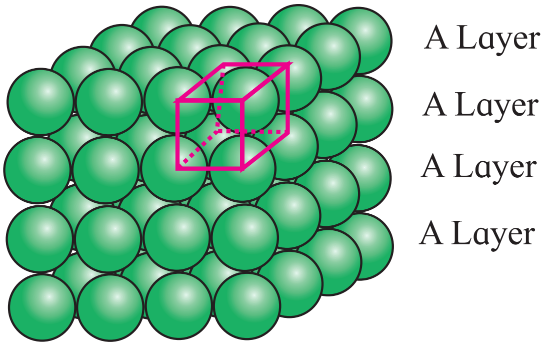


Fig. 1.4 : Stacking of square closed packed layers

It can be seen that in the simple cubic structure, each sphere touches six neighbouring spheres, four in its own layer, one in the layer above and one in the layer below. Hence, coordination number of each sphere is 6. Polonium is the only metal that crystallizes in simple cubic closed packed structure.

ii. Stacking of two hexagonal close packed layers : To generate a close packed three dimensional structure, hexagonal close packed layers are arranged in a particular manner. In doing so, spheres of the second layer are placed in the depression of the first layer (Fig. 1.5). If the first layer is labelled as 'A' layer, the second layer is labelled as 'B' layer because the two layers are aligned differently. It is evident from the Fig. 1.5 that all triangular voids of the first layers are not covered by the spheres of the second layer. The triangular voids that are covered by spheres of the second layer generate tetrahedral void(Fig. 1.6). A tetrahedral void is surrounded by four spheres. On joining the centres of these four spheres a tetrahedron is formed which encloses the tetrahedral voids (Fig. 1.6). The remaining triangular voids of the first layer have above them the triangular voids of the second layer. The overlapping triangular voids from the two layers together form an octahedral void which is surrounded by six spheres (Fig. 1.7).

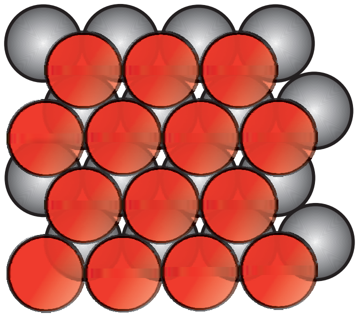


Fig. 1.5 : Two layers of closed packed spheres

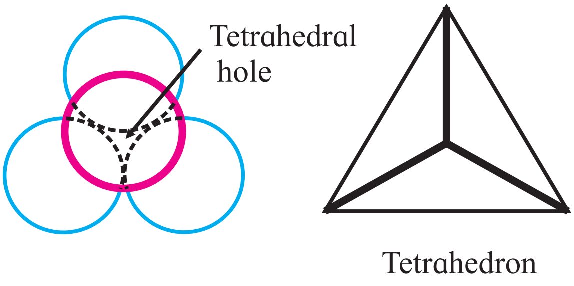


Fig. 1.6 : Tetrahedral void

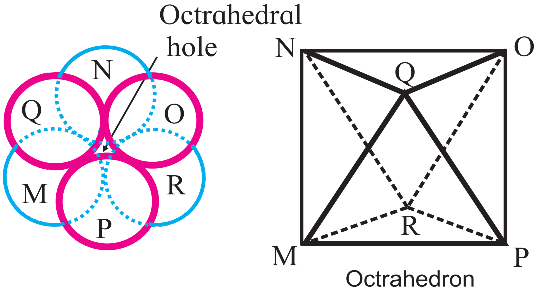


Fig. 1.7 : Octahedral void

Remember...

It is important to note that the triangular shapes of depressions in A and B layer do not overlap. The apices of two triangular depressions in A and B layer point in opposite directions.

The depressions in which spheres of second layer rest are tetrahedral voids while the depressions in which no sphere rests are octahedral voids.

iii. Placing third hexagonal close packed layer : There are two ways of placing the third hexagonal close packed layer on the second.

One way of doing this is to align the spheres of the third layer with the spheres of the first layer. The resulting pattern of the layers will be 'ABAB....'. This arrangement results in **hexagonal close packed (hcp)** structure (Fig. 1.8(a)). Metals such as Mg, Zn, have hcp crystal structure.

The second way of placing the third hexagonal close packed layer on the second is to cover the octahedral voids by spheres of the third layer. In such placing, the spheres of the third layer do not align with the spheres of the second or the spheres of the first layer. The third layer is, therefore, called 'C' layer. The spheres of the fourth layer get aligned with the spheres of the first layer. Hence, the fourth layer is called 'A' layer. This pattern of stacking hexagonal close packed layers is called 'ABCABC....'. This arrangement results **in cubic close packed (ccp)** structure (Fig. 1.8(b)). This is same as fcc structure. Metals such as copper and Ag have ccp (or fcc) crystal structure.

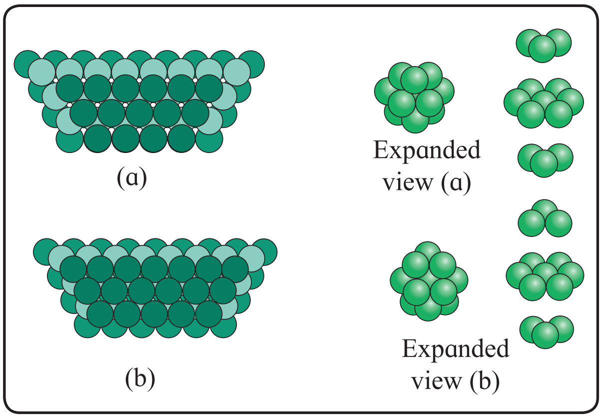


Fig. 1.8 : Formation of hexagonal closed packed structures

1.6.2 Coordination number in close packed structure

a. In the simple cubic (sc) crystal structure, that results from stacking of square close packed layers, each sphere is surrounded by 6 neighbouring spheres, 4 in its own layer, 1 above and 1 below. Hence coordination number of any sphere in sc is 6.

b. In both **hcp** and **ccp/fcc** structures that result from stacking of hexagonal close packed layers in two different ways, each sphere is surrounded by 12 neighbouring spheres, 6 in its own layer, 3 above and 3 below. Hence, the coordination number of any sphere in hcp or ccp/fcc structure is 12.

1.6.3 Number of voids per atom in hcp and ccp : The tetrahedral and octahedral voids occur in hcp and ccp/fcc structures. There are two tetrahedral voids associated with each atom. The number of octahedral voids is half that of tetrahedral voids. Thus, there is one octahedral void per atom.

Remember...

If N denotes number of particles, then number of tetrahedral voids is 2N and that of octahedral voids is N.

1.7 Packing efficiency : Like coordination number, the magnitude of packing efficiency gives a measure of how tightly particles are packed together.

Packing efficiency is the fraction or a percentage of the total space occupied by the spheres (particles).

Packing efficiency =

$$\frac{\text{volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100 \qquad \text{............ (1.5)}$$

1.7.1 Packing efficiency of metal crystal in simple cubic lattice is obtained by the following steps.

Step 1 : Radius of sphere : In simple cubic unit cell, particles (spheres) are at the corners and touch each other along the edge. A face of simple cubic unit cell is shown in Fig. 1.9. It is evident that

$$a = 2r \quad \text{or} \quad r = a/2 \qquad \text{............ (1.6)}$$

where r is the radius of atom and ‘a’ is the length of unit cell edge.

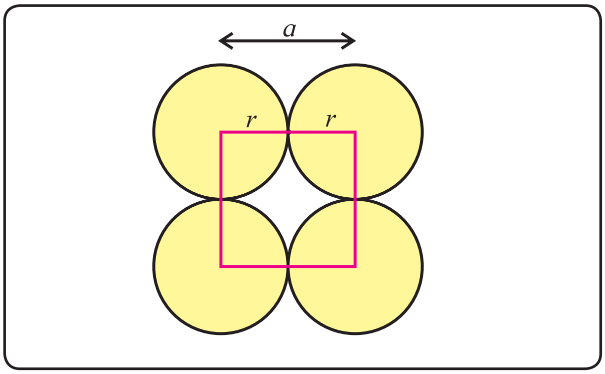


Fig. 1.9 : Face of simple cubic unit cell

Step 2 : Volume of sphere : Volume of a sphere = $(4/3\pi)(r^3)$. Substitution for r from Eq. (1.6) gives

Volume of one particle

$$= (4/3\pi)\ (a/2)^3 = \frac{\pi a^3}{6} \quad \text{.........} (1.7)$$

Step 3 : Total volume of particles : Because simple cubic unit cell contains only one particle,

volume occupied by particle in unit cell $= \dfrac{\pi a^3}{6}$

Step 4 : Packing efficiency

Packing efficiency

$$= \frac{\text{volume occupied by particle in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{\pi a^3/6}{a^3} \times 100 = \frac{100\pi}{6} = \frac{100 \times 3.142}{6} = 52.36\%$$

Thus, in simple cubic lattice, 52.36 % of total space is occupied by particles and 47.64% is empty space, that is, void volume.

1.7.2 Packing efficiency of metal crystal in body-centred cubic lattice

Step 1 : Radius of sphere (particle) :

In bcc unit cell, particles occupy the corners and in addition one particle is at the centre of the cube. Figure 1.10 shows that the particle at the centre of the cube touches two corner particles along the diagonal of the cube. To obtain radius of the particle (sphere) Pythagorus theorem is applied.

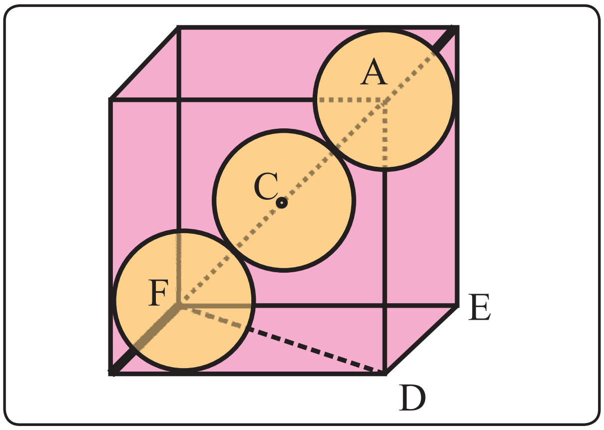


Fig. 1.10 : bcc unit cell

- For triangle FED, ∠ FED = 90^0.

$\therefore$ $FD^2 = FE^2 + ED^2 = a^2 + a^2 = 2a^2$ (because FE = ED = a) ....(1.8)

- For triangle AFD, ∠ ADF = 90^0

$$\therefore\ AF^2 = AD^2 + FD^2 \quad \text{..........} (1.9)$$

Substitution of Eq. (1.8) into Eq. (1.9) yields

$$AF^2 = a^2 + 2a^2 = 3a^2 \text{ (because } AD = a)$$

or $AF = \sqrt{3}\ a$ ....(1.10)

The Fig. 1.10 shows that AF = 4r.

Substitution for AF from equation (1.10) gives

$\sqrt{3}a = 4r$ and hence, $r = \dfrac{\sqrt{3}}{4}\ a$ ....(1.11)

Step 2 : Volume of sphere : Volume of sphere particle = $4/3\ \pi\ r^3$. Substitution for r from Eq. (1.11), gives

$$\text{volume of one particle} = \frac{4}{3}\ \pi\ (\sqrt{3}/4a)^3$$

$$= \frac{4}{3}\ \pi \times \frac{(\sqrt{3})^3}{64}\ a^3$$

$$= \frac{\sqrt{3}\pi\ a^3}{16}$$

Step 3 : Total volume of particles : Unit cell bcc contains 2 particles. Hence, volume occupied by particles in bcc unit cell

$$= 2 \times \frac{2\sqrt{3}\ \pi a^3}{16}$$

$$= \frac{\sqrt{3}\ \pi a^3}{8} \quad \text{..........} (1.12)$$

Step 4 : Packing efficiency

Packing efficiency

$$= \frac{\text{volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{\sqrt{3}\pi a^3}{8a^3} \times 100 = 68\ \%$$

Thus, 68% of the total volume in bcc unit lattice is occupied by atoms and 32 % is empty space or void volume.

1.7.3 Packing efficiency of metal crystal in face-centred cubic lattice (or ccp or hcp lattice)

Step 1 : Radius of particle/sphere : The corner particles are assumed to touch the particle at the centre of face ABCD as shown in Fig. 1.11.

The triangle ABC is right angled with $\angle ABC = 90^0$. According to Pythagorus theorem,

$AC^2 = AB^2 + BC^2 = a^2 + a^2 = 2a^2$

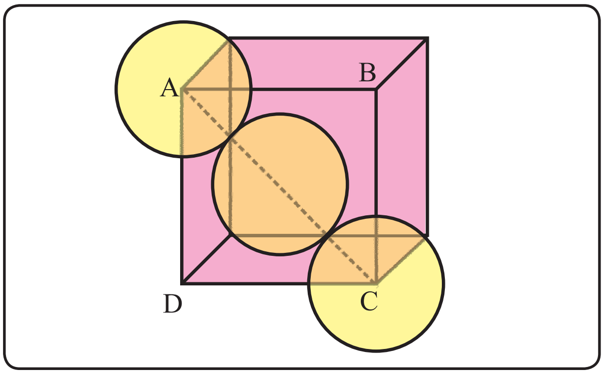


Fig. 1.11 : fcc unit cell

(because AB = BC = a)

Hence, $AC = \sqrt{2}\ a$ .... (1.13)

Figure 1.11 shows that AC = 4 r. Substitution for AC from Eq. (1.13) gives

$$\sqrt{2}a = 4r \text{ or } r = \frac{\sqrt{2}}{4}a = \frac{a}{2\sqrt{2}} \qquad \text{.......... (1.14)}$$

Step 2 : Volume of sphere : Volume of one particle $= \frac{4}{3}\pi r^3$. Substitution for r from Eq. (1.14) gives

Volume of one particle $= \frac{4}{3}\pi\left(\frac{a}{2\sqrt{2}}\right)^3$

$$= \frac{4}{3}\pi a^3 \times \left(\frac{1}{2\sqrt{2}}\right)^3$$

$$= \frac{\pi a^3}{12\sqrt{2}}$$

Step 3 : Total volume of particles : The unit cell of fcc lattice contains 4 particles. Hence, volume occupied by particles in fcc unit cell

$$= 4 \times \frac{\pi a^3}{12\sqrt{2}} = \frac{\pi a^3}{3\sqrt{2}}$$

Step 4 : Packing efficiency : Packing efficiency

$$= \frac{\text{volume occupied by particles in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{\pi a^3}{3\sqrt{2}\,a^3} \times 100 = \frac{\pi}{3\sqrt{2}} \times 100 = 74\%$$

Thus in fcc/ccp/hcp crystal lattice, 74% of the total volume is occupied by particles and 26% is void volume or empty space.

Table 1.3 shows the expressions for various parameters of particles in terms of unit cell dimension for cubic systems.

Use your brain power

Which of the three lattices, sc, bcc and fcc has the most efficient packing of particles? Which one has the least efficient packing?

Table 1.3 : Edge length and particle parameters in cubic system

Unit cell	Relation between a and r	Volume of one particle	Total volume occupied by particles in unit cell
1. sc	$r = a/2 = 0.5000a$	$\pi a^3/6 = 0.5237\ a^3$	$\pi a^3/6 = 0.5237\ a^3$
2. bcc	$r = \sqrt{3}a/4 = 0.4330a$	$\sqrt{3}\ \pi a^3/16 = 0.34a^3$	$\sqrt{3}\ \pi a^3/8 = 0.68a^3$
3. fcc/ ccp	$r = \sqrt{2}a/4 = 0.3535a$	$\pi a^3/12\sqrt{2} = 0.185a^3$	$\pi a^3/3\sqrt{2} = 0.74a^3$

Table 1.4 shows the summary of coordination number of particles and packing efficiency in various cubic systems.

Table 1.4 : Coordination number and packing efficiency in systems

Lattice	Coordination number of atoms	Packing efficiency
1. sc	**6 :** four in the same layer, one directly above and one directly below	52.4 %
2. bcc	**8 :** four in the layer below and one in the layer above	68 %
3. fcc/ccp/ hcp	**12 :** six in its own layer, three above and three below	74 %

1.7.4 Number of particles and unit cells in x g of metallic crystal :

The number of particles and the number of unit cells in given mass of a metal can be calculated from the known parameters of unit cell, namely, number of particles 'n' per unit cell and volume 'a^3' of unit cell. Density (ρ) and molar mass (M) of a metal are related to each other through unit cell parameters as shown below :

$$\rho = \frac{\text{mass}}{\text{volume}}$$

$$= \frac{\text{number of particles in unit cell}}{\text{volume of unit cell}} \times \frac{M}{N_A}$$

$$\therefore \rho = \frac{n}{a^3} \times \frac{M}{N_A}$$

$$\therefore M = \rho \frac{a^3 N_A}{n}$$

where 'n' is the number of particles in unit cell and 'a^3' is the volume of unit cell.

- **Number of particles in 'x' g metal :**

$\because$ Molar mass, M, contains N_A particles

$\therefore$ x g of metal contains $\frac{xN_A}{M}$ particles.

substitution of M gives

$$\text{Number of particles in 'x' g} = \frac{xN_A}{\rho a^3 N_A/n}$$

$$= \frac{xn}{\rho a^3}$$

- **Number of unit cells in 'x' g metal :**

$\because$ 'n' particles correspond to 1 unit cell

$\therefore \frac{xn}{\rho a^3}$ particles correspond to $\frac{xn}{\rho a^3} \times \frac{1}{n}$ unit cells.

$\therefore$Number of unit cells in 'x' g metal $= \frac{x}{\rho a^3}$

- **Number of unit cells in volume 'V' of metal =** $\frac{V}{a^3}$

Problem 1.2 A compound made of elements C and D crystallizes in fcc structure. Atoms of C are present at the corners of the cube. Atoms of D are at the centres of faces of the cube. What is the formula of the compound?

Solution:

i. C atoms are present at the 8 corners. The contribution of each corner atom to the unit cell is 1/8 atom. Hence, the number of C atom that belongs to the unit cell = 8×(1/8) = 1

ii. D atoms are present at the centres of six faces of unit cell. Each face-centre atom is shared between two cubes. Hence, centribution of each face centre atom to the unit cell is 1/2 atom.

The number of D atoms that belong to unit cell = 1/2×6 =3

There are one C atom and three D atoms in the unit cell.

$\therefore$ Formula of compound = CD_3

Problem 1.3 : The unit cell of metallic silver is fcc. If radius of Ag atom is 144.4 pm, calculate (a) edge length of unit cell(b) volume of Ag atom, (c) the percent of the volume of a unit cell, that is occupied by Ag atoms, (d) the percent of empty space.

Solution:

(a) For fcc unit cell, $r = 0.3535\ a$

$r = 144.4 \text{ pm} = 144.4 \times 10^{-12} \text{ m}$

$= 144.4 \times 10^{-10} \text{ cm}$

$$a = \frac{r}{0.3535} = \frac{144.4 \times 10^{-10}\text{cm}}{0.3535}$$

$= 4.085 \times 10^{-8} \text{ cm}$

(b) Volume of Ag atom $= \frac{4}{3} \pi r^3$

$$= \frac{4}{3} \times 3.142 \times (144.4 \times 10^{-10} \text{ cm})^3$$

$= 1.261 \times 10^{-23} \text{ cm}^3$

(c) In fcc unit cell, there are 4 Ag atoms

Volume occupied by 4 Ag atoms

$= 4 \times 1.26 \times 10^{-23} \text{ cm}^3$

$= 5.044 \times 10^{-23} \text{ cm}^3$

Total volume of unit cell $= a^3$

$= (4.085 \times 10^{-8} \text{ cm})^3$

$= 6.817 \times 10^{-23} \text{ cm}^3$

Percent of volume occupied by Ag atoms

$$= \frac{\text{volume occupied by atoms in unit cell}}{\text{total volume of unit cell}} \times 100$$

$$= \frac{5.044 \times 10^{-23}\text{cm}^3}{6.817 \times 10^{-23}\text{cm}^3} = 74\%$$

(d) Percent empty space = 100 - 74 = 26%

Problem 1.4 : A compound is formed by two elements A and B. The atoms of element B forms ccp structure. The atoms of A occupy 1/3rd of tetrahedral voids. What is the formula of the compound ?

Solution : The atoms of element B form ccp structure. The number of tetrahedral voids generated is twice the number of B atoms.

Thus, number of tetrahedral voids = 2B

The atoms A occupy (1/3) of these tetrahedral voids.

Hence, number of A atoms = 2B×1/3

Ratio of A and B atoms = 2/3 B: 1B

= 2/3:1 = 2:3

Formula of compound = A_2B_3

Problem 1.5 : Niobium forms bcc structure. The density of niobium is 8.55 g/cm^3 and length of unit cell edge is 330.6 pm. How many atoms and unit cells are present in 0.5 g of niobium?

Solution:

i. Number of atoms in x g niobium $= \frac{xn}{\rho a^3}$

x = 0.5 g, $n = 2$ (for bcc structure),

$\rho = 8.55 \text{ g/cm}^3$,

$a = 330.6\text{pm} = 3.306 \times 10^{-8}\text{cm}$.

Number of atoms in 0.5 g of niobium

$$= \frac{0.5 \text{ g} \times 2}{8.55 \text{ g cm}^{-3} \times (3.306 \times 10^{-8} \text{ cm})^3}$$

$= 3.25 \times 10^{21}$

ii. Number of unit cells in x g $= \frac{x}{\rho a^3}$

Number of unit cells in 0.5 g of niobium

$$= \frac{0.5 \text{ g} \times 2}{8.55 \text{ g cm}^{-3} \times (3.306 \times 10^{-8}\text{cm})^3}$$

$= 1.62 \times 10^{21}$

Problem 1.6 : A compound forms hcp structure. What is the number of (a) octahedral voids (b) tetrahedral voids (c) total voids formed in 0.4 mol of it.

Solution :

Number of atoms in 0.4 mol = $0.4 \times N_A$

$= 0.4 \times 6.022 \times 10^{23} = 2.4098 \times 10^{23}$

(a) Number of octahedral voids = number of atoms = 2.4098×10^{23}

(b) Number of tetrahedral voids

$= 2\times$number of atoms

$= 2\times2.4098\times10^{23}$

$= 4.818\times10^{23}$

(c) Total number of voids

$= 2.409\times10^{23} + 4.818\times10^{23}$

$= 7.227 \times 10^{23}$

1.8 Crystal defects or imperfections :

The real, naturally occurring crystalline substances do not have perfect crystal structures. They have some disorders or irregularities in the stacking of atoms. Such irregularities in the arrangement of constituent particles of a solid crystal are called defects or imperfections.

Defects are created during the process of crystallization. The imperfections are more if the crystallization occurs at a faster rate. It means that the defects can be minimized by carrying out crystallization at a slower rate.

In fact ideal crystals with no imperfections are possible only at the absolute zero of temperature. Above this temperature no crystalline materials are 100 % pure. They contain defects.

Whatever be the nature of a crystal defect, electrical neutrality of the solid is maintained.

It is important to note that sometimes defects are to be intentionally created for manipulating the desired properties in crystalline solids.

There are three types of defects: point defects, line defects and plain defects. Only point defects will be discussed in this chapter.

1.8.1 Point defects :

These defects are irregularities produced in the arrangement of basis at lattice points in crystalline solids.

There are three major classes of point defects: stoichiometric point defects, impurity defects and nonstoichiometric point defects.

a. Stoichiometric point defects : Chemical formula of a compound shows fixed ratio of number of atoms or number of cations and anions. This fixed ratio is the stoichiometry of the compound.

In stoichiometric defect, the stoichiometry remains unchanged. In other words, the ratio of number of atoms or number of cations and anions of compound remains the same as represented by its chemical formula.

There are four types of stoichiometric point defects: vacancy defect, self interstitial defect, Schottky defect and Frenkel defect.

i. Vacancy defect : During crystallization of a solid, a particle is missing from its regular site in the crystal lattice. The missing particle creates a vacancy in the lattice structure. Thus, some of the lattice sites are vacant because of missing particles as shown in Fig. 1.12. The crystal is, then, said to have a vacancy defect. The vacancy defect can also be developed when the substance is heated.

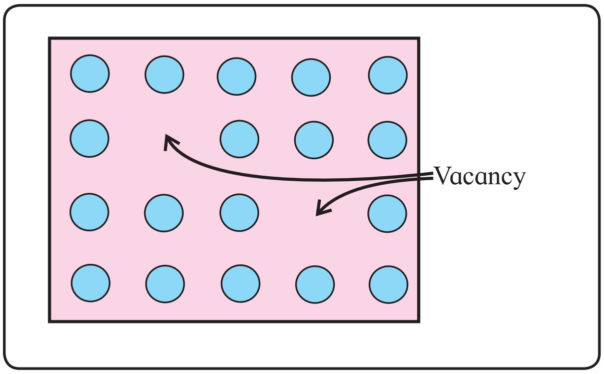


Fig. 1.12 : Vacancy defect

Due to the absence of particles, the mass of the substance decreases. However, the volume remains unchanged. As a result the density of the substance decreases.

ii. Self interstitial defect in elemental solid

Interstitial sites in a crystal are the spaces or voids in between the particles at lattice points. When some particles of a crystalline elemental solid occupy interstitial sites in the crystal structure, it is called self interstitial defect.

This defect occurs in the following two ways :

Firstly, an extra particle occupies an empty interstitial space in the crystal structure as shown in Fig. 1.13. This extra particle is same as those already present at the lattice points.

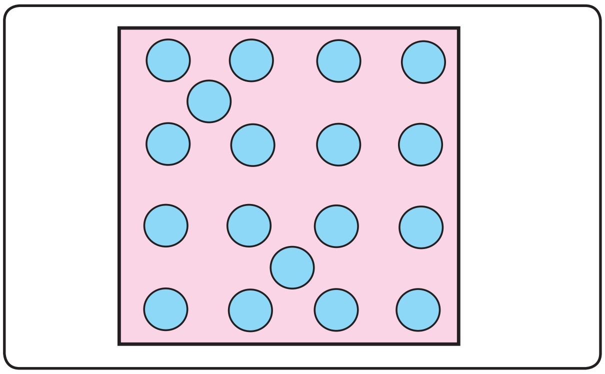


Fig. 1.13 : Self interstitial defect

The extra particles increase the total mass of substance without increasing volume. Hence its density increases.

Secondly, in an elemental solid a particle gets shifted from its original lattice point and occupies an interstitial space in the crystal as shown in the Fig. 1.14.

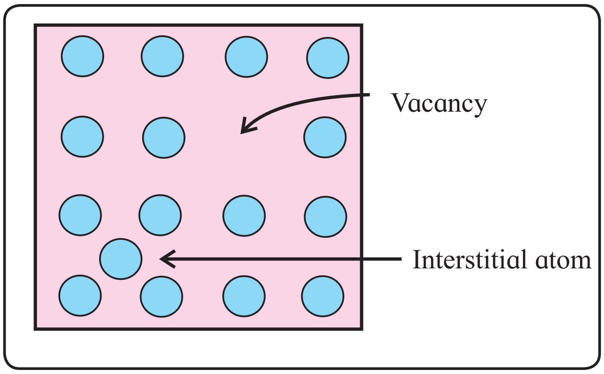


Fig. 1.14 : Self interstitial defect

It is interesting to note that in this second case, because of the displacement of a particle a vacancy defect is created at its original regular lattice site. At the same time interstitial defect results at its new position. We can, therefore, say that in this defect there is a combination of vacancy defect and self interstitial defect.

This defect preserves the density of the substance because there is neither loss nor gain in mass of a substance.

iii. Schottky defect : In an ionic solid, equal number of cations and anions are missing from their regular positions in the crystal lattice creating vacancies as shown in Fig. 1.15. It means that a vacancy created by a loss of cation is always accompanied by a vacancy formed by a loss of anion.

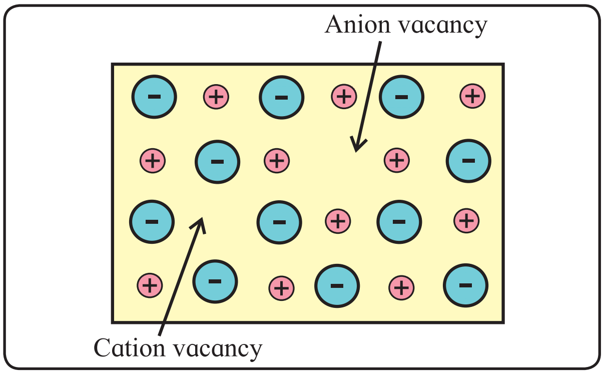


Fig. 1.15 : Schottky defect

Thus, there exist two holes per ion pair lost, one created by missing cation and the other by a missing anion. Such a paired cation-anion vacancy defect is a Schottky defect.

Conditions for the formation of Schottky defect

i. Schottky defect is found in ionic compounds with the following characteristics :

- High degree of ionic character.
- High coordination number of anion
- Small difference between size of cation and anion. The ratio r_{cation}/r_{anion} is not far below unity.

Consequences of Schottky defect

- As the number of ions decreases, mass decreases. However, volume remains unchanged. Hence, the density of a substance decreases.
- The number of missing cations and anions is equal, the electrical neutrality of the compound is preserved.

This defect is found in ionic crystals such as NaCl, AgBr and KCl.

iv. Frenkel defect : Frenkel defect arises when an ion of an ionic compound is missing from its regular lattice site and occupies interstitial position between lattice points as shown in Fig. 1.16.

The cations are usually smaller than anions. It is, therfore, more common to find the cations occupying interstitial sites. It is easier for the smaller cations to accomodate the interstitial spaces.

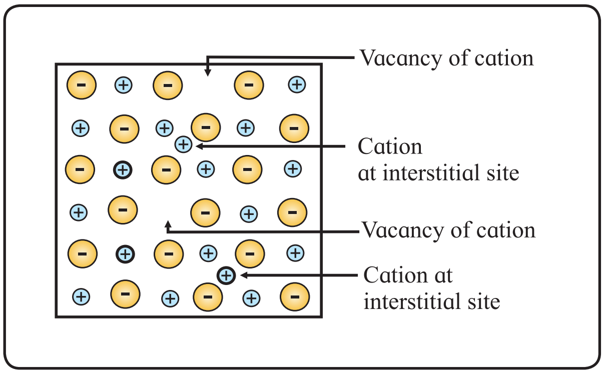


Fig. 1.16 : Frenkel defect

Do you know ?

Frenkel defect is not found in pure alkali metal halides because cations of allkali metals due to large size cannot occupy interstitial space.

It is important to note that the smaller cation is displaced from its normal site to an interstitial space. It, therefore, creates a vacancy defect at its original position and interstitial defect at its new location in the same crystal. Frenkel defect can be regarded as the combination of vacancy defect and interstitial defect.

Conditions for the formation of Frenkel defect

- Frenkel defect occurs in ionic compounds with large difference between sizes of cation and anion.
- The ions of ionic compounds must be having low coordination number.

Consequences of Frenkel defect

- As no ions are missing from the crystal lattice as a whole, the density of solid and its chemical properties remain unchanged.
- The crystal as a whole remains electrically neutral because the equal numbers of cations and anions are present.

This defect is found in ionic crystals like ZnS, AgCl, AgBr, AgI, CaF_2.

b. Impurity defect : Impurity defect arises when foreign atoms, that is, atoms different from the host atoms, are present in the crystal lattice. There are two kinds of impurity defects : Substitutional and interstitial impurity defects.

i. Substitutional impurity defect : In this defect, the foreign atoms are found at the lattice sites in place of host atoms. The regular atoms are displaced from their lattice sites by impurity atoms.

For example :

- **Solid solutions of metals (alloys) :** Brass is an alloy of Cu and Zn. In brass, host Cu atoms are replaced by impurity of Zn atoms. The Zn atoms occupy regular sites of Cu atoms as shown in Fig. 1.17.

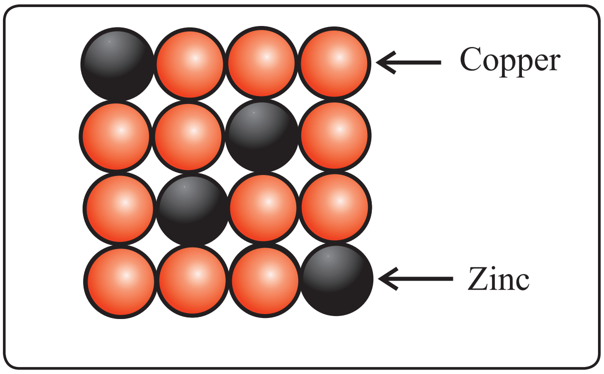


Fig. 1.17 : Brass

- **Vacancy through aliovalent impurity :**

Vacancies are created by the addition of impurities of aliovalent ions (that is, ions with oxidation state (o.s.) different from that of host ions) to an ionic solid.

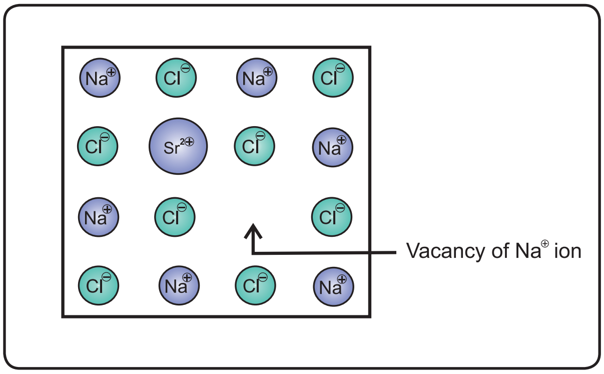


Fig. 1.18 : Vacancy through aliovalent ion

Suppose that a small amount of $SrCl_2$ impurity is added to NaCl during its crystallization. The added $Sr^{2\oplus}$ ions (O.S. + 2) occupy some of the regular sites of $Na^{\oplus}$ host ions (O.S.+1).

In order to maintain electrical neutrality, every $Sr^{2\oplus}$ ion removes two $Na^{\oplus}$ ions. One of the vacant lattice sites created by removal of two $Na^{\oplus}$ ions is occupied by one $Sr^{2\oplus}$ ion. The other site of $Na^{\oplus}$ ion remains vacant as shown in Fig. 1.18.

ii. Interstitial impurity defect : In this defect, the impurity atoms occupy interstitial spaces of lattice structure. For example in steel, Fe atoms occupy normal lattice sites. The carbon atoms are present at interstitial spaces, as shown in Fig. 1.19.

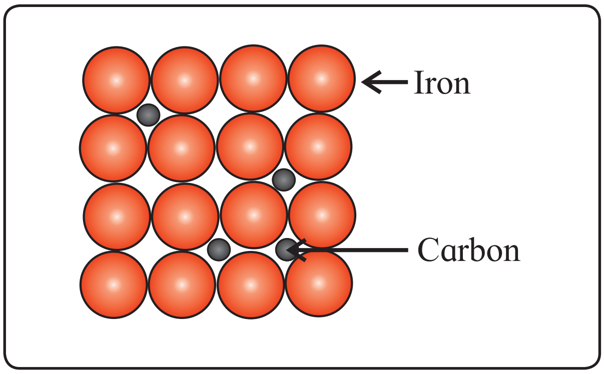


Fig. 1.19 : Stainless steel

c. Nonstoichiometric defects :

Nonstoichiometric defect arises when the ratio of number of atoms of one kind to that of other kind or the ratio of number of cations to anions becomes different from that indicated by its chemical formula. In short, stoichiometry of the compound is changed.

It is important to note that the change in stoichiometry does not cause any change in the crystal structure.

There are two types of nonstoichiometric defects

i. Metal deficiency defect : This defect is possible only in compounds of metals that show variable oxidation states.

In some crystals, positive metal ions are missing from their original lattice sites. The extra negative charge is balanced by the presence of cation of the same metal with higher oxidation state than that of missing cation.

For example, in the compound NiO one $Ni^{2\oplus}$ ion is missing creating a vacnacy at its lattice site. The deficiency of two positive charges is made up by the presence of two $Ni^{3\oplus}$ ions at the other lattice sites of $Ni^{2\oplus}$ ions as shown in Fig. 1.20. The composition of NiO then becomes $Ni_{0.97}O_{1.0}$

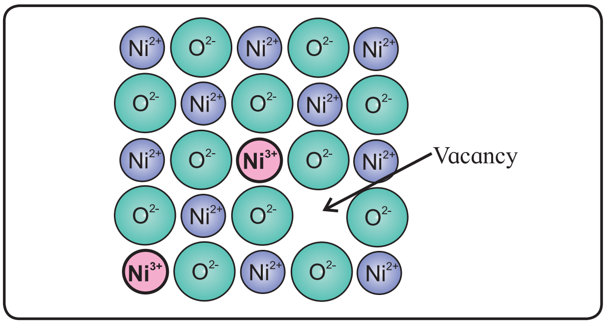


Fig. 1.20 : Nonstoichiometric $Ni_{0.97}O_{1.0}$

ii. Metal excess defect : There are two types of metal excess defects.

- **A neutral atom or an extra positive ion occupies interstitial position :** ZnO presents two ways of metal excess defect. In the first case in ZnO lattice one neutral

Zn atom is present in the interstitial space as shown in Fig. 1.21(a)

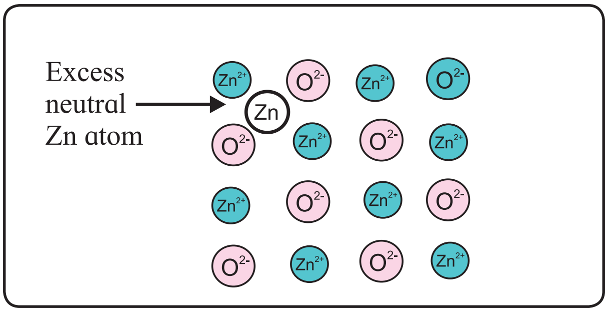


Fig. 1.21 (a) : Neutral Zn atom at interstitial site

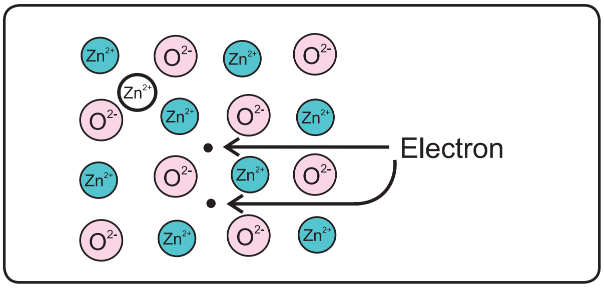


Fig. 1.21 (b) : Zn^{2+} ions and electrons at interestitial sites

In the second case, when ZnO is heated it decomposes as :

$$ZnO \longrightarrow Zn^{2\oplus} + 1/2\ O_2 + 2e^{\ominus}$$

The excess $Zn^{2\oplus}$ ions are trapped in interstitial site in the lattice. The electrons also diffuse in the crystal to occupy interstitial sites as shown in Fig. 1.21(b).

In both the cases, nonstoichiometric formula of ZnO is $Zn_{1+x}O_{1.0}$

Can you think ?

When ZnO is heated it turns yellow and returns back to original white colour on cooling. What could be the reason ?

- **By anion vacancies (Colour or F-centres)**

This type of defect imparts colour to the colourless crystal. For example, when NaCl crystal is heated in the atmosphere of sodium vapour, sodium atoms are deposited on the crystal surface. $Cl^{\ominus}$ ions diffuse to the crystal surface creating vacancies at their regular sites. These $Cl^{\ominus}$ ions combine with Na atoms on the surface to form NaCl, by releasing electron from sodium atom.

$$Na + Cl^{\ominus} \longrightarrow NaCl + e^{\ominus}$$

The electrons released diffuse into the crystal and occupy vacant sites of anions as shown in Fig. 1.22. The anion vacant sites occupied by electrons are F-centres or colour-centres.

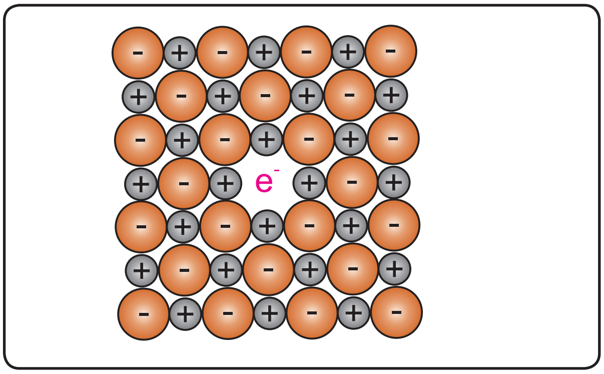


Fig. 1.22 : An F-centre in a crystal

NaCl shows yellow colour due to the formation of F-centre. The crystal of NaCl has excess Na. The nonstoichiometric formula of NaCl is the $Na_{1+x}Cl_{1.0}$

1.9 Electrical properites of solids

Can you recall ?

- What is electrical conductivity ?
- What is meant by the terms electrical 'insulator' and 'semiconductor' ?

Solids show very wide range of electrical conductivity. Accordingly solids are classified into the following three categories : conductors, insulators and semiconductors.

i. Conductors : Solids having electrical conductivities in the range 10^4 to 10^7 $Ohm^{-1}m^{-1}$ are called conductors. Metals and electrolytes (ionic solids) are examples of electrical conductors. Metals conduct electricity by movement of electrons while electrolytes conduct electricity by movement of ions. In this section we will study some aspects of electronic conduction of electricity.

ii. Insulators : Solids having low electrical conductivities in the range 10^{-20} to 10^{-10} $Ohm^{-1}m^{-1}$ are called insulators. Most nonmetals and molecular solids belong to this category.

iii. Semiconductors : Solids having electrical conductivities in the range 10^{-6} to 10^{4} Ohm^{-1} m^{-1} are semiconductors. This range is intermediate between conductors and insulators. Metalloids like silicon, germanium belong to this category.

1.9.1 Band theory : Electrical conductivities of solid metals, nonmetals and metalloids are explained in terms of band theory. A band is made of closely spaced electronic energy levels. Band formation can be correlated to formation of molecular orbitals (MOs) by interaction of atomic orbitals. (Refer to Std. XI Chemistry Textbook, chapter 5).

Can you recall ?

- How many molecular orbitals are formed by interaction of two atomic orbitals ?
- What is metallic bond ?

According to MO theory interaction of atomic orbitals of combining atoms results in formation of equal number of MOs which spread over the entire molecule. Similar to this, interaction of energy levels of electrons in the closely spaced constituent atoms in solids result in formation of bands. Band theory considers formation of two types of bands, namely, conduction band and valence band. Another important concept of band theory is the band gap.

i. Conduction band : The highest energy band containing electrons is the conduction band. It is formed by interaction of the outermost energy levels of closely spaced atoms in solids. Conduction band may be partially occupied or vacant. Electrons in conduction band are mobile and delocalized over the entire solid. They conduct electricity when electrical potential is applied.

ii. Valence band : The band having lower energy than conduction band is the valence band.

The electrons in valence band are not free to move because they are tightly bound to the respective nuclei.

iii. Band gap : The energy difference between valence band and conduction band is called band gap. Size of the band gap decides whether electrons from valence band can be promoted to vacant conduction band or not when band gap is too large to promote electrons from valence band to vacant conduction band by thermal energy, it is called **forbidden zone**. When band gap is small, electrons from higher energy levels in valence band can be promoted to conduction band by absorption of energy (such as thermal, electromagnetic).

Do you know ?

The band gap energy values of a few solids are as shown here.

Solid	E_{gap} eV
Diamond	5.47
Sodium	0
Silicon	1.12
Germanium	0.67

The electrical properties of metallic conductors, insulators and semiconductors are explained in terms of band theory as follows :

1.9.2 Metals : Metals are good conductors of electricity. The outermost electrons of all the atoms in the metallic crystal occupy conduction band. The number of electrons in conduction band of metals is large. Hence metals are good conductors of electricity. The conduction bands in metals can be further labelled as 's' band (Fig. 1.23 (a)), overlapping s and p bands (Fig. 1.23(b)) and so on. This depends on the atomic orbitals involved in band formation. Band formation in metallic conductors, thus, results in delocalization of the outermost electrons of all the metal atoms leaving behind metal ions. This is described as 'cations of metal are immersed in the sea of electrons'.

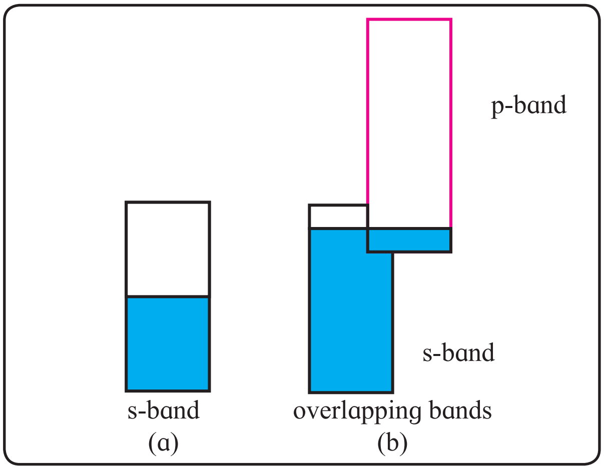


Fig. 1.23: Metalic conductor

The cations of metal atoms occupying lattice sites vibrate about their mean positions. At higher temperatures, metal cations undergo increased vibrational motion about their lattice sites. The flow of electrons is interrupted by increased vibrational motion. As a result conductivity of metals decreases with increase in temperature. (Refer to Std. XI Physics chapter 11).

Do you know ?

- **Metallic sodium** is an example of conductor where the conduction band is partially filled and there is no band gap. Electronic configuration of Na is $[Ar]3s^1$. Interaction of the partially filled 3s AOs of all the Na atoms gives rise to same number of MOs. All these closely spaced MOs together form a continuous band of energies which is called 3s band. Lower half of 3s band corresponds of BMOs and is filled while the upper half of 3s band corresponds to AMOs and is empty. There is no gap between these two halves. The 3s band in sodium is the conduction band which contains same number of electrons as the sodium atoms. This is responsible for the high conductivity of metallic sodium.
- **Metallic magnesium** is an example of conductor with overlapping bands. Electronic configuration of Mg is $[Ar]3s^2 3p^0$. Interaction of completely filled 3s AOs of all the Mg atoms gives rise to the same number of MOs all of which are filled. These together form the 3s band which is a completely filled band. Interaction of vacant 3p AOs of all the Mg atoms gives rise to the same number of vacant MOs together called 3p band. This is the vacant band. The filled 3s band and vacant 3p band overlap each other. As a result, higher energy electrons move from 3s band to 3p band.

1.9.3 Insulators : In insulators the valence band is completely filled with electrons and the conducation band is empty.

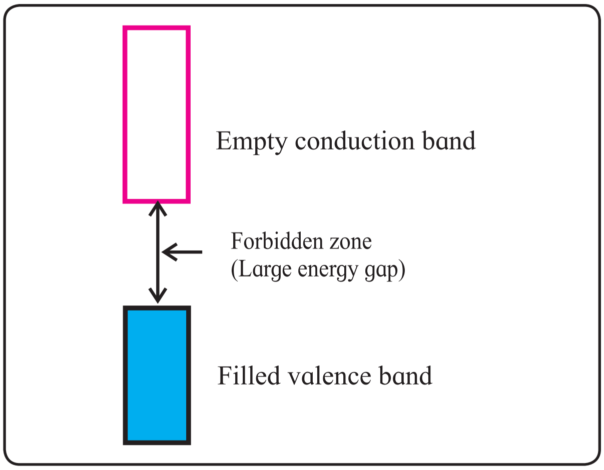


Fig. 1.24: Insulators

The valence band and conduction band in insulators are separated by a large energy gap called forbidden zone as shown in Fig. 1.24. Here, thermal energy is insufficient to promote electrons from valence band to conduction band.

As a result the conduction band remains vacant. The material is, therefore, an insulator.

1.9.4 Semiconductors :

Electrical conductivity of a semiconductor material is intermediate between that of metals and insulators. The metalloids Si and Ge are semiconductors.

Like insulators, the valence band in semiconductor is completely filled with electrons and conduction band is empty. However, the energy gap between the two bands is smaller than that in an insulator. (Fig. 1.25)

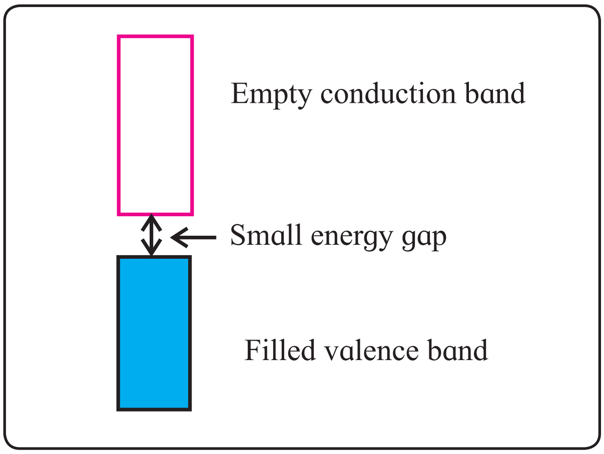


Fig. 1.25 : Semiconductors

At a temperature above absolute zero a few electrons in the valence band have enough thermal energy to jump through the small band gap and occupy higher energy conduction band. The conduction band, thus, becomes partially filled and the valence band becomes partially empty.

The electrons in conduction band are free to move. When electric potential is applied to a semiconductor, it conducts a small amount of electicity.

Such a pure semiconductor material which has a very low but finite electrical conductivity is called **intrinsic semiconductor**.

The electrical conductivity of a semiconductor increases with increasing temperature. This is because, the number of electrons with sufficient energy so as to get promoted to the conduction band increases as temperature rises. Thus, at higher temperatures, there are more mobile electrons in the conduction band and more vacancies in the valence band than at lower temperature. In fact semiconductors are insulators at low temperatures and conductors at high temperatures.

Remember...

Electrical conductivity of metals decreases and that of semiconductor increases with increasing temperature.

1.9.5 Extrinsic semiconductors and doping :

The conductivity of a semiconductor can be increased by doping. The process of addition of minute quantity of impurities to a semiconductor to increase its conductivity is called **doping**. The added impurity is called **dopant**.

A doped semiconductor, having higher conductivity than pure intrinsic semiconductor, is an **extrinsic semiconductor**.

There are two types of extrinsic semiconductors, namely, **n-type** and **p-type** semiconductors.

i. n-type semiconductor : n-type semiconductor contains increased number of electrons in the conduction bond.

An n-type semiconductor is obtained by adding group 15 element to intrinsic semiconductor which belongs to group 14.

Can you tell ?

Let a small quantity of phosphorus be doped into pure silicon.

- Will the resulting material contain the same number of total number of electrons as the original pure silicon ?
- Will the material be electrically neutral or charged ?

Consider, for example, doping of Si with phosphorus. Si has a crystal structure in which each Si atom is linked tetrahedrally to four other Si atoms. When small quantity of phosphorous is added to pure Si, the P atoms occupy some vacant sites in the lattice in place of Si atoms, as shown in Fig. 1.26. The overall crystal structure of Si remains unchanged.

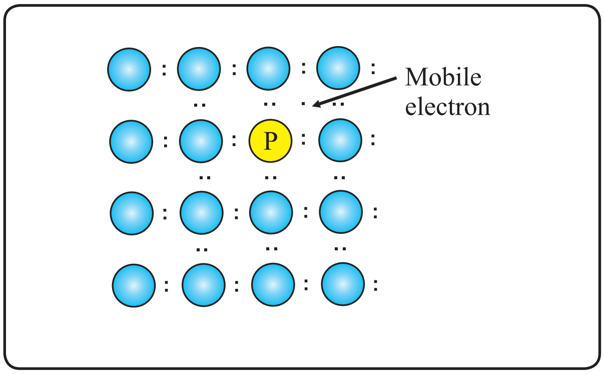


Fig. 1.26 : P atom occupying regular site of Si atom

Four of the five valence electrons of P are utilized in bonding the closest to four Si atoms. Thus, P has one extra electron than needed for bonding. Therefore, Si doped with P has more number of electrons in the conduction band than those in the conduction band in pure Si as shown in Fig. 1.27. It is thus transperent that the conductivity of Si doped with P is higher than that of pure Si. The electrons in conduction band move under the influence of an applied potential and conduct electricity.

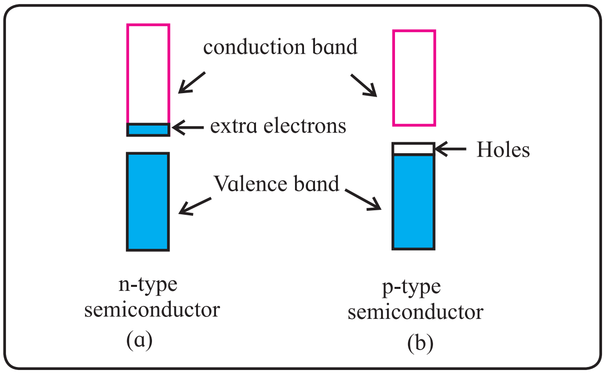


Fig. 1.27 : n-type and p-type semiconductor

Because the charge carriers are the increased number of electrons, Si or Ge doped with group 15 elements such as P, As, Sb or Bi is an n-type semiconductor.

ii. p-type semiconductor : A p-type semiconductor is produced by doping a pure semiconductor material (Si or Ge) with an impurity of group 13 elements. These elements contain less number of valence electrons than that of the pure semiconductor.

Consider, for example, pure Si doped with boron. The B atoms occupy normal positions of some of the Si atoms in the lattice as shown in Fig. 1.28. Boron atom has only three valence electrons. It does not have enough electrons to form bonds with its four Si neighbours.

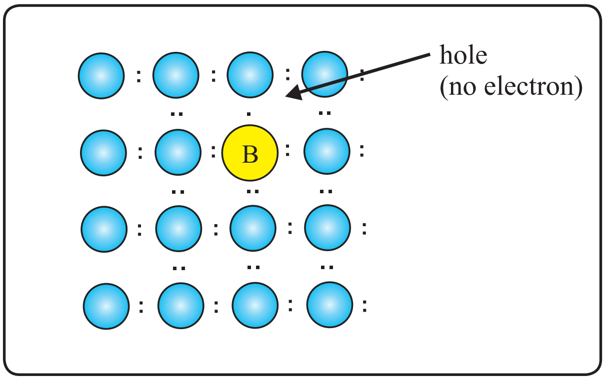


Fig. 1.28 : B atom occupying regular site of Si atom

B atom forms bonds with three Si atoms only. The missing fourth electron creates an electron vacancy. It is called a **hole**.

Fig. 1.28 shows the holes in the valence band of p-type semiconductor.

A hole has a tendency to accept electron from its close vicinity. Thus, a hole behaves as if it has a positive charge. The electrons in partially filled valence band move under the influence of an applied potential. The holes move in the opposite direction.

Remember...

- Whether intrinsic or extrinsic semiconductor, the material is electrically neutral.
- An n-type semiconductor such as Si doped with P has more electrons than those needed for bonding and thus has electrons in the partially filled conduction band.
- A p-type semiconductor such as Si doped with B has the less electrons than needed for bonding and thus has vacancies (holes) in the valence band.

Because the charge carriers are holes which behave like positive charge, the Si or Ge doped with group 13 elements like B, Ga or In, is a p-type semiconductor.

1.10 Magnetic properties of solids : Magnetic properties of solids can be understood easily in terms of classical picture of electron. The electrons spin about their own axis. The spinning electrons act like tiny magnets because their spinning action generates induced magnetic field.

If an orbital contains one electron, the unbalanced spin exhibits magnetism. However, when electrons are paired their spin is balanced and no magnetic property is observed. On the basis of magnetic properties solids are classified into three major classes : diamagnetic, paramagnetic and ferromagnetic.

i. Diamagnetic solids : The substances with all electrons paired, are weakly repelled by magnetic fields. These substances are said to be diamagnetic.

Pairing of electrons balances the spins and hence, cancels their magnetic moments.

N_2, F_2, NaCl, H_2O and benzene are some examples of diamagnetic substances.

ii. Paramagnetic solids : The substances with unpaired electrons are weakly attracted by magnetic field. These substances are called paramagnetic substances.

The spinning of unpaired electron gives rise to a magnetic moment. The substance is attracted by magnetic field because of magnetic moment. It is important to understand that these substances exhibit magnetism in presence of external magnetic field only. They lose magnetism when the external magnetic field is removed.

Oxygen, $Cu^{2\oplus}$, $Fe^{3\oplus}$, $Cr^{3\oplus}$ are some examples of paramagnetic substances.

iii. Ferromagnetism : The substances containing large number of unpaired electrons are attracted strongly by magnetic field. These substances are said to be ferromagnetic.

These substances can be permanently magnetised. They retain magnetism even after the removal of external magnetic field.

Some example of ferromagnetic substances are Fe, Co, Ni, Gd, CrO_2.

Exercises

1. Choose the most correct answer.

i. Molecular solids are
   a. crystalline solids
   b. amorphous solids
   c. ionic solids
   d. metallic solids

ii. Which of the follwong is n-type semiconductor?
   a. Pure Si
   b. Si doped with As
   c. Si doped with Ga
   d. Ge doped with In

iii. In Frenkel defect
   a. electrical neutrality of the substance is changed.
   b. density of the substance is changed.
   c. both cation and anion are missing
   d. overall electical neutrality is preserved.

iv. In crystal lattice formed by bcc unit cell the void volume is
   a. 68 % b. 74 %
   c.32 % d. 26 %

v. The coordination number of atoms in bcc crystal lattice is

a. 2 b. 4

c. 6 d. 8

vi. Which of the following is not correct?

a. Four spheres are involved in the formation of tetrahedral void.

b. The centres of spheres in octahedral voids are at the apices of a regular tetrahedron.

c. If the number of atoms is N the number of octahedral voids is 2N.

d. If the number of atoms is N/2, the number of tetrahedral voids is N.

vii. A compound forms hcp structure. Number of octahedral and tetrhedral voids in 0.5 mole of substance is respectively

a. 3.011×10^{23}, 6.022×10^{23}

b. 6.022×10^{23}, 3.011×10^{23}

c. 4.011×10^{23}, 2.011×10^{23}

d. 6.011×10^{23}, 12.022×10^{23}

vii. Pb has fcc structure with edge length of unit cell 495 pm. Radius of Pb atom is

a. 205 pm b. 185 pm

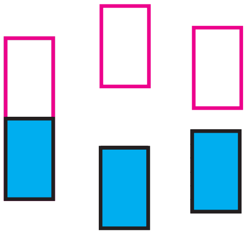
c. 260 pm d. 175 pm

2. Answer the following in one or two sentences

i. What are the types of particles in each of the four main classes of crystalline solids ?

ii. Which of the three types of packing used by metals makes the most efficient use of space and which makes the least efficient use?

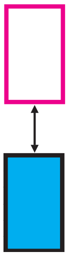
iii. The following pictures show population of bands for materials having different electrical properties. Classify them as insulator, semiconductor or a metal.



iv. What is the unit cell?

v. How does electrical conductivity of a semiconductor change with temperature? Why?

vi. The picture represents bands of MOs for Si. Label valence band, conduction band and band gap.



vii. A solid is hard, brittle and electrically nonconductor. Its melt conducts electricity. What type of solid is it?

viii. Mention two properties that are common to both hcp and ccp lattices.

ix. Sketch a tetrahedral void.

x. What are ferromagnetic substances?

3. Answer the following in brief.

i. What are valence band and conduction band?

ii. Distinguish between ionic solids and molecular solids.

iii. Calculate the number of atoms in fcc unit cell.

iv. How are the spheres arranged in first layer of simple cubic close-packed structures? How are the successive layers of spheres placed above this layer?

v. Calculate the packing efficiency of metal crystal that has simple cubic structure.

vi. What are paramagnetic substances? Give examples.

vii. What are the consequences of Schottky defect?

viii. Cesium chloride crystallizes in cubic unit cell with $Cl^{\ominus}$ ions at the corners and a $Cs^{\oplus}$ ion in the centre of the cube. How many CsCl molecules are there in the unit cell?

ix. Cu crystallizes in fcc unit cell with edge length of 495 pm. What is the radius of Cu atom?

x. Obtain the relationship between density of a substance and the edge length of unit cell.

4. **The density of iridium is 22.4 g/cm^3. The unit cell of iridium is fcc. Calculate the radius of iridium atom. Molar mass of iridium is 192.2 g/mol. (136 pm)**
5. **Aluminium crystallizes in cubic close packed structure with unit cell edge length of 353.6 pm. What is the radius of Al atom? How many unit cells are there in 1.00 cm^3 of Al? (125 pm, 2.26×10^{22})**
6. **In an ionic crystalline solid atoms of element Y form hcp lattice. The atoms of element X occupy one third of tetrahedral voids. What is the formula of the compound ? (X_2Y_3)**
7. **How are tetrahedral and octahedral voids formed?**
8. **Third layer of spheres is added to second layer so as to form hcp or ccp structure. What is the difference between the addition of third layer to form these hexagonal close-packed structures?**
9. **An element with molar mass 27 g/mol forms cubic unit cell with edge length of 405 pm. If density of the element is 2.7 g/cm^3. What is the nature of cubic unit cell? (fcc or ccp)**
10. **An element has a bcc structure with unit cell edge length of 288 pm. How many unit cells and number of atoms are present in 200 g of the element? (1.16×10^{24}, 2.32×10^{24})**
11. **Distinguish with the help of diagrams metal conductors, insulators and semiconductors from each other.**
12. **What are n-type semiconductors? Why is the conductivity of doped n-type semiconductor higher than that of pure semiconductor? Explain with diagram.**
13. **Explain with diagram, Frenkel defect. What are the conditions for its formation? What is its effect on density and electrical neutrality of the crystal?**
14. **What is an impurity defect? What are its types? Explain the formation of vacancies through aliovalent impurity with example.**

Activity :

- **With the help of plastic balls, prepare models of**
  1. **tetrahedral and octahedral voids.**
  2. **simple cubic, bcc and fcc unit cells.**
  3. **ccp and hcp lattices.**
- **Draw structures of network of carbon atoms in diamond and graphite. Discuss with reference to the following points :**
  1. **Are the outermost electrons of carbons in diamond localized or delocalized ?**
  2. **Is the energy gap between BMOs and AMOs in diamond expected to be large or small ?**

2. SOLUTIONS

2.1 Introduction

You are familiar with mixtures. The mixture is a combination of two or more substances. Air is a mixture of gases, rock is a mixture of two or more minerals and so forth.

Recall that the mixtures are (a) homogeneous in which mixing of components is uniform or (b) heterogeneous which have nonuniform mixing of components.

We studied in standard XI, that homogeneous mixtures are classified according to the size of their constituent particles as colloids or as true solutions. In this chapter we deal with the properties of homogeneous mixtures especially of true solutions.

Can you recall ?
The size of particles of colloids and those of true solutions.

The solutions are commonly found in all life processes. The body fluids are solutions. The solutions are also important for industrial processes, and many other areas.

Can you recall ?
The terms solute and solvent.

The solution is a homogeneous mixture of two or more pure substances. A true solution consists of a solvent and one or more solutes. We explore the properties of binary true solutions containing only one solute.

2.2 Types of solutions

We generally think that a solution is a either solid dissolved in liquid or a mixture of two liquids. There are other types of solutions as well. The solute and the solvent may be in any of three states namely, solid, liquid or gas. The solutions thus may involve any combination of these three states of their components. This gives rise to nine types of solutions depending on the states of solute and solvent. These are summarised in table 2.1.

Table 2.1 : Types of solutions

No.	State of solute	State of solvent	Some examples
1	Solid	Liquid	Sea water, benzoic acid in benzene, sugar in water
2	Solid	Solid	Metal alloys such as brass, bronze.
3	Solid	Gas	Iodine in air
4	Liquid	Liquid	Gasoline, ethanol in water.
5	Liquid	Solid	Amalgams of mercury with metals as mercury in silver
6	Liquid	Gas	Chloroform in nitrogen
7	Gas	Liquid	Carbonated water (CO_2 in water), oxygen in water.
8	Gas	Solid	H_2 in palladium
9	Gas	Gas	Air (O_2, N_2, Ar and other gases)

Our focus, in this chapter, will be on the solution of solid in liquid with some attention to a solution of gas in liquid. The solvent in most of the cases will be water.

Can you recall ?
The different units used to express the concentrations of solutions.

2.3 Capacity of solution to dissolve solute

Chemists need to know the capacity of solutions to dissolve a solute. Suppose that a solute is added to a solvent. It dissolves readily at first. The dissolution then slows down as more solute is added. If we continue the addition of solute, the dissolution stops. The solution at this point is said to be saturated. A dynamic equilibrium can be reached where the number of solute molecules leaving the crystal to pass into solution is equal to the number returning from the solution to the crystal. Thus,

$$\text{Solute + solvent} \underset{\text{crystallization}}{\overset{\text{dissolution}}{\rightleftharpoons}} \text{Solution}$$

A saturated solution contains maximum amount of solute dissolved in a given amount of solvent at a given temperature. A solution containing greater than the equilibrium amount of solute is said to be supersaturated solution. Such solutions are unstable. The precipitation occurs by the addition of a tiny crystal of solute and the supersaturated solution changes to saturated solution.

2.4 Solubility : The solubility of a solute is its amount per unit volume of saturated solution at a specific temperature. The solubility of a solute is its maximum concentration and expressed in the concentration units mol L^{-1}.

2.4.1 Factors affecting solubility : The extent to which a substance dissolves in a solvent varies greatly with different substances. It depends on the nature of solute and solvent, temperature and pressure.

i. Nature of solute and solvent : Generally the compounds with similar chemical character are more readily soluble in each other than those with entirely different chemical characters. The saying that ‘like dissolves like’ guides to predict the solubility of a solute in a given solvent.

Thus, substances having similar intermolecular forces are likely to be soluble in each other. Generally polar solutes dissolve in polar solvents. This is because in these, solute-solute, solute-solvent and solvent-solvent interactions are all of similar magnitude. For example, NaCl dissolves in water. The strong ion-dipole interactions of $Na^{\oplus}$ and $Cl^{\ominus}$ ions with water molecules, hydrogen bonding between water molecules and ion-ion attractions between $Na^{\oplus}$ and $Cl^{\ominus}$ ions are comparable.

Can you recall ?

The types of force between molecules.

Nonpolar organic compounds like cholesterol dissolves in nonpolar solvent such as benzene.

Can you tell ?

Why naphthalene dissolves in benzene but not in water?

Sugar dissolves in water! The dissolution of sugar in water is due to intermolecular hydrogen bonding between sugar and water.

ii. Effect of temperatute on solubility : How solubility of substance changes with temperature depends on enthalpy of solution. Many solids, for example KCl, dissolve in water by endothermic process, that is, with the absorption of heat. When temperature is increased by adding heat to the system, the solubility of substance increases according to the Le-Chatelier principle. Addition of heat causes a stress on the saturated solution. This stress favours endothermic process.

Can you recall ?

Le-Chatelier principle, exothermic and endothermic processes.

On the other hand, when the substance dissolves in water by an exothermic process its solubility decreases with an increase of temperature. The substances such as $CaCl_2$ and $Li_2SO_4.H_2O$ dissolve in water releasing heat.

Can you tell ?

Anhydrous sodium sulphate dissolves in water with the evolution of heat. What is the effect of temperature on its solubility ?

It is important to understand that there is no direct correlation between solubility and exothermicity or endothermicity. For example, dissolution of $CaCl_2$ in water is exothermic and that of NH_4NO_3 is endothermic. The solubility of these increases with the temperature.

Figure 2.1 shows the result of experimental determination of solubilities of some ionic solids in water at various temperatures. Following are some experimental observations from Fig 2.1

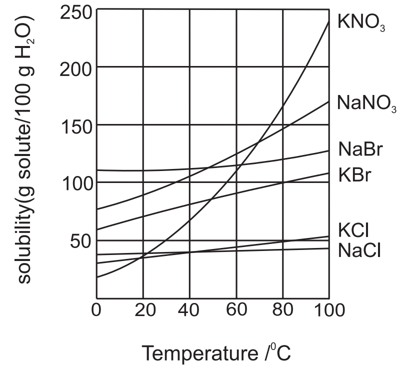


Fig. 2.1 : Variation of solubilities of some ionic solids with temperature

i. Solubilities of NaBr, NaCl and KCl change slightly with temperature.

ii. Solubilities of KNO_3, $NaNO_3$ and KBr increase appreciably with increasing temperature.

iii. Solubility of Na_2SO_4 decreases with increase of temperature.

The solubility of gases in water usually decreases with increase of temperature. When gases are dissolved in water, the gas molecules in liquid phase are condensed. The condensation is an exothermic process. The solubility of gases in water must decrease as temperature is raised.

In united states about 1000000 billion galons of water from rivers and lakes are used for industrial cooling. The cooling process heats water. The hot water then returns to rivers and lakes. The solubility of oxygen decreases in hot water thereby affecting the life of cold blooded animals like fish.

iii. Effect of pressure on solubility

Pressure has no effect on the solubilities of solids and liquids as they are incompressible. However pressure greatly affects solubility of gases in liquids. The solubility of gases increases with increasing pressure. The quantitative relationship between gas solubility in a liquid and pressure is given by Henry's law.

Henry's law: It states that the solubility of a gas in a liquid is directly proportional to the pressure of the gas over the solution. Thus,

$$S \propto P \text{ or } S = K_H P \qquad \text{.........} (2.1)$$

where, S is the solubility of the gas in mol L^{-1}, P is the pressure of the gas in bar over the solution. K_H, the proportionality constant is called Henry's law constant.

$$\text{Units of } K_H : K_H = \frac{S}{P} = \frac{\text{mol L}^{-1}}{\text{bar}} = \text{mol L}^{-1}\text{ bar}^{-1}$$

When $P = 1$ bar, $K_H = S$. Thus, K_H is the solubility of the gas in a liquid when its pressure over the solution is 1 bar.

Demonstration of Henry's law.

Before sealing the bottle of soft drink, it is pressurised with a mixture of air, CO_2 saturated with water vapour. Because of high partial pressure of CO_2, its amount dissolved in soft drink is higher than the solubility of CO_2 under normal conditions.

When the bottle of soft drink is opened, excess dissolved CO_2 comes out with effervescence.

Exceptions to Henry's law

Gases like NH_3 and CO_2 do not obey Henry's law. The reason is that these gases react with water.

$$NH_3 + H_2O \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

Because of these reactions, NH_3 and CO_2 gases have higher solubilities than expected by Henry's law.

Do you know ?

O_2 gas has very low solubility in water. However, its solubility in blood is exceedingly high. This is because of binding of O_2 molecule to haemoglobin present in blood.

$Hb + 4O_2 \rightleftharpoons Hb(O_2)_4$

Problem 2.1 : The solubility of N_2 gas in water at 25 ^{0}C and 1 bar is 6.85×10^{-4} mol L^{-1}. Calculate (a) Henry's law constant (b) molarity of N_2 gas dissolved in water under atmospheric conditions when partial pressure of N_2 in atmosphere is 0.75 bar.

Solution :

a. $K_H = \frac{S}{P} = \frac{6.85 \times 10^{-4} \text{ mol dm}^{-3}}{1 \text{ bar}}$

$= 6.85 \times 10^{-4} \text{ mol L-}^{1} \text{ bar}^{-1}$

b. $S = K_H P = 6.85 \times 10^{-4} \text{ mol L-}^{1} \text{ bar}^{-1}$

$\times 0.75 \text{ bar}$

$= 5.138 \times 10^{-4} \text{ mol L-}^{1}$

Problem 2.2 : The Henry's law constant of methyl bromide (CH_3Br), is 0.159 mol L^{-1} bar^{1} at 25^{0}C. What is the solubility of methyl bromide in water at 25^{0}C and at pressure of 130 mmHg?

Solution :

According to Henry's law

$S = K_H P$

1. $K_H = 0.159 \text{ mol L-}^{1} \text{ bar}^{1}$

2. $P = 130 \text{ mm Hg} \times \frac{1}{760 \text{ mm Hg/atm}}$

$= 0.171 \text{ atm} \times 1.013 \text{ bar/atm}$

$= 0.173 \text{ bar}$

Hence, $S = 0.159 \text{ mol L-}^{1} \text{ bar}^{1} \times 0.173 \text{ bar}$

$= 0.271 \text{ M}$

2.5 Vapour pressure of solutions of liquids in liquids :

Consider a binary solution of two volatile liquids A_1 and A_2. When the solution is placed in a closed container, both the liquids vaporize. Eventually an equilibrium is established between vapor and liquid phases. Both the components are present in the vapour phase. The partial pressure of the components are related to their mole fractions in the solution. This realationship is given by Raoult's law.

2.5.1 Raoult's law : It states that the partial vapour pressure of any volatile component of a solution is equal to the vapour pressure of the pure component multiplied by its mole fraction in the solution.

Suppose that for a binary solution of two volatile liquids A_1 and A_2, P_1 and P_2 are their partial vapour pressures and x_1 and x_2 are their mole fractions in solution. Then according to Raoult's law,

we write $P_1 = x_1 P_1^0$ and $P_2 = x_2 P_2^0$ .... (2.2)

where P_1^0 and P_2^0 are vapour pressures of pure liquids A_1 and A_2, respectively.

According to Dalton's law of partial pressures, the total pressure P above the solution is,

$$P = P_1 + P_2$$
$$= P_1^0 x_1 + P_2^0 x_2 \qquad \text{......... (2.3)}$$

Since $x_1 = 1 - x_2$, the Eq. (2.2) can also be written as

$$P = P_1^0 (1-x_2) + P_2^0 x_2$$
$$= P_1^0 - P_1^0 x_2 + P_2^0 x_2$$
$$= (P_2^0 - P_1^0)\, x_2 + P_1^0 \qquad \text{......... (2.4)}$$

Because P_1^0 and P_2^0 are constants, a plot of P versus x_2 is a straight line as shown in the Fig 2.2. The figure also shows the plots of P_1 versus x_1 and P_2 versus x_2 according to the equations 2.2. These are straight lines passing through origin.

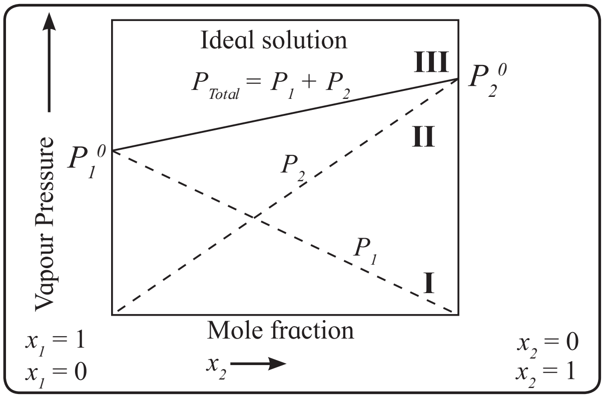


Fig. 2.2 : Variation of vapour pressure with mole fraction of solute

i. For P_1^0 versus x_2 straight line,

$P = P_1^0$ at $x_2 = 0$ and $P = P_2^0$ at $x_2 = 1$

ii. For P_1 versus x_1 straight line,

$P_1 = 0$ at $x_1 = 0$ and $P_1 = P_1^0$, at $x_1 = 1$

iii. For P_2 versus x_2 straight line,

$P_2 = 0$ at $x_2 = 0$ and $P_2 = P_2^0$ at $x_2 = 1$

Composition of vapour phase :

The composition of vapour in equilibrium with the solution can be determined by Dalton's law of partial pressures.

If we take y_1 and y_2 as the mole fractions of two components in the vapour, then $P_1 = y_1P$ and $P_2 = y_2P$

where P_1 and P_2 are the partial pressures of two components in the vapour and P is the total vapour pressure.

Problem 2.3 : The vapour pressures of pure liquids A and B are 450 mm Hg and 700 mm Hg, respectively at 350 K. Find the composition of liquid and vapour if total vapour pressure is 600 mm.

Solution : i. Compositions of A and B in the solution are x_1 and x_2

$$P = (P_2^0 - P_1^0)\,x_2 + P_1^0$$

$P_1^0 = 450$ mmHg, $P_2^0 = 700$ mmHg,

$P = 600$ mmHg

Hence, 600 mm Hg = (700 mm Hg - 450 mm Hg)x_2 + 450 mm Hg

$= 250x_2 + 450$

$600 - 450 = 150 = 250x_2$ or $x_2 = \frac{150}{250} = 0.6$

$x_1 = 1-x_2 = 1-0.6 = 0.4$

ii. Compositions of A and B in vapour are y_1 and y_2 respectively.

$P_1 = y_1P$ and $P_2 = y_2P$, $P_1 = P_1^0x_1$ and

$P_2 = P_2^0x_2$

$$y_1 = \frac{P_1}{P} = \frac{P_1^0x_1}{P} = \frac{450 \text{ mm Hg} \times 0.4}{600 \text{ mmHg}}$$

$= 0.3$

$y_2 = 1 - y_1 = 1 - 0.3 = 0.7$

2.5.2 Ideal and nonideal solutions

1. Ideal solutions

i. Ideal solutions obey Raoult's law over entire range of concentrations.

ii. No heat is evolved or absorbed when two components forming an ideal solution are mixed. Thus, the enthalpy of mixing is zero. $\Delta_{\text{mix}}H = 0$

iii. There is no volume change when two components forming an ideal solution are mixed. Thus volume of an ideal solution is equal to the sum of volumes of two components taken for mixing.

$\Delta_{\text{mix}}V = 0$

iv. In an ideal solution solvent-solute, solute-solute and solvent-solvent molecular interactions are comparable.

v. The vapour pressure of ideal solution always lies between vapour pressures of pure components, as shown in Fig. 2.2.

It is important to understand that perfectly ideal solutions are uncommon and solutions such as benzene + toluene behave nearly ideal.

2. Nonideal solutions

i. These solutions do not obey Raoult's law over the entire range of concentrations.

ii. The vapour pressures of these solutions can be higher or lower than those of pure components.

iii. Deviation from the Raoult's law : These solutions show two types of deviation from the Raoult's law.

A. Positive deviations from Raoult’s law -

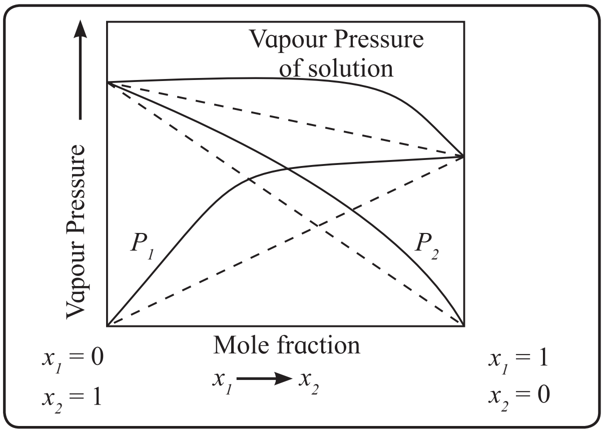


Fig. 2.3 : Positive derivations from Raoult's law

The solutions in which solute-solvent intermolecular attractions are weaker than those between solute-solute molecules and solvent-solvent molecules, exhibit positive deviations. The vapour pressures of such solutions are higher than those of pure components as shown in Fig. 2.3. The solutions of ethanol and acetone, carbon disulphide and acetone show positive deviations from the Raoult’s law.

B. Negative deviations from Raoult’s law

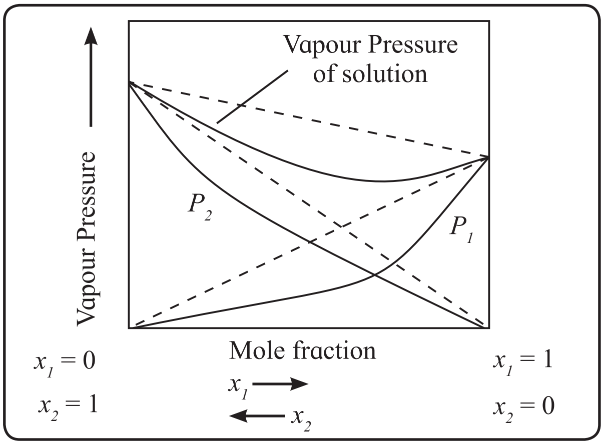


Fig. 2.4 : Negative derivations from Raoult's law

The solutions in which the interactions between solvents and solute molecules are stronger than solute-solute or solvent-solvent interactions, exhibit negative deviations.The vapour pressures of such solutions are lower than those of pure components as shown in Fig. 2.4. The solutions of phenol and aniline, chloroform and acetone exhibit negative deviations from the Raoult’s law.

2.6 Colligative properties of nonelectrolyte solutions :

The physical properties of solutions that depend on the number of solute particles in solutions and not on their nature are called colligative properties. These are

1. vapour pressure lowering
2. boiling point elevation
3. freezing point depression
4. osmotic pressure

While dealing with colligative properties of nonelectrolyte solutions, the relatively dilute solutions with concentrations 0.2 M or less are considered.

2.7 Vapour pressure lowering :

When a liquid in a closed container is in equilibrium with its vapours, the pressure exerted by the vapour on the liquid is its vapour pressure.

Can you recall ?
Vapour pressure of a liquid

i. Experiments have shown that when a nonvolatile, nonionizable solid is dissolved in a liquid solvent, the vapour pressure of the solution is lower than that of pure solvent. In other words the vapour pressure of a solvent is lowered by dissolving a nonvoltile solute into it. When the solute is nonvolatile it does not contribute to the vapour pressure above the solution. Therefore, the vapour pressure of solution is equal to the vapour pressure of solvent above the solution.

ii. If P_1^0 is the vapour pressure of pure solvent and P_1 is the vapour pressure of solvent above the solution, then

$$P_1 < P_1^0$$

The vapour pressure lowering is

$$\Delta P = P_1^0 - P_1 \qquad \text{.........} \ (2.5)$$

iii. Why the vapour pressure of solution containing nonvolatile solute is lower than that of pure solvent? Vapour pressure of a liquid depends on the ease with which the molecules escape from the surface of liquid. When nonvolatile solute is dissolved in a solvent, some of the surface molecules of solvent are replaced by nonvolatile solute molecules. These solute molecules do not contribute to vapour above the solution. Thus, the number of solvent molecules available for vaporization per unit surface area of solution is less than the number at the surface of pure solvent. As a result the solvent molecules at the surface of solution vaporize at a slower rate than pure solvent. This results in lowering of vapour pressure.

2.7.1 Raoult's law for solutions of nonvolatile solutes : We saw in section 2.5.1 that Raoult's law expresses the quantitative relationship between vapour pressure of solution and vapour pressure of solvent.

In solutions of nonvolatile solutes, the law is applicable only to the volatile solvent. The law states that the vapour pressure of solvent over the solution is equal to the vapour pressure of pure solvent multiplted by its mole fraction in the solution. Thus

$$P_1 = P_1^0 x_1$$

A plot of P_1 versus x_1 is a straight line as shown in Fig. 2.5

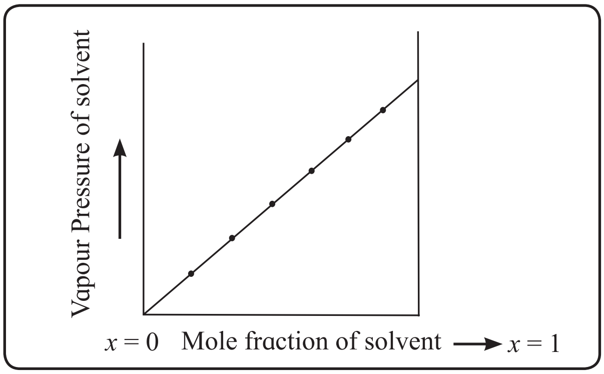


Fig. 2.5 : Variation of vapour pressure of solution with mole fraction of solvent

For a binary solution containing one solute,

$$x_1 = 1 - x_2$$

It therefore, follows that

$$\begin{aligned} P_1 &= P_1^0 x_1 \\ &= P_1^0 (1 - x_2) \\ &= P_1^0 - P_1^0 x_2 \end{aligned}$$

or $$P_1^0 - P_1 = P_1^0 x_2$$

The Eq. (2.5) defines $P_1^0 - P_1$ as ΔP, the lowering of vapour pressure. Hence

$$\Delta P = P_1^0 x_2 \qquad \text{......... (2.6)}$$

The Eq. (2.6) shows that ΔP depends on x_2 that is on number of solute particles. Thus, ΔP, the lowering of vapour pressure is a colligative property.

2.7.2 Relative lowering of vapour pressure

The ratio of vapour pressure lowering of solvent divided by the vapour pressure of pure solvent is called relative lowering of vapour pressure. Thus

Relative vapour pressure lowering

$$= \frac{\Delta P}{P_1^0} = \frac{P_1^0 - P_1}{P_1^0} \qquad \text{......... (2.7)}$$

The Eq. (2.6) shows that

$$\frac{\Delta P}{P_1^0} = x_2 = \frac{P_1^0 - P_1}{P_1^0} \qquad \text{......... (2.8)}$$

Thus, relative lowering of vapour pressure is equal to the mole fraction of solute in the solution. Therefore, relative vapour pressure lowering is a colligative property.

2.7.3 Molar mass of solute from vapour pressure lowering : We studied that the relative lowering of vapour pressure is equal to the mole fraction x_2 of solute in the solution.

From Eq. 2.6, it follows that :

$$\frac{\Delta P}{P_1^0} = x_2 \qquad \text{......... (2.8)}$$

Recall (Chapter 10, sec 10.5.6) that the mole fraction of a component of solution is equal to its moles divided by the total moles in the solution. Thus,

$$x_2 = \frac{n_2}{n_1 + n_2}$$

where n_1 and n_2 are the moles of solvent and solute respectively, in the solution.

We are concerned only with dilute solutions hence $n_1 >> n_2$ and $n_1+n_2 \approx n_1$. The mole fraction x_2 is then given by

$$x_2 = \frac{n_2}{n_1} \quad \text{and}$$

$$\frac{\Delta P}{P_1^0} = \frac{n_2}{n_1} \qquad \text{.........} (2.9)$$

Suppose that we prepare a solution by dissolving W_2 g of a solute in W_1 g of solvent. The moles of solute and solvent in the solution are then,

$$n_2 = \frac{W_2}{M_2} \text{ and } n_1 = \frac{W_1}{M_1} \qquad \text{.........} (2.10)$$

where M_1 and M_2 are molar masses of solvent and solute, respectively. Substitution of Eq. (2.10) into Eq. (2.9) yields

$$x_2 = \frac{\Delta P}{P_1^0} = \frac{W_2/M_2}{W_1/M_1}$$

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{\Delta P}{P_1^0} = \frac{W_2 M_1}{M_2 W_1} \qquad \text{.........} (2.11)$$

Knowing all other quantities, molar mass of solute M_2 can be calculated.

Problem 2.4 : A solution is prepared by dissolving 394 g of a nonvolatile solute in 622 g of water. The vapour pressure of solution is found to be 30.74 mm Hg at 30 ^{0}C. If vapour pressure of water at 30 ^{0}C is 31.8 mm Hg, what is the molar mass of solute?

Solution :

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{\Delta P}{P_1^0} = \frac{W_2 M_1}{M_2 W_1}$$

$W_2 = 394$ g, $W_1 = 622$ g, $M_1 = 18$ g mol^{-1},

$P_1 = 30.74$ mm Hg, $P_1^0 = 31.8$ mm Hg

Substitution of these quantities into the equation gives

$$\frac{31.8 \text{ mm Hg} - 30.74 \text{ mm Hg}}{31.8 \text{ mm Hg}} = \frac{394 \text{ g} \times 18 \text{ gmol}^{-1}}{M_2 \times 622 \text{ g}}$$

$$0.0333 = \frac{11.4 \text{ g mol}^{-1}}{M_2}$$

$$M_2 = \frac{11.4 \text{ g mol}^{-1}}{0.0333} = 342 \text{ g mol}^{-1}$$

Problem 2.5 : The vapour pressure of pure benzene (molar mass 78 g/mol) at a certain temperature is 640 mm Hg. A nonvolatile solute of mass 2.315 g is added to 49 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molar mass of solute?

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

$P_1^0 = 640$ mm Hg, $P_1 = 600$ mm Hg,
$W_1 = 49$ g, $W_2 = 2.315$ g

$$\text{Hence, } \frac{640 \text{ mm Hg- } 600 \text{ mm Hg}}{640 \text{ mm Hg}}$$

$$= \frac{2.315 \text{ g - } 78 \text{ g/mol}}{40 \text{ g} \times M_2}$$

$$\frac{40 \text{ mm Hg}}{640 \text{ mm Hg}} = \frac{2.315 \text{ g - } 78 \text{ g/mol}}{40 \text{ g} \times M_2}$$

$$M_2 = \frac{2.315 \text{ g - } 78 \text{ g/mol} \times 640 \text{ mm Hg}}{40 \text{ mm Hg} \times 40 \text{ g}}$$

$$= 72.23 \text{ g mol}$$

2.8 Boiling point elevation : Recall that the boiling point of liquid is the temperature at which its vapour pressure equals the applied pressure. For liquids in open containers the applied pressure is atmospheric pressure.

It has been found that the boiling point of a solvent is elevated by dissolving a nonvolatile solute into it. Thus, the solutions containing nonvolatile solutes boil at temperatures higher than the boiling point of a pure solvent.

If T_b^0 is the boiling point of a pure solvent and T_b that of a solution, $T_b > T_b^0$. The difference between the boiling point of solution and that of pure solvent at any given constant pressure is called the boiling point elevation.

$$\Delta T_b = T_b - T^0_b \qquad \text{.........}(2.12)$$

2.8.1 Boiling point elevation as a consequence of vapour pressure lowering : To understand the elevation of boiling point, let us compare the vapour pressures of solution and those of pure solvent. The vapour pressures of solution and of pure solvent are plotted as a function of temperature as shown in Fig. 2.6.

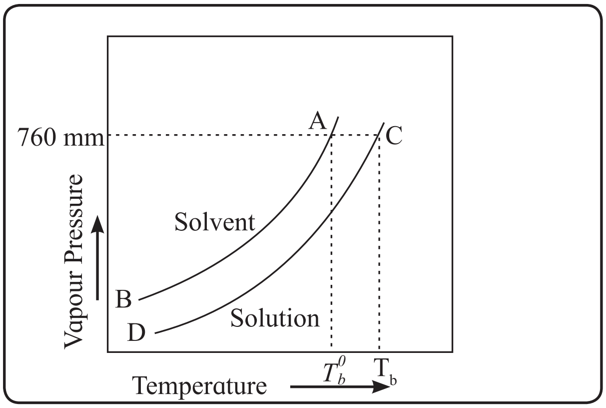


Fig. 2.6 : Vapour pressure-temperature of pure solvent and solution

As stated in section 2.7 that at any temperature the vapour pressure of solution is lower than that of pure solvent. Hence, the vapour pressure-temperature curve of solution (CD) lies below that of solvent (AB). The difference between the two vapour pressures increases as temperature and vapour pressure increase as predicted by the equation

$$\Delta P = x_2 P_1^0$$

The intersection of the curve CD with the line corresponding to 760 mm is the boiling point of solution. The similar intersection of the curve AB is the boiling point of pure solvent. It is clear from the figure that the boiling point (T_b) of the solution is higher than that of pure solvent (T_b^0)

At the boiling point of a liquid, its vapour pressure is equal to 1 atm. In order to reach boiling point, the solution and solvent must be heated to a temperature at which their respective vapour pressures attain 1 atm. At any given temperature the vapour pressure of solution is lower than that of pure solvent. Hence, the vapour pressure of solution needs higher temperature to reach 1 atm than that needed for vapour pressure of solvent. In other words the solution must be heated to higher temperature to cause it to boil than the pure solvent.

2.8.2 Boiling point elevation and concentration of solute : The boiling point elevation is directly proportional to the molality of the solution. Thus,

$$\Delta T_b \propto m \quad \text{or} \quad \Delta T_b = K_b m \quad \text{......... (2.13)}$$

where m is the molality of solution. The proportionality constant K_b is called boiling point elevation constant or molal elevation constant or ebullioscopic constant.

If $m = 1$, $\Delta T_b = K_b$

Thus, ebullioscopic constant is the boiling point elevation produced by 1 molal solution.

Units of K_b : $K_b = \frac{\Delta T_b}{m} = \frac{\text{K}}{\text{mol kg}^{-1}} = \text{K kg mol}^{-1}$

Remember...

K_b and ΔT_b are the differences between two temperatures. Hence, their values will be the same in K or in ^{0}C.

We are dealing with the systems whose temperature is not constant. Therefore, we cannot express the concentration of solution in molarity which changes with temperature whereas molality is temperature independent.

Therefore the concentration of solute is expressed in mol/kg (molality) rather than mol/L (molarity).

2.8.3 Molar mass of solute from boiling point elevation

The Eq. (2.13) is $\Delta T_b = K_b m$

Suppose we prepare a solution by dissolving W_2 g of solute in W_1 g of solvent.

Moles of solute in W_1 g of solvent $= \frac{W_2}{M_2}$ where M_2 is the molar mass of solute.

Mass of solvent $= W_1 \text{ g} = \frac{W_1 \text{g}}{1000 \text{ g/kg}} = \frac{W_1}{1000}$ kg

Recall the expression of molality, m.

$$m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

$$= \frac{W_2/M_2 \text{ mol}}{W_1/1000 \text{ kg}} = \frac{1000\, W_2}{M_2 W_1} \text{ mol kg}^{-1} \text{ ....(2.14)}$$

Substitution of this value of m in Eq. (2.13) gives

$$\Delta T_b = K_b \frac{1000\ W_2}{M_2 W_1}$$

Hence,

$$M_2 = \frac{1000\ K_b W_2}{\Delta T_b W_1} \qquad \text{......... (2.15)}$$

Problem 2.6 : The normal boiling point of ethyl acetate is 77.06 ^{0}C. A solution of 50 g of a nonvolatile solute in 150 g of ethyl acetate boils at 84.27 ^{0}C. Evaluate the molar mass of solute if K_b for ethyl acetate is 2.77 ^{0}C kg mol^{-1}.

Solution :

$$M_2 = \frac{1000\ K_b W_2}{\Delta T_b W_1}$$

$W_2 = 50$ g, $W_1 = 150$ g,

$\Delta T_b = T_b - T^0_b = 84.27\ ^0\text{C} - 77.06\ ^0\text{C}$

$= 7.21^0\text{C} = 7.21$ K

$K_b = 2.77\ ^0\text{C kg mol}^{-1} = 2.77 \text{ K kg mol}^{-1}$

Substitution of these in above equation

$$M_2 = \frac{1000 \text{ g Kg}^{-1} \times 2.77 \text{ K kg mol}^{-1} \times 50 \text{ g}}{7.21 \text{ K} \times 150 \text{ g}}$$

$= 128$ g mol^{-1}

Problem 2.7 : 3.795 g of sulphur is dissolved in 100 g of carbon disulfide. This solution boils at 319.81 K. What is the molecular formula of sulphur in solution? The boiling point of the solvent is 319.45 K.

(Given that K_b for CS_2 = 2.42 K kg mol^{-1} and atomic mass of S = 32 u

$$M_2 = \frac{1000\ K_b W_2}{\Delta T_b W_1}$$

$W_1 = 100$ g, $W_2 = 3.795$ g

$\Delta T_b = (319.81 - 319.45)\text{K} = 0.36$ K

$$M_2 = \frac{1000 \text{ g kg}^{-1} \times 2.42 \text{ K kg mol}^{-1} \times 3.795 \text{ g}}{0.36 \text{ K} \times 100 \text{ g}}$$

$= 255.10$ g mol^{-1}

Atomic mass of S = 32 u

Therefore number of atoms in a molecule of sulphur

$$= \frac{\text{molar mass of S}}{\text{atomic mass of S}} = \frac{255.1}{32}$$

$= 7.92 \approx 8$

The molecular formula would be S_8 in CS_2

2.9 Depression in freezing point

Recall that freezing point of a liquid is the temperature at which liquid and solid are in equilibrium and the two phases have the same vapour pressure.

The general experimental observation is that the freezing point of a solvent is lowered by dissolving a nonvolatile solute into it. Thus, freezing point of solution containing a nonvolatile solute is lower than that of pure solvent.

If T_f^0 is the freezing point of pure solvent and T_f that of a solution in which nonovolatile solute is dissolved, $T_f^0 > T_f$. The difference between the freezing point of pure solvent and that of the solution is depression in freezing point.

Thus $\Delta T_f = T_f^0 - T_f$ .... (2.16)

2.9.1 Freezing point depression as a consequence of vapour pressure lowering

The effect of dissolution of a nonvolatile solute into a solvent on freezing point of solvent can be understood in terms of the vapour pressure lowering.

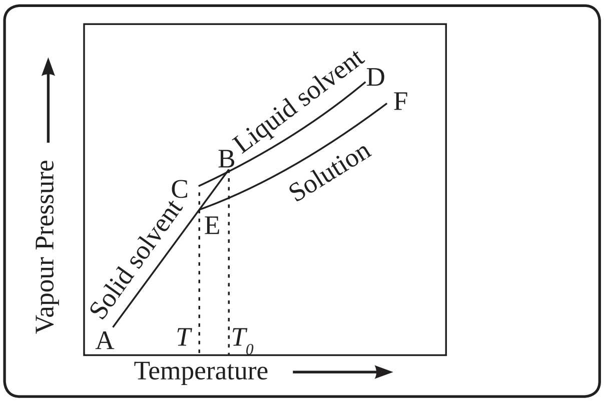


Fig. 2.7 : Variation of vapour pressure with temperature of pure solvent, solid solvent and solution

Consider the vapoure pressure-temperature diagram as shown in Fig. 2.7. The diagram consists of three curves. AB is the vapour pressure curve of solid solvent while CD is the vapour pressure curve of pure liquid solvent. EF is the vapour pressure curve of solution that always lies below the pure solvent.

It is important to note that solute does not dissolve in solid solvent.

The curves AB and CD intersect at point B where solid and liquid phases of pure solvent are in equilibrium. The two phases have the same vapour pressure at B. The temperature corresponding to B is the freezing point of solvent (T_f^0).

Similarly at E, the point of intersection of EF and AB, the solid solvent and solution are in equilibrium. They have the same vapour pressure at E. The temperature corresponding to E is the freezing point of solution, T_f.

It is clear from the figure that freezing point of solution T_f is lower than that of pure solvent T_f^0. It is obvious because the vapour pressure curve of solution lies below that of solvent.

Why freezing point of solvent is lowered by dissolving a nonvolatile solute into it? At the freezing point of a pure liquid the attractive forces among molecules are large enough to cause the change of phase from liquid to solid.

In a solution, the solvent molecules are separated from each other because of solute molecules. Thus, the separation of solvent molecules in solution is more than that in pure solvent. This results in decreasing the attractive forces between solvent molecules. Consequently, the temperature of the solution is lowered below the freezing point of solvent to cause the phase change.

2.9.2 Freezing point depression and concentration of solute : As varified experimentally for a dilute solution the freezing point depression (ΔT_f) is directly proportional to the molality of solution. Thus,

$$\Delta T_f \propto m \quad \text{or} \quad \Delta T_f = K_f m \text{ .... } (2.17)$$

The proportionality constant K_f is called freezing point depression constant or cryoscopic constant.

If $m = 1$, $\Delta T_f = K_f$. The cryoscopic constant thus is the depression in freezing point produced by 1 molal solution of a nonvolatile solute.

Unit of K_f: $\frac{\Delta T_f}{m} = \frac{\text{K or } ^0\text{C}}{\text{mol kg}^{-1}}$

$= \text{K kg mol}^{-1}$ or $^0\text{C kg mol}^{-1}$

2.9.3 Molar mass of solute from freezing point depression

Refer to Eq. (2.17), $\Delta T_f = K_f m$

The molality m of the solution is given by Eq. (2.14) as

$$\text{m} = \frac{1000\text{W}_2}{M_2\text{W}_1}$$

Substitution of Eq. (2.14) into Eq. (2.17) gives

$$\Delta T_f = K_f \frac{1000\text{W}_2}{M_2\text{W}_1}$$

$$\text{Hence, } M_2 = \frac{1000K_f\text{W}_2}{\Delta T_f\text{W}_1} \text{ .... } (2.18)$$

Problem 2.8 : 1.02 g of urea when dissolved in 98.5 g of certain solvent decreases its freezing point by 0.211K. 1.609 g of unknown compound when dissolved in 86 g of the same solvent depresses the freezing point by 0.34 K. Calculate the molar mass of the unknown compound.

(Molar mass of urea = 60 g mol^{-1})

Solution :

Urea	Unknown compound
$\text{W}_2 = 1.02$ g	$\text{W}_2' = 1.609$ g
$\text{W}_1 = 98.5$ g	$\text{W}_1' = 86$ g
$\Delta T_f = 0.211$ K	$\Delta T_f' = 0.34$ K
$M_2 = 60$ gmol^{-1}	$M_2' = ?$

$$1000K_f = \frac{M_2 \times \Delta T_f \times \text{W}_1}{\text{W}_2}$$

$$1000K_f = \frac{M_2' \times \Delta T_f' \times W_1'}{W_2'}$$

$$= \frac{60 \text{ g mol}^{-1} \times 0.211 \text{ K} \times 98.5 \text{ g}}{1.02 \text{ g}}$$

$$= \frac{M_2' \times 0.34\text{K} \times 86 \text{ g}}{1.609 \text{ g}}$$

$$\frac{1247.01 \text{ g K mol}^{-1}}{1.02} = \frac{M_2' \times 29.24 \text{ K}}{1.609}$$

$$1222.55 \text{ g K mol}^{-1} = M_2' \times 18.173$$

$$M_2' = \frac{1222.55 \text{ g K mol}^{-1}}{18.175 \text{ K}} = 67.3 \text{ g mol}^{-1}$$

2.10 Osmotic pressure : Besides the boiling point elevation and freezing point depression, the osmotic pressure is associated with vapour pressure lowering and can be used to determine molar masses of dissolved solutes.

Semipermeable membrane : The osmotic pressure phenomenon involves the use of semipermeable membrane.

It is a film such as cellophane which has pores large enough to allow the solvent molecules to pass through them. These pores are small enough not to allow the passage of large solute molecules or ions of high molecular mass through them. The semipermeable membrane selectively allows passage of solvent molecules.

2.10.1 Osmosis : When a solution and pure solvent or two solutions of different concentrations are separated by a semipermeable membrane, the solvent molecules pass through the membrane.

What is the direction of flow of solvent molecules? It is important to understand that the passage of solvent molecules through the semipermeable membrane takes place in both directions, since solvent is on both sides of the membrane. However, the rate of passage of solvent molecules into the solution or from more dilute solution to more concentrated solution is found to be greater than the rate in the reverse direction. This is favourable since the vapour pressure of solvent is greater than that of solution. The net spontaneous flow of solvent molecules into the solution or from more dilute solution to more concentrated solution through a semipermeable membrane is called osmosis. See Fig. 2.8.

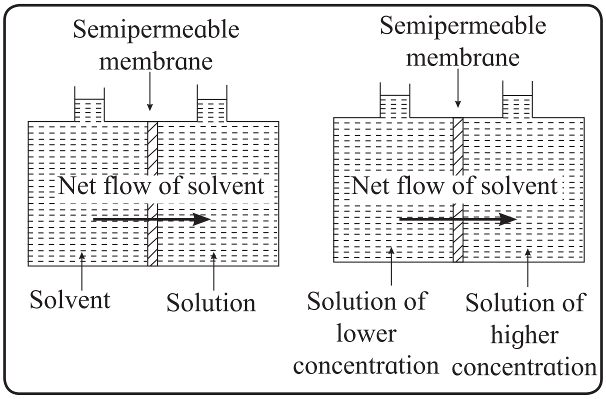


Fig. 2.8 : Osmosis

As a result of osmosis, the amount of liquid on the pure solvent side or more dilute solution side decreases. Consequently, the amount of liquid on the other side increases. This results in decrease of the concentration of solution.

2.10.2 Osmotic pressure : Osmosis can be demonstrated with experimental set up shown in Fig. 2.9

Semipermeable membrane is firmly fastened across the mouth of thistle tube. The solution of interest is placed inside an inverted thistle tube. This part of the tube and the membrane are then immersed in a container of pure water.

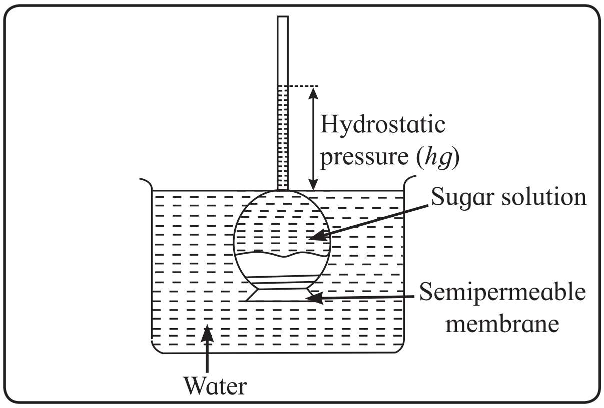


Fig. 2.9 : Osmosis and osmotic pressure

As a result, some of the solvent passes through the membrane into the solution. It causes the liquid level in the tube to rise. The liquid column in the tube creates hydrostatic pressure that pushes the solvent back through the membrane into the container. The column of liquid in the tube continues to rise and eventually stops rising. At this stage hydrostatic pressure developed is sufficient to force solvent molecules back through the membrane into the container at the same rate they enter the solution.

An equilibrium is thus established where rates of forward and reverse passages are equal. The height of liquid column in the tube remains constant. This implies that the hydrostatic pressure has stopped osmosis.

Remember...

It is important to note that osmotic pressure is not the pressure produced by a solution. It exists only when the solution is separated from the solvent by a suitable kind of semipermeable membrane.

The hydrostatic pressure that stops osmosis is an osmotic pressure (π) of the solution. The hydrostatic pressure is equal to hρg where *h* is the height of liquid column in the tube, ρ is density of solution and *g* is acceleration due to gravity.

2.10.3 Isotonic, hypertonic and hypotonic solutions

i. Isotonic solutions : Two or more solutions having the same osmotic pressure are said to be **isotonic solutions**.

For example, 0.1 M urea solution and 0.1 M sucrose solution are isotonic because their osmotic pressures are equal. Such solutions have the same molar concentrations but different concentrations in g/L. If these solutions are separated by a semipermeable membrane, there is no flow of solvent in either direction.

ii. Hypertonic and hypotonic solutions :

If two solutions have unequal osmotic pressures, the more concentrated solution with higher osmotic pressure is said to be **hypertonic solution**.

The more dilute solution exhibiting lower osmotic pressure is said to be **hypotonic solution**.

For example, if osmotic pressure of sucrose solution is higher than that of urea solution, the sucrose solution is hypertonic to urea solution, and the urea solution is hypotonic to sucrose solution.

2.10.4 Osmotic pressure and concentration of solution

For very dilute solutions, the osmotic pressure follows the equation,

$$\pi = \frac{n_2 RT}{V} \qquad \text{.........} (2.19)$$

where *V* is the volume of a solution in dm^3 containing n_2 moles of nonvolatile solute. R is the gas constant equal to 0.08206 dm^3 atm $K^{-1}mol^{-1}$ and π is osmotic pressure in atm.

The term n_2/V is concentration in molarity (*M*). Eq. (2.19) thus can be written as

$$\pi = MRT \qquad \text{.........} (2.20)$$

Note that the solute concentration is expressed in molarity while calculating osmotic pressure rather than molality. The reason is that osmotic pressure measurements are made at a specific constant temperature. It is not necessary to express concentration in a temperature independent unit like molality.

2.10.5 Molar mass of solute from osmotic pressure

Consider Eq. (2.19) $\pi = \frac{n_2 RT}{V}$

If the mass of solute in *V* litres of solution is W_2 and its molar mass is M_2 then $n_2 = W_2/M_2$. With this value of n_2, Eq. (2.19) becomes

$$\pi = \frac{W_2 RT}{M_2 V} \text{ or } M_2 = \frac{W_2 RT}{\pi V} \qquad \text{.........}(2.21)$$

Remember...

Osmotic pressure is much larger and therefore more precisely measurable property than other colligative properties. It is therefore, useful to determine molar masses of very expensive substances and of the substances that can be prepared in small quantities.

2.10.6 Reverse osmosis : As mentioned earlier osmosis is a flow of solvent through a semipermeable membrane into the solution.

The direction of osmosis can be reversed by applying a pressure larger than the osmotic pressure.

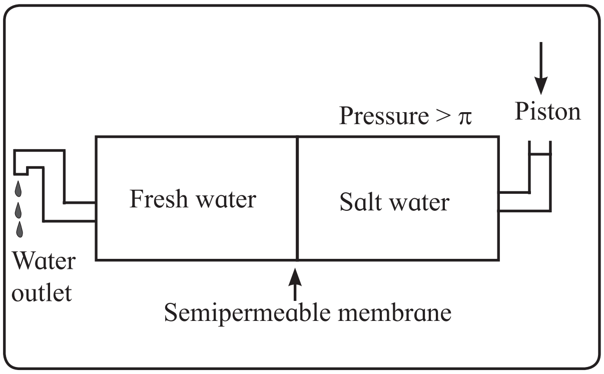


Fig. 2.10 : Reverse osmosis

The pure solvent then flows from solution into pure solvent through semi-permeable membrane. This phenomenon is called reverse osmosis. Fig. 2.10 shows the schematic set up for reverse osmosis. Fresh water and salty water are separated by a semipermeable membrane. When the pressure larger than the osmotic pressure of solution is applied to solution, pure water from salty water passes into fresh pure water through the membrane.

Problem 2.9 : What is the molar mass of a solute if a solution prepared by dissolving 0.822 g of it in 300 mdm^3 of water has an osmotic pressure of 149 mm Hg at 298 K?

Solution :

$$M_2 = \frac{W_2RT}{\pi V}$$

$W_2 = 0.822$ g

$R = 0.08205$ dm^3 atm K^{-1} mol^{-1}

$T = 298$K

$$\pi = 149\ (\text{mmHg}) = \frac{149\ (\text{mmHg})}{760\ (\text{mmHg/atm})}$$

$= 0.196$ atm

$V = 300$ mL $= 0.3$dm^3

$$M_2 = \frac{0.822\ \text{g} \times 0.08205\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 298\text{K}}{0.196\ \text{atm} \times 0.3\text{dm}^3}$$

$= 342$ g mol^{-1}

2.11 Collgative properties of electrolytes

Can you recall ?

Electrolytes and nonelectrolytes.

Solutions of nonelectrolytes in water exhibit colligative properties as described in the preceeding sections. These solutions also give, for the dissolved substances, the molar masses expected from their chemical formulae.

The study of colligative properties of electrolytes, however, require a different approach than used for colligative properties of nonelectrolytes. Following are the experimental observations for the colligative behavior of electrolytes.

i. The solutions of elctrolytes also exhibit colligative properties which do not obey the relations of nonelectrolytes.

ii. The colligative properties of the solutions of electrolytes are greater than those to be expected for solutions of nonelectrolytes of the same concentration.

iii. The molar masses of electrolytes in aqueous solutions determined by colligative properties are found to be considerably lower than the formula masses.

Why the colligative properties of electrolyte solutions are greater than those for nonelectrolyte solutions of the same concentration? Recall that electrolytes dissociate into two or more ions when dissolved in water whereas nonelctrolytes do not. Stated differently, one formula unit of electrolyte dissolved in water produces two or more ions. Consequently number of particles in solution increases.

The colligative properties of electrolyte solutions are thus higher than the nonelectrolyte solutions.

If 1.25 m sucrose solution has ΔT_f of 2.32^0C, what will be the expected value of ΔT_f for 1.25m $CaCl_2$ solution?

For example, when NaCl is dissolved in water, it produces two ions, $Na^{\oplus}$ and $Cl^{\ominus}$, whereas sucrose does not dissociate. It is expected then that the colligative property of 0.1 *m* NaCl is twice that of 0.1 *m* sucrose solution.

2.11.1 van't Hoff factor(i)

To obtain the colligative properties of electrolyte solutions by using relations for nonelectrolytes, van't Hoff suggested a factor *i*. It is defined as the ratio of colligative property of a solution of electrolyte divided by the collogative property of nonelectrlyte solution of the same concentration. Thus

$$i = \frac{\text{colligative property of elctrolyte solution}}{\text{colligative property of nonelectrolyte solution of the same concentration}}$$

$$= \frac{(\Delta T_f)}{(\Delta T_f)_0} = \frac{(\Delta T_b)}{(\Delta T_b)_0} = \frac{(\Delta P)}{(\Delta P)_0} = \frac{(\pi)}{(\pi)_0} \quad \text{......... (2.22)}$$

where quantities without subscript refer to electrolytes and those with subscript to nonelectrolytes.

The van't Hoff factor *i* is also defined in an alternative but exactly equivalent manner as

$$i = \frac{\text{actual moles of particles in solution after dissociation}}{\text{moles of formula units dissolved in solution}} \quad \text{......... (2.23)}$$

$$= \frac{\text{formula mass of substance}}{\text{observed molar mass of substance}}$$

$$= \frac{M_{\text{theoretical}}}{M_{\text{observed}}} \quad \text{......... (2.24)}$$

Thus, *i* is equal to 1 for nonelctrolyte, 2 for KNO_3 and NaCl, 3 for Na_2SO_4 and $CaCl_2$ and so forth. The colligative properties of these electrolytes are, therefore, twice and thrice respectively as those of noneletrolytes of the same concentration.

The foregoing arguments are valid only for infinitely dilute solutions where the dissociation of electrolytes is complete.

In reality especially at high concentrations, the colligative properties of strong electrolytes and their i values are usually smaller than expected. The reason is that the electrostatic forces between oppositely charged ions bring about the formation of ion pairs. Each ion pair consists of one or more cations and one or more anions held together by electrostatic attractive forces. This results in decrease in the number of particles in solution causing reduction in the expected i value and colligative properties.

2.11.2 Modification of expressions of colligative properties : The expressions of colligative properties mentioned earlier for nonelectrolytes are to be modified so as to make them applicable for electrolyte solutions. The modified equations are

i. $\Delta P = i \; P_1^0 x_2 = i\dfrac{W_2 M_1}{M_2 W_1}$

ii. $\Delta T_b = iK_b m = i\dfrac{1000\, K_b W_2}{M_2 W_1}$

iii. $\Delta T_f = i\; K_f m = i\; \dfrac{1000\, K_f W_2}{M_2 W_1}$

iv. $\pi = i\; MRT = i\dfrac{W_2 RT}{M_2 V}$

2.11.3 van't Hoff factor and degree of dissociation : A discussion of colligative properties of electrolytes in the preceeding sections is based on the fact that the elctrolytes are completely dissociated in their aqueous solutions. This is approximately true for solutions of strong electrolytes and not for weak electrolytes that dissociate to a small extent. The weak electrolytes involve the concept of degree of dissociation (∝), that changes the van't Hoff factor.

Relation between van't Hoff factor and degree of dissociation

Consider an elctrolyte A_xB_y that dissociates in aqueous solution as

$$\mathrm{AxBy} \rightleftharpoons x\,\mathrm{A}^{y\oplus} + y\,\mathrm{B}^{z\ominus} \quad ....(2.25)$$

Initially : 1 mol 0 0

At equilibrium :

(1-∝) mol (x ∝ mol) (y ∝) mol

If ∝ is the degree of dissociation of elctrolyte, then the moles of cations are ∝x and those of anions are ∝y at equilibrium. We have dissolved just 1 mol of electrolyte initially. ∝ mol of eletrolyte dissociates and (1-∝) mol remains undissociated at equilibrium.

Total moles after dissociation

$$= (1-\propto) + (x\propto) + (y\propto)$$

$$= 1+\propto(x+y-1)$$

$$= 1+\propto(n-1) \quad .... (2.26)$$

where, n = x+y = moles of ions obtained from dissociation of 1 mole of electrolyte.

The van't Hoff factor given by Eq. (2.23) is

$$i = \frac{\text{actual moles of particles in solution after dissociation}}{\text{moles of formula units dissolved in solution}}$$

$$= \frac{1 + \propto(n-1)}{1}$$

Hence $i = 1 + \propto(n-1)$ or $\propto = \dfrac{i-1}{n-1}$ ....(2.27)

Problem 2.10 : 0.2 *m* aqueous solution of KCl freezes at -0.680 ⁰C. Calculate van't Hoff factor and osmotic pressure of solution at 0 ⁰C.(K_f = 1.86 K kg mol⁻¹)

Solution :

$$\Delta T_f = K_f m$$

$$\Delta T_f = 0.680\ \mathrm{K},\ m = 0.2\ \mathrm{mol\ kg^{-1}}$$

$$(\Delta T_f)_0 = 1.86\ \mathrm{K\ kg\ mol^{-1}} \times 0.2\ \mathrm{mol\ kg^{-1}}$$

$$= 0.372\ \mathrm{K}$$

$$i = \frac{(\Delta T_f)}{(\Delta T_f)_0} = \frac{0.680\ \mathrm{K}}{0.372\ \mathrm{K}} = 1.83$$

$$(\pi)_0 = MRT$$

$$= \frac{n_2}{V} RT$$

$$= \frac{0.2\ \mathrm{mol} \times 0.08205\ \mathrm{L\ atm.mol^{-1}K^{-1}} \times 273\mathrm{K}}{1\mathrm{L}}$$

$$= 4.48\ \mathrm{atm}$$

$$i = 1.83 = \frac{\pi}{\pi_0}$$

$$\pi = 1.83 \times 4.48\ \mathrm{atm}$$

$$\pi = 8.2\ \mathrm{atm}$$

Problem 2.11 : 0.01*m* aqueous formic acid solution freezes at -0.021 ⁰C. Calculate its degree of dissociation. K_f = 1.86 K kg mol⁻¹

$$\Delta T_f = i K_f m$$

$$\Delta T_f = 0\ ^0\mathrm{C} - (-0.021\ ^0\mathrm{C}) = 0.021\ ^0\mathrm{C}$$

$$m = 0.01\ \mathrm{mol\ kg^{-1}}$$

$$0.021 = i \times 1.86\ \mathrm{K\ kg\ mol^{-1}} \times 0.01\ \mathrm{mol\ kg^{-1}}$$

$$\mathrm{i} = \frac{0.021}{1.86 \times 0.01} = 1.13$$

$$\propto = \frac{\mathrm{i} - 1}{\mathrm{n} - 1} = \mathrm{i} - 1 \text{ because } \mathrm{n} = 2$$

Hence, ∝ = 1.13 - 1 = 0.13 = 13%

Problem 2.12 : 3.4 g of $CaCl_2$ is dissolved in 2.5 L of water at 300 K. What is the osmotic pressure of the solution? van't Hoff factor for $CaCl_2$ is 2.47.

Solution :

$$\pi = iMRT = \mathrm{i}\frac{W_2 RT}{M_2 V}$$

i = 2.47, W_2 = 3.4 g, R = 0.08206 dm³atm K⁻¹ mol⁻¹, T = 300 K, M_2 = 40+71 = 111 g mol⁻¹, V = 2.5 dm³

$$\pi = 2.47 \times \frac{3.4\ \cancel{\mathrm{g}} \times 0.08206\ \cancel{\mathrm{dm}}^3\mathrm{atm}\ \cancel{\mathrm{K}}^{-1}\cancel{\mathrm{mol}}^{-1} \times 300\ \cancel{\mathrm{K}}}{111\ \cancel{\mathrm{g}}\ \cancel{\mathrm{mol}}^{-1} \times 2.5\ \cancel{\mathrm{dm}}^3}$$

$$= 0.745\ \mathrm{atm}$$

Problem 2.13 : Which of following solutions will have maximum boiling point elevation and which have minimum freezing point depression assuming the complete dissociation? (a) 0.1 *m* KCl (b) 0.05 *m* NaCl (c) 1*m* $AlPO_4$ (d) 0.1 *m* $MgSO_4$

Solution : Boiling point elevation and freezing point depression are colligative properties that depend on number of particles in solution. The solution having more number of particles will have large boiling point elevation and that having less number of particles would show minimum freezing point depression.

(a) $\underset{0.1m}{KCl} \longrightarrow \underset{0.1m}{K^{\oplus}} + \underset{0.1m}{Cl^{\ominus}}$ Total particles in solution = 0.2 mol

(b) $\underset{0.05m}{NaCl} \longrightarrow \underset{0.05m}{Na^{\oplus}} + \underset{0.05m}{Cl^{\ominus}}$ Total particles in solution = 0.1 mol

(c) $\underset{1m}{AlPO_4} \longrightarrow \underset{1m}{Al^{3\oplus}} + \underset{1m}{PO_4^{3\ominus}}$ Total particles in solution = 2.0mol

(d) $\underset{0.1m}{MgSO_4} \longrightarrow \underset{0.1m}{Mg^{2\oplus}} + \underset{0.1m}{SO_4^{2\ominus}}$ Total particles in solution = 0.2mole

$AlPO_4$ solution contains highest moles and hence highest number particles and in turn, the maximum ΔT_b. NaCl solution has minimum moles and particles. It has minimum ΔT_f.

Arrange the following solutions in order of increasing osmotic pressure. Assume complete ionization. a) 0.5m Li_2SO_4 b) 0.5m KCl c) 0.5m $Al_2(SO_4)_3$ d) 0.1m $BaCl_2$.

Problem 2.14 : Assuming complete dissociation, calculate the molality of an aqueous solution of KBr whose freezing point is -2.95⁰C. K_f for water is 1.86 K kg mol^{-1}

Solution :

$$KBr = K^{\oplus} + Br^{\ominus},$$

$$i = \frac{\text{moles of particles after dissociation}}{\text{moles of particles dissolved}}$$

$$= \frac{2}{1} = 2$$

$$\Delta T_f = iK_f m$$

$$\Delta T_f = 0\ ^0C - (-2.95\ ^0C) = 2.95\ ^0C$$

$$m = \frac{\Delta T_f}{iK_f} = \frac{2.95\ K}{2 \times 1.86\ K\ kg\ mol^{-1}}$$

$$= 0.793\ mol\ kg^{-1}$$

Exercises

1. Choose the most correct option.

i. The vapour pressure of a solution containing 2 moles of a solute in 2 moles of water (vapour pressure of pure water = 24 mm Hg) is

a. 24 mm Hg b. 32 mm Hg
c. 48 mm Hg d. 12 mm Hg

ii. The colligative property of a solution is

a. vapour pressure b. boiling point
c. osmotic pressure d. freezing point

iii. In calculating osmotic pressure the concentration of solute is expressed in

a. molarity b. molality
c. mole fraction d. mass percent

iv. Ebullioscopic constant is the boiling point elevation when the concentration of solution is

a. 1m b. 1M c. 1 mass%
d. 1 mole fraction of solute.

v. Cryoscopic constant depends on

a. nature of solvent
b. nature of solute
c. nature of solution
d. number of solvent molecules

vi. Identify the correct statement

a. vapour pressure of solution is higher than that of pure solvent.
b. boiling point of solvent is lower than that of solution
c. osmotic pressure of solution is lower than that of solvent
d. osmosis is a colligative property.

vii. A living cell contains a solution which is isotonic with 0.3 M sugar solution. What osmotic pressure develops when the cell is placed in 0.1 M KCl solution at body temperature?

a. 5.08 atm   b. 2.54 atm
c. 4.92 atm   d. 2.46 atm

viii. The osmotic pressure of blood is 7.65 atm at 310 K. An aqueous solution of glucose isotonic with blood has the percentage (by volume)

a. 5.41 %   b. 3.54 %
c. 4.53 %   d. 53.4 %

ix. Vapour pressure of a solution is

a. directly proportional to the mole fraction of the solute
b. inversely proportional to the mole fraction of the solute
c. inversely proportional to the mole fraction of the solvent
d. directly proportional to the mole fraction of the solvent

x. Pressure cooker reduces cooking time for food because

a. boiling point of water involved in cooking is increased
b. heat is more evenly distributed in the cooking space
c. the higher pressure inside the cooker crushes the food material
d. cooking involves chemical changes helped by a rise in temperature.

xi. Henry's law constant for a gas CH_3Br is 0.159 moldm^{-3} atm at 250 ^{0}C. What is the solubility of CH_3Br in water at 25 ^{0}C and a partial pressure of 0.164 atm?

a. 0.0159 mol L^{-1} b. 0.164 mol L^{-1}
c. 0.026 M   d. 0.042 M

xii. Which of the following statement is NOT correct for 0.1 M urea solution and 0.05 M sucrose solution?

a. osmotic pressure exhibited by urea solution is higher than that exhibited by sucrose solution
b. urea solution is hypertonic to sucrose solution
c. they are isotonic solutions
d. sucrose solution is hypotonic to urea solution

2. Answer the following in one or two sentences

i. What is osmotic pressure?

ii. A solution concentration is expressed in molarity and not in molality while considering osmotic pressure. Why?

iii. Write the equation relating boiling point elevation to the concentration of solution.

iv. A 0.1 m solution of K_2SO_4 in water has freezing point of -4.3 ^{0}C. What is the value of van't Hoff factor if K_f for water is 1.86 K kg mol^{-1}?

v. What is van't Hoff factor?

vi. How is van't Hoff factor related to degree of ionization?

vii. Which of the following solutions will have higher freezing point depression and why ?

a. 0.1 *m* NaCl b. 0.05 *m* $Al_2(SO_4)_3$

viii. State Raoult's law for a solution containing a nonvolatile solute

ix. What is the effect on the boiling point of water if 1 mole of methyl alcohol is added to 1 dm^3 of water? Why?

x. Which of the four colligative properties is most often used for molecular mass determination? Why?

3. Answer the following.

i. How vapour pressure lowering is related to a rise in boiling point of solution?

ii. What are isotonic and hypertonic solutions?

iii. A solvent and its solution containing a nonvolatile solute are separated by a semipermable membrane. Does the flow of solvent occur in both directions? Comment giving reason.

iv. The osmotic pressure of $CaCl_2$ and urea solutions of the same concentration at the same temperature are respectively 0.605 atm and 0.245 atm. Calculate van't Hoff factor for $CaCl_2$

v. Explain reverse osmosis.

vi. How molar mass of a solute is determined by osmotic pressure measurement?

vii. Why vapour pressure of a solvent is lowered by dissolving a nonvolatile solute into it?

viii. Using Raoult's law, how will you show that $\Delta P = P_1^0 x_2$? Where x_2 is the mole fraction of solute in the solution and P_1^0 vapour pressure of pure solvent.

ix. While considering boiling point elevation and freezing point depression a solution concentration is expressed in molality and not in molarity. Why?

4. Derive the relationship between degree of dissociation of an electrolyte and van't Hoff factor.

5. What is effect of temperature on solubility of solids in water? Give examples.

6. Obtain the relationship between freezing point depression of a solution containing nonvolatile nonelctrolyte and its molar mass.

7. Explain with diagram the boiling point elevation in terms of vapour pressure lowering.

8. Fish generally needs O_2 concentration in water at least 3.8 mg/L for survival. What partial pressure of O_2 above the water is needed for the survival of fish? Given the solubility of O_2 in water at 0^0C and 1 atm partial pressure is 2.2×10^{-3} mol/L (0.054 atm)

9. The vapour pressure of water at 20 ^{0}C is 17 mm Hg. What is the vapour pressure of solution containing 2.8 g urea in 50 g of water? (16.17 mm Hg)

10. A 5% aqueous solution (by mass) of cane sugar (molar mass 342 g/mol) has freezing point of 271K. Calculate the freezing point of 5% aqueous glucose solution. (269.06 K)

11. A solution of citric acid $C_6H_8O_7$ in 50 g of acetic acid has a boiling point elevation of 1.76 K. If K_b for acetic acid is 3.07 K kg mol^{-1}, what is the molality of solution? (0.573 m)

12. An aqueous solution of a certain organic compound has a density of 1.063 gmL^{-1}, an osmotic pressure of 12.16 atm at 25^{0}C and a freezing point of -1.03^{0}C. What is the molar mass of the compound? (334 g/mol)

13. A mixture of benzene and toluene contains 30% by mass of toluene. At 30^{0}C, vapour pressure of pure toluene is 36.7 mm Hg and that of pure benzene is 118.2 mm Hg. Assuming that the two liquids form ideal solutions, calculate the total pressure and partial pressure of each constituent above the solution at 30^{0}C. (86.7 mm, P = 96.5 mm)

14. At 25 ^{0}C a 0.1 molal solution of CH_3COOH is 1.35 % dissociated in an aqueous solution. Calculate freezing point and osmotic pressure of the solution assuming molality and molarity to be identical. (-0.189 ^{0}C, 2.48 atm)

15. A 0.15 m aqueous solution of KCl freezes at -0.510 ^{0}C. Calculate *i* and osmotic pressure at 0 ^{0}C. Assume volume of solution equal to that of water (1.83, 6.15 atm)

Activity :

Boil about 100 mL of water in a beaker. Add about 10 to 15 g of salt (NaCl) to the boiling water. Write your observations and conclusions.

3. IONIC EQUILIBRIA

Can you recall ?

- What is chemical equilibrium ?
- What are electrolytes ?

3.1 Introduction : The equilibrium between ions and unionized molecules in solution is called ionic equilibrium. The principles of chemical equilibrium we studied in standard XI will be applied to ionic equilibria. In this chapter with the help of these principles we determine equilibrium constants and concentrations of ions and unionized species. In particular examine the following ionic equilibria :

- $H^{\oplus}$ and $OH^{\ominus}$ ions and unionized water molecules.
- Ionization of weak acids and weak bases.
- Reactions between ions of salt and ions of water.
- Solid salt and its ions in water.

3.2 Types of electrolyte : The substances which give rise to ions when dissolved in water are electrolytes. The non electrolytes are those which do not ionize and exist as molecules in aqueous solutions.

The electrolytes are classified into strong and weak electrolytes. This classification is based on their extent of ionisation in dilute aqueous solutions.

3.2.1 Strong electrolyte : The electrolytes ionizing completely or almost completely are strong electrolytes. For example : strong acids, strong bases and salts.

3.2.2 Weak electrolyte : The electrolytes which dissociate to a smaller extent in aqueous solution are weak electrolytes. Weak acids and weak bases belong to this class.

The weak electrolytes dissociate only partially in dilute aqueous solutions. An equilibrium thus can be established between the ions and nonionized molecules. The ionization reaction therein is represented as double arrow($\rightleftharpoons$) between the ions and nonionized molecule.

Use your brain power

Which of the following is a strong electrolyte ?

HF, AgCl, $CuSO_4$, CH_3COONH_4, H_3PO_4.

3.2.3 Degree of dissociation ($\propto$) : The degree of dissociation of an electrolyte is defined as a fraction of total number of moles of the electrolyte that dissociates into its ions when the equilibrium is attained. It is denoted by symbol $\propto$ and given by

$$\propto = \frac{\text{number of moles dissociated}}{\text{total number of moles}} \qquad \text{......(3.1)}$$

$$\text{Percent dissociation} = \propto \times 100 \qquad \text{....... (3.2)}$$

If 'c' is the molar concentration of an electrolyte the equilibrium concentration of cation or anion is ($\propto \times c$) mol dm^{-3}.

3.3 Acids and Bases : Acids and bases are familiar chemical compounds. Acetic acid is found in vinegar, citric acid in lemons, magnesium hydroxide in antacids, ammonia in household cleaning products. The tartaric acid is present in tamarind paste. These are some acids and bases we come across in everyday life.

3.3.1 Arrhenius theory of acids and bases

According to this theory acids and bases are defined as follows :

Acid : Acid is a substance which contains hydrogen and gives rise to $H^{\oplus}$ ions in aqueous solution. For example :

$$HCl\ (aq) \xrightarrow{water} H^{\oplus}(aq) + Cl^{\ominus}(aq)$$

$$CH_3COOH(aq) \overset{water}{\rightleftharpoons} CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

Arrhenius described $H^{\oplus}$ ions in water as bare ions; they hydrate in aqueous solutions and thus represented as hydronium ions $H_3O^{\oplus}$. We herewith conveniently represent them as $H^{\oplus}$.

Do you know ?

Hydrochloric acid, HCl present in the gastric juice is secreted by our stomach and is essential for digestion of food.

Base : Base is a substance that contains OH group and produces hydroxide ions ($OH^{\ominus}$) ions in aqueous solution. For example,

$$NaOH\ (aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$$

Arrhenius theory accounts for properties of different acids and bases and is applicable only to aqueous solutions. It does not account for the basicity of NH_3 and Na_2CO_3 which do not have OH group.

3.3.2 Bronsted - Lowry theory :

J. N. Bronsted and T. M. Lowry (1923) proposed a more general theory known as the Bronsted-Lowry proton transfer theory. According to this theory acids and bases are defined as follows.

Acid : Acid is a substance that donates a proton ($H^{\oplus}$) to another substance.

Base : Base is a substance that accepts a proton ($H^{\oplus}$) from another substance.

For example :

$$\underset{Acid_1}{HCl} + \underset{Base_2}{NH_3} \rightleftharpoons \underset{Acid_2}{NH_4^{\oplus}} + \underset{Base_1}{Cl^{\ominus}}$$

In the above reaction HCl and $NH_4^{\oplus}$ are proton donors and act as acids. The NH_3 and $Cl^{\ominus}$ are proton acceptors and act as bases. Further it follows that the products of the Bronsted-Lowry acid-base reactions are acids bases.

The base produced by accepting the proton from an acid is the conjugate base of that acid. Likewise the acid produced when a base accepts a proton is called the conjugate acid of that base. A pair of an acid and a base differing by a proton is said to be a **conjugate acid-base pair**.

$$\underset{Acid_1}{HCl(aq)} + \underset{Base_2}{H_2O(l)} \rightleftharpoons \underset{Acid_2}{H_3O^{\oplus}(aq)} + \underset{Base_1}{Cl^{\ominus}(aq)}$$

conjugate acid-base pair$_2$

conjugate acid-base pair$_1$

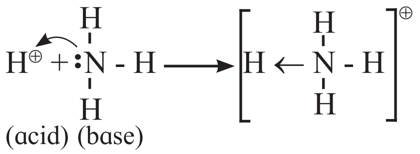
3.3.3 Lewis theory :

A more generalized acid-base concept was put forward by G.N. Lewis in 1923. According to this theory acids and bases are defined as follows.

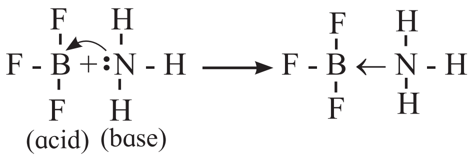
Acid : Any species that accepts a share in an electron pair is called Lewis acid.

Base : Any species that donates a share in an electron pair is called Lewis base.

For example :



$$\underset{(acid)}{H^{\oplus}} + \underset{(base)}{:NH_3} \longrightarrow [H \leftarrow NH_3]^{\oplus}$$



$$\underset{(acid)}{BF_3} + \underset{(base)}{:NH_3} \longrightarrow F_3B \leftarrow NH_3$$

Use your brain power

- All Bronsted bases are also Lewis bases, but all Bronsted acids are not Lewis acids. Explain.

Amphoteric nature of water : Water has the ability to act as an acid as well as a base. Such behaviour is known as amphoteric nature of water. For example :

$$H_2O(l) + NH_3(aq) \rightleftharpoons OH^{\ominus}(aq) + NH_4^{\oplus}(aq)$$

Acid

$$H_2O(l) + HCl(aq) \rightleftharpoons H_3O^{\oplus}(aq) + Cl^{\ominus}(aq)$$

Base

H_2O acts as an acid towards NH_3 and as a base towards HCl. Therefore H_2O is amphoteric.

3.4 Ionisation of acids and bases

Acids and bases are classified as strong acids and strong bases, weak acids and weak bases on the basis of their **extent of dissociation**. Strong acids and bases are almost completely dissociated in water. For example :

$$HCl\ (aq) \longrightarrow H^{\oplus}(aq) + Cl^{\ominus}\ (aq)$$

$$NaOH\ (aq) \longrightarrow Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

Typical strong acids are HCl, HNO_3, H_2SO_4, HBr and HI while typical strong bases may include NaOH and KOH.

Weak acids and weak bases are partially dissociated in water. The solution of a weak acid or a weak base contains undissociated molecules along with a small number of ions at equilibrium. For example :

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^{\oplus}(aq) + OH^{\ominus}(aq)$$

Note that HCOOH, HF, H_2S are examples of weak acids while $Fe(OH)_3$, $Cu(OH)_2$ are examples of weak bases.

3.4.1 Dissociation constant of weak acids and weak bases :

The dissociation of a weak acid HA in water is expressed as

$$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$$

The equilibrium constant called acid-dissociation constant for this equilibrium is :

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]} \qquad .... (3.3)$$

Similarly the dissociation of weak base BOH in water is represented as :

$$BOH(aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$$

The equilibrium constant called base-dissociation constant for this equilibrium is,

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]} \qquad .... (3.4)$$

Thus, the dissociation constant of a weak acid or a weak base is defined as **the equilibrium constant for dissociation equilibrium of weak acid or weak base, respectively**.

3.4.2 Ostwald's dilution law :

Arrhenius concept of acids and bases was expressed quantitatively by F. W. Ostwald in the form of the dilution law in 1888.

a. Weak acids : Consider an equilibrium of weak acid HA that exists in solution partly as the undissociated species HA and partly $H^{\oplus}$ and $A^{\ominus}$ ions. Then

$$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$$

The acid dissociation constant is given by Eq. (3.3)

$$K_a = \frac{[H^{\oplus}][A^{\ominus}]}{[HA]}$$

Suppose 1 mol of acid HA is initially present in volume V dm^3 of the solution. At equilibrium the fraction dissociated would be $\propto$, where $\propto$ is degree of dissociation of the acid. The fraction of an acid that remains undissociated would be $(1 - \propto)$.

	$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{\ominus}(aq)$		
Amount present at equilibrium/ mol	$(1-\propto)$	$\propto$	$\propto$
concentration at equilibrium/ mol dm^{-3}	$\frac{1-\propto}{V}$	$\frac{\propto}{V}$	$\frac{\propto}{V}$

Thus, at equilibrium $[HA] = \frac{1-\propto}{V}$, mol dm^{-3},

$[H^{\oplus}] = [A^{\ominus}] = \frac{\propto}{V}$ mol dm^{-3}.

Substituting these in Eq. (3.3)

$$K_a = \frac{(\propto/V)\,(\propto/V)}{(1-\propto)/V} = \frac{\propto^2}{(1-\propto)V} \qquad \text{....... (3.5)}$$

If c is the initial concentration of an acid in mol dm^{-3} and V is the volume in dm^3 mol^{-1} then $c = 1/V$. Replacing $1/V$ in Eq. (3.5) by c we get

$$K_a = \frac{\propto^2 c}{1-\propto} \qquad \text{.......(3.6)}$$

For the weak acid HA, $\propto$ is very small, or $(1 - \propto) \cong 1$. With this Eq. (3.5) and (3.6) reduce.

$$K_a = \propto^2/V \text{ and } K_a = \propto^2 c \qquad \text{........... (3.7)}$$

$$\propto = \sqrt{\frac{K_a}{c}} \text{ or } \propto = \sqrt{K_a.V} \qquad \text{........... (3.8)}$$

The Eq. (3.8) implies that the degree of dissociation of a weak acid is inversely proportional to the square root of its concentration or directly proportional to the square root of volume of the solution containing 1 mol of the weak acid.

b. Weak base : Consider 1 mol of weak base BOH dissolved in V dm^3 of solution. The base dissociates partially as

$$BOH\ (aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$$

The base dissociation constant is

$$K_b = \frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]}$$

Let the fraction dissociated at equilibrium is $\propto$ and that remains undissociated is $(1 - \propto)$.

	$BOH(aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$		
Amount present at equilibrium	$(1-\propto)$	$\propto$	$\propto$
concentration at equilibrium	$\frac{1-\propto}{V}$	$\frac{\propto}{V}$	$\frac{\propto}{V}$

A equilibrium,

$[BOH] = \frac{1-\propto}{V}$ mol dm^{-3},

$[B^{\oplus}] = [OH^{\ominus}] = \frac{\propto}{V}$ mol dm^{-3}.

Substitution of these concentrations in Eq. (3.4), gives

$$K_b = \frac{(\propto/V)\,(\propto/V)}{(1-\propto)/V} = \frac{\propto^2}{(1-\propto)V} \qquad \text{.......... (3.9)}$$

Similar arguments in the case of weak acid, led to

$$K_b = \frac{\propto^2 c}{(1-\propto)} \qquad \text{........... (3.10)}$$

$$\propto = \sqrt{K_b.V}\ ,\ \propto = \sqrt{\frac{K_b}{c}} \qquad \text{........... (3.11)}$$

The degree of dissociation of a weak base is inversely proportional to square root of its concentration and is directly proportional to square root of volume of the solution containing 1 mol of weak base.

Problem 3.1 : A weak monobasic acid is 0.05% dissociated in 0.02 M solution. Calculate dissociation constant of the acid.

Solution : The dissociation constant of acid is given by $K_a = \propto^2 c$. Here,

$$\propto = \frac{\text{percent dissociation}}{100}$$

$$= \frac{0.05}{100} = 5 \times 10^{-4}$$

$c = 0.02$ M $= 2 \times 10^{-2}$ M

Hence $K_a = (5 \times 10^{-4})^2 \times 2 \times 10^{-2}$

$= 25 \times 10^{-8} \times 2 \times 10^{-2}$

$= 50 \times 10^{-10} = 5 \times 10^{-9}$

Problem 3.2 : The dissociation constant of NH_4OH is 1.8×10^{-5}. Calculate its degree of dissociation in 0.01 M solution.

Solution : The degree of dissociation is given by $\propto = \sqrt{K_b/c}$. Here,

$K_b = 1.8 \times 10^{-5}$; $c = 0.01 = 1 \times 10^{-2}$ M

$$\text{Hence, } \propto = \sqrt{\frac{1.8 \times 10^{-5}}{1 \times 10^{-2}}} = \sqrt{1.8 \times 10^{-3}}$$

$$= \sqrt{18 \times 10^{-4}} = 4.242 \times 10^{-2} = 0.04242$$

Problem 3.3 : A weak monobasic acid is 12% dissociated in 0.05 M solution. What is percent dissociation in 0.15 M solution.

Solution : If $\propto_1$ and $\propto_2$ are the values of degree of dissociation at two different concentrations c_1 and c_2 respectively, then

$K_a = \propto_1^2 c_1 = \propto_2^2 c_2$ Therefore $\propto_1^2 c_1 = \propto_2^2 c_2$

$\propto_1 = \dfrac{12}{100}$ $c_1 = 0.05$ M, $c_2 = 0.15$ M,

$\propto_2 = ?$

Substituting of these values in the equation gives

$$(0.12)^2 \times 0.05 = \propto_2^2 \times 0.15$$

$$\propto_2^2 = \frac{(12)^2 \times 0.05}{0.15} = 0.0048$$

Hence $\propto_2 = 0.0693$ %

$\therefore$ percent dissociation = 6.93 %

Problem 3.4 : Calculate $[H_3O^\oplus]$ in 0.1 mol dm^3 solution of acetic acid.

Given : $K_a\ [CH_3COOH] = 1.8 \times 10^{-5}$

Solution : Let $\propto_1$ be the degree of dissociation. Concentrations of various species involved at equilibrium are as follows.

$$\underset{(1-\propto)c}{CH_3COOH} + H_2O \rightleftharpoons \underset{\propto c}{CH_3COO^\ominus} + \underset{\propto c}{H_3O^\oplus}$$

$$\propto = \sqrt{\frac{K_a}{c}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}}$$

$$= 1.34 \times 10^{-2}$$

$$[H_3O^\oplus] = \propto \times c = 1.34 \times 10^{-2} \times 0.1$$

$$= 1.34 \times 10^{-3} \text{ mol/L}$$

3.5 Autoionization of water : Pure water ionizes to a very small extent. The ionization equilibrium of water is represented as,

$$H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^\oplus(aq) + OH^\ominus(aq)$$

The equilibrium constant (*K*) for the ionization of water is given by

$$K = \frac{[H_3O^\oplus][OH^\ominus]}{[H_2O(l)]^2} \quad \text{............ (3.12)}$$

$$\text{or } K[H_2O]^2 = [H_3O^\oplus][OH^\ominus] \quad \text{............ (3.13)}$$

A majority of H_2O molecules are undissociated, consequently concentration of water $[H_2O]$ can be treated as constant. Then

$[H_2O]^2 = K'$. Substituting this in Eq. (3.13) we get,

$$K \times K' = [H_3O^\oplus][OH^\ominus] \quad \text{............ (3.14)}$$

$$K_w = [H_3O^\oplus][OH^\ominus]$$

where $K_w = KK'$ is called ionic product of water. The product of molar concentrations of hydronium (or hydrogen) ions and hydroxyl ions at equilibrium in pure water at the given temperature is called ionic product of water.

In pure water $H_3O^\oplus$ ion concentration always equals the concentration of $OH^\ominus$ ion. Thus at 298 K this concentration is found to be 1.0×10^{-7} mol/L.

$$K_w = (1.0 \times 10^{-7})\,(1.0 \times 10^{-7})$$

$$K_w = 1.0 \times 10^{-14} \quad \text{............ (3.15)}$$

Internet my friend

Find out the values of ionic product K_w of water at various temperatures.

273 K, 283K, 293K, 303K, 313K, 323 K

3.6 pH Scale : Instead of writing concentration of $H_3O^\oplus$ ions in mol dm^{-3}, sometimes it is convenient to express it on the logarithmic scale. This is known as pH scale.

Sorensen in 1909 defined the pH of a solution as the negative logarithm to the base 10, of the concentration of $H^\oplus$ ions in solution in mol dm^{-3}. Expressed mathematically as

$pH = -\log_{10}[H^\oplus]$

Similarly pOH of a solution can be defined as the negative logarithm to the base 10, of the molar concentration of $OH^\ominus$ ions in solution.

Thus, $pOH = -\log_{10}[OH^\ominus]$ .... (3.16)

3.6.1 Relationship between pH and pOH

The ionic product of water is

$K_w = [H_3O^\oplus][OH^\ominus]$

Now, $K_w = 1 \times 10^{-14}$ at 298 K and thus

$[H_3O^\oplus][OH^\ominus] = 1.0 \times 10^{-14}$

Taking logarithm of both the sides, we write

$\log_{10}[H_3O^\oplus] + \log_{10}[OH^\ominus] = -14$

$-\log_{10}[H_3O^\oplus] + \{-\log_{10}[OH^\ominus]\} = 14$

From Eq. (3.16) and (3.17)

$pH + pOH = 14$ .... (3.18)

3.6.2 Acidity, basicity and neutrality of aqueous solutions

1. Neutral solution : For pure water or any aqueous neutral solution at 298 K

$[H_3O^\oplus] = [OH^\ominus] = 1.0 \times 10^{-7}$ M

Hence, $pH = -\log_{10}[H^\oplus] = -\log_{10}[1 \times 10^{-7}] = 7$

2. Acidic solution : In acidic solution, there is excess of $H_3O^\oplus$ ions, or $[H_3O^\oplus] > [OH^\ominus]$ Hence, $[H_3O^\oplus] > 1 \times 10^{-7}$ and $pH < 7$

3. Basic solution : In basic solution, the excess of $OH^\ominus$ ions are present that is $[H_3O^\oplus] < [OH^\ominus]$ or $[H_3O^\oplus] < 1.0 \times 10^{-7}$ with $pH > 7$.

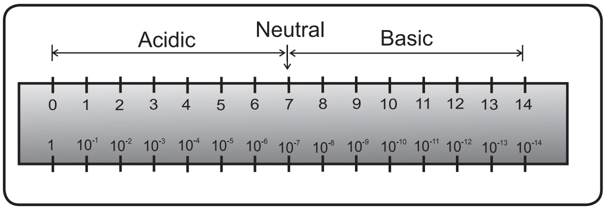


Fig. 3.1 : *pH* scale

Problem 3.5 : Calculate pH and pOH of 0.01 M HCl solution.

Solution : HCl is a strong acid. It dissociates almost completely in water as

$HCl\ (aq) + H_2O(l) \longrightarrow H_3O^\oplus(aq) + Cl^\ominus\ (aq)$

Hence, $[H_3O^\oplus] = c = 0.01M = 1 \times 10^{-2}$ M

$pH = -\log_{10}[H_3O^+] = -\log_{10}[1 \times 10^{-2}] = 2$

We know that $pH + pOH = 14$

$\therefore pOH = 14 - pH = 14 - 2 = 12$

Problem 3.6 : pH of a solution is 3.12. Calculate the concentration of $H_3O^\oplus$ ion.

Solution : pH is given by

$pH = -\log_{10}[H_3O^\oplus]$

$$\begin{aligned}\log_{10}[H_3O^\oplus] &= -pH \\ &= -3.12 \\ &= -3 - 0.12 + 1 - 1 \\ &= (-3 - 1) + 1 - 0.12 \\ &= -4 + 0.88 = \bar{4}.88\end{aligned}$$

Thus $[H_3O^\oplus]$ = antilog $[\bar{4}.88]$

$= 7.586 \times 10^{-4}$ M

Problem 3.7 : A weak monobasic acid is 0.04 % dissociated in 0.025M solution. What is pH of the solution ?

Solution : A weak monobasic acid HA dissociates as :

$HA + H_2O(l) \rightleftharpoons H_3O^\oplus(aq) + A^\ominus(aq)$

Percent dissociation = $\propto \times 100$

$$\text{or } \propto = \frac{\text{percent dissociation}}{100}$$

$$= \frac{0.04}{100} = 4 \times 10^{-4}$$

Now $[H_3O^\oplus] = \propto \times c$

$= 4 \times 10^{-4} \times 0.025\ M = 10^{-5}$ M

$\therefore pH = -\log_{10}[H_3O^\oplus] = -\log_{10}[10^{-5}] = 5$

Use your brain power

- Suppose that *pH* of monobasic and dibasic acid is the same. Does this mean that the molar concentrations of both acids are identical ?
- How *pH* of pure water vary with temperature ? Explain.

Problem 3.8 : The *pH* of monoacidic weak base is 11.2. Calculate its percent dissociation in 0.02 M solution.

Solution : *pOH* of the solution is given as :

$$pOH = 14 - pH = 14 - 11.2 = 2.8$$

$$pOH = -\log_{10}[OH^{\ominus}]$$

$$\log_{10}[OH^{\ominus}] = -pOH$$

$$= -2.8 = -2 - 0.8 - 1 + 1$$

$$= -3 + 0.2 = \bar{3}.2$$

$$[OH^{\ominus}] = \text{antilog } \bar{3}.2 = 1.585 \times 10^{-3} \text{ mol/dm}^3$$

For monoacidic base,

$$BOH\ (aq) \rightleftharpoons B^{\oplus}(aq) + OH^{\ominus}(aq)$$

$$[OH^{\ominus}] = \alpha c$$

$$\alpha = \frac{[OH^{\ominus}]}{c} = \frac{1.585 \times 10^{-3}}{0.02} = 0.07925$$

$$\text{Percent dissociation} = \alpha \times 100$$

$$= 0.07925 \times 100$$

$$= 7.925\ \%$$

Do you know ?

- *pH* is crucial for digestion of food and other biochemical reactions in our body.
- *pH* of gastric juice is about 2.
- *pH* of blood is maintained within range 7.36 to 7.42.
- Enzymes function effectively only at a certain *pH*. For example trypsin acts best for alkaline *pH*.

3.7 Hydrolysis of salts

3.7.1 Types of salts

These are of four types

I. Salts derived from **strong acid and strong base**. For example : NaCl, Na_2SO_4, $NaNO_3$, KCl, KNO_3.

II. Salts derived from **strong acids and weak bases**. For example : NH_4Cl, $CuSO_4$, NH_4NO_3, $CuCl_2$.

III. Salts derived from **weak acids and strong bases**. For example : CH_3COONa, KCN, Na_2CO_3.

IV. Salts derived from **weak acids and weak bases**. For example : CH_3COONH_4, NH_4CN.

3.7.2 Concept of hydrolysis :

When a salt is dissociated in water, it dissociates completely into its constituent ions. The solvent water dissociates slightly as,

$$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

Pure water is neutral and $[H_3O^{\oplus}] = [OH^{\ominus}]$. If the ions of the salt do not interact with water, the hydronium and hydroxyl ion concentrations remain equal and the solution is neutral. When one or more of the salt ions react with water, the equality of concentrations of $H_3O^{\oplus}$ and $OH^{\ominus}$ ions is disturbed. The solution, does not remain neutral and becomes acidic or basic depending on the type of the salt. Such a reaction between the ions of salt and the ions of water is called hydrolysis of salt. **Hydrolysis of salt is defined as the reaction in which cations or anions or both ions of a salt react with ions of water to produce acidity or alkalinity (or sometimes even neutrality).**

3.7.3 Salts of strong acids and strong bases

NaCl is a salt of strong acid HCl and a strong base NaOH. When it is dissolved in water, it dissociates completely into its ions.

$$NaCl\ (aq) \longrightarrow Na^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The ions $Na^{\oplus}$ and $Cl^{\ominus}$ have no tendency to react with water. This is because the possible products, NaOH and HCl of such reactions are strong electrolytes and dissociate completely in aqueous solutions.

In other words,

$$Na^{\oplus}(aq) + Cl^{\ominus}(aq) + H_2O \longrightarrow \underset{\text{(strong acid)}}{HCl(aq)} + \underset{\text{(strong base)}}{NaOH(aq)}$$

[Possible products]

$$HCl(aq) + NaOH(aq) + H_2O \longrightarrow H_3O^{\oplus}(aq) + Cl^{\ominus}(aq) + Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

Thus the reactants and the products are the same. This implies that neither the cation nor anion of the salt reacts with water or there is no hydrolysis. Equality $H_3O^{\oplus} = OH^{\ominus}$ produced by ionization of water is not disturbed and solution is neutral. It may be concluded that salt of strong acid and strong base does not undergo hydrolysis.

3.7.4 Salts of strong acids and weak bases :

$CuSO_4$ is salt of strong acid H_2SO_4 and weak base $Cu(OH)_2$. When $CuSO_4$ is dissolved in water, it dissociates completely as,

$$CuSO_4(aq) \longrightarrow Cu^{2\oplus}(aq) + SO_4^{2\ominus}(aq)$$

$SO_4^{2\ominus}$ ions of salt have no tendency to react with water because the possible product H_2SO_4 is strong electrolyte. The reaction of $Cu^{2\oplus}$ ions with $OH^{\ominus}$ ions form unionized $Cu(OH)_2$. The hydrolytic equilibrium for $CuSO_4$ is then written as,

$$Cu^{2\oplus}(aq) + 4H_2O(l) \rightleftharpoons Cu(OH)_2(aq) + 2H_3O^{\oplus}(aq)$$

Due to the presence of excess of $H_3O^{\oplus}$ ions, the resulting solution of $CuSO_4$ becomes acidic and turns blue litmus red.

Formation of sparingly soluble $Cu(OH)_2$ by hydrolysis makes the aqueous solution of $CuSO_4$ turbid. If H_2SO_4, that is $H_3O^{\oplus}$ ions are added, the hydrolytic equilibrium shifts to the left. A turbidity of $Cu(OH)_2$ dissolves to give a clear solution. To get clear solution of $CuSO_4$, the addition of H_2SO_4 would be required.

3.7.5 Salts of weak acids and strong bases

CH_3COONa is a salt of weak acid CH_3COOH and strong base NaOH, when dissolved in water, it dissociates completely.

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus}(aq) + Na^{\oplus}(aq)$$

Water dissociates slightly as,

$$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^{\oplus}(aq) + OH^{\ominus}(aq)$$

Solution of CH_3COONa contains $Na^{\oplus}$, $H_3O^{\oplus}$, $CH_3COO^{\ominus}$, $OH^{\ominus}$. The $Na^{\oplus}$ ions of salt have no tendency to react with $OH^{\ominus}$ ions of water since the possible product of the reaction is NaOH, a strong electrolyte.

On the other hand the reaction of $CH_3COO^{\ominus}$ ions of salt with the $H_3O^{\oplus}$ ions from water produces unionized CH_3COOH.

$$CH_3COO^{\ominus}(aq) + H_2O\ (l) \rightleftharpoons CH_3COOH(aq) + OH^{\ominus}(aq)$$

Thus, the hydrolytic equilibrium for CH_3COONa is,

$$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + Na^{\oplus}(aq) + OH^{\ominus}(aq)$$

As a result of excess $OH^{\ominus}$ ions produced the solution becomes basic. The solution of CH_3COONa is therefore basic.

Can you tell ?

Why an aqueous solution of NH_4Cl is acidic while that of HCOOK basic ?

Remember...

As a general rule the solutions of salts of strong acids and strong bases are neutral, the solutions of salts of strong acids and weak bases are acidic and the solutions of salts of strong bases and weak acids are basic.

3.7.6 Salts of weak acids and weak bases:

When salt BA of weak acid HA and weak base BOH is dissolved in water, it dissociates completely as

$$BA(aq) \longrightarrow B^{\oplus}(aq) + A^{\ominus}(aq)$$

The hydrolysis reaction involves the interaction of both the ions of the salt with water,

$$B^{\oplus}(aq) + A^{\ominus}(aq) + H_2O \rightleftharpoons \underset{\text{(weak base)}}{BOH} + \underset{\text{(weak acid)}}{HA}$$

The solution may turn out acidic, basic or neutral depending on the relative strength of weak base and weak acid formed in the hydrolysis.

i. if, $K_a > K_b$, the solution will be acidic.

ii. if, $K_a < K_b$, the solution will be basic.

iii. if, $K_a = K_b$, the solution will be neutral.

i. Salt of weak acid and weak base for which $K_a > K_b$.

NH_4F is a salt of weak acid HF ($K_a = 7.2 \times 10^{-4}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$). Here, K_a is greater than K_b. The salt hydrolyses as

$$NH_4^{\oplus}(aq) + F^{\ominus}(aq) + H_2O \rightleftharpoons \underset{\text{(weak base)}}{NH_4OH(aq)} + \underset{\text{(weak acid)}}{HF(aq)}$$

The acid HF is slightly stronger than base NH_4OH. The two ions react with water as

$$NH_4^{\oplus}(aq) + 2H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq) \qquad \text{............ (3.19)}$$

$$F^{\ominus}(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^{\ominus}(aq) \qquad \text{............ (3.20)}$$

The $NH_4^{\oplus}$ ions hydrolyse to a slightly greater extent than the $F^{\ominus}$ ions. That means the reaction produces more $H_3O^{\oplus}$ ions than the $OH^{\ominus}$ ions produced in reaction (3.20). In other words, $NH_4^{\oplus}$ ions are slightly stronger as acid than $F^{\ominus}$ ions as base. The solution of NH_4F is thus only slightly acidic and turns blue litmus red.

ii. Salt of weak acid and weak base for which $K_a < K_b$: NH_4CN is the salt of weak acid HCN ($K_a = 4.0 \times 10^{-10}$) and weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$) showing that $K_a < K_b$. When NH_4CN is dissolved in water, it hydrolyses as

$$NH_4^{\oplus}(aq) + CN^{\ominus}(aq) + H_2O(l) \rightleftharpoons \underset{\text{(weak base)}}{NH_4OH(aq)} + \underset{\text{(weak acid)}}{HCN(aq)}$$

The base NH_4OH is stronger than the acid HCN. The ions of the salt react with water as,

$$NH_4^{\oplus}(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq) \qquad \text{............ (3.21)}$$

$$CN^{\ominus}(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^{\ominus}(aq) \qquad \text{............ (3.22)}$$

The $CN^{\ominus}$ ions hydrolyse to a greater extent than $NH_4^{\oplus}$ ions, The reaction (3.22) produces more $OH^{\ominus}$ ions than the $H_3O^{\oplus}$ ions produced in reaction (3.21). The solution of NH_4CN is, basic and turns red litmus blue.

iii. Salt of weak acid and weak base for which $K_a = K_b$.

CH_3COONH_4 is a salt of weak acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and weak base, NH_4OH ($K_b = 1.8 \times 10^{-5}$).

When the salt CH_3COONH_4 is dissolved in water, it undergoes hydrolysis :

$$CH_3COO^{\ominus}(aq) + NH_4^{\oplus}(aq) + H_2O(l) \rightleftharpoons \underset{\text{(weak acid)}}{CH_3COOH(aq)} + \underset{\text{(weak base)}}{NH_4OH(aq)}$$

The ions of the salt react with water as

i. $CH_3COO^{\ominus}(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^{\ominus}(aq)$

ii. $NH_4^{\oplus}(aq) + 2H_2O(l) \rightleftharpoons NH_4OH(aq) + H_3O^{\oplus}(aq)$

As $K_a = K_b$, the relative strength of acid and base produced in hydrolysis is the same. Therefore, the solution is neutral. Hydrolysis of $NH_4^{\oplus}$ produces as many $H_3O^{\oplus}$ ions as that of $CH_3COO^{\ominus}$ produces $OH^{\ominus}$ ions.

3.8 Buffer solutions : Buffer solution is defined as a solution which resists drastic changes in pH when a small amount of strong acid or strong base or water is added to it.

Can you think ?

Home made jams and gellies without any added chemical preservative additives spoil in a few days whereas commercial jams and jellies have a long shelf life. Explain. What role does added sodium benzoate play?

3.8.1 Types of buffer solutions

There are two types of buffer solutions. Acidic buffer used to maintain an acidic pH, while basic buffer maintains alkaline pH.

a. Acidic buffer solution : A solution containing a weak acid and its salts with strong base is called an acidic buffer solution.

For example : A solution containing weak acid such as CH_3COOH and its salt such as CH_3COONa is an acidic buffer solution.

pH of acidic buffer is given by the equation

$$pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]} \qquad \text{...........} (3.23)$$

$$\text{where } pK_a = -\log_{10}K_a \qquad \text{...........} (3.24)$$

and K_a is the dissociation constant of the acid.

b. Basic buffer solution : A solution containing a weak base and its salt with strong acid is the basic buffer solution.

For example : A solution containing a weak base such as NH_4OH and its salt such as NH_4Cl is a basic buffer solution.

The *pOH* of basic buffer is given by,

$$pOH = pK_b + \log_{10}\frac{[\text{salt}]}{[\text{base}]} \qquad \text{...........} (3.25)$$

where $pK_b = -\log_{10}K_b$ .... (3.26)and K_b is the dissociation constant for the base. Equations (3.26) and (3.25) are known to **Henderson Hasselbalch equation**.

3.8.2 Buffer action : Let us consider sodium acetate - acetic acid buffer. Here sodium acetate is a strong electrolyte which dissociates completely in water producing large concentration of $CH_3COO^{\ominus}$ as follows :

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus}(aq) + Na^{\oplus}(aq)$$

On the other hand since the acetic acid is a weak acid, the concentration of undissociated CH_3COOH molecules is usually high. If a strong acid is added to this solution the added $H^{\oplus}$ ions will be consumed by the conjugate base $CH_3COO^{\ominus}$ present in large concentration. Similarly, if small amount of base is added, the added $OH^{\ominus}$ ions will be neutralized by the large concentration of acetic acid as shown in the following reactions :

$$CH_3COO^{\ominus}(aq) + H^{\oplus}(aq) \longrightarrow CH_3COOH(aq)$$

(large concentraion) (added acid)

$$CH_3COOH(aq) + OH^{\ominus}(aq) \longrightarrow CH_3COO^{\ominus}(aq) + H_2O(l)$$

(large concentraion) (added acid)

The acid or base added thus can not change the $[H^{\oplus}]$ or $[OH^{\ominus}]$ concentrations and, *pH* of the buffer remains unchanged. Dilution does not have any effect on *pH* of buffer. This is because the concentration ratio term in Eq. (3.23) and Eq. (3.25) remains the same. The dilution does not change this ratio.

3.8.3 Properties of buffer solution

The *pH* of a buffer solution does not change appereciably

i. by addition of small amount of either strong acid or strong base, ii. on dilution or iii. when it is kept for long time.

Can you tell ?

It is enough to add a few mL of a buffer solution to maintain its *pH*. Which property of buffer is used here?

3.8.4 Applications of buffer solution

Buffer solution finds extensive applications in a variety of fields. Some of its applications are given.

i. In biochemical system : *pH* of blood in our body is maintained at 7.36 - 7.42 due to $(HCO_3^{\ominus} + H_2CO_3)$ buffer. A mere change of 0.2 *pH* units can cause death. The saline solution used for intravenous injection must contain buffer system to maintain the proper *pH* of the blood.

ii. Agriculture : The soils get buffered due to presence of salts such as carbonate, bicarbonate, phosphates and organic acids. The choice of fertilizers depends upon *pH* of soil.

iii. Industry : Buffers play an important role in paper, dye, ink, paint and drug industries.

iv. Medicine : Penicillin preparations are stabilized by addition of sodium citrate as buffer. When citric acid is added to milk of magnesia ($Mg(OH)_2$), magnesium citrate is formed, which is a buffer.

v. Analytical chemistry : In qualitative analysis, a *pH* of 8 to 10 is required for precipitation of cations IIIA group. It is maintained with the use of ($NH_4OH + NH_4Cl$) buffer.

Problem 3.9 : Calculate the *pH* of buffer solution containing 0.05 mol NaF per litre and 0.015 mol HF per litre. [$K_a = 7.2 \times 10^{-4}$ for HF]

Solution : The *pH* of acidic buffer is given by Henderson-Hasselbalch equation

$$pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$$

$$\therefore pK_a = -\log_{10}K_a \quad = -\log_{10} 7.2 \times 10^{-4}$$

$$= 4 - \log_{10} 7.2 = 4 - 0.8573 = 3.1427$$

[salt] = 0.05 M, [acid] = 0.015M

Substitution in the above equation gives

$$pH = 3.1427 + \log_{10}\frac{0.05}{0.015}$$

$$= 3.1427 + \log 3.33$$

$$= 3.1427 + 0.5224 = 3.6651 \approx 3.67$$

Problem 3.10 : Calculate the *pH* of buffer solution composed of 0.1 M weak base BOH and 0.2 M of its salt BA. [$K_b = 1.8 \times 10^{-5}$ for the weak base]

Solution : *pOH* of basic buffer is given by Henderson-Hasselbalch equation

$$pOH = pK_b + \log_{10}\frac{[\text{salt}]}{[\text{base}]}$$

$$\therefore pK_b = -\log_{10}K_b$$

$$= -\log_{10}(1.8 \times 10^{-5}) = 5 - \log_{10} 1.8$$

$$= 5 - 0.2553 = 4.7447$$

[salt] = 0.02 M, [acid] = 0.1M

Substitution of these in the above equation gives

$$pOH = 4.7447 + \log\frac{0.02}{0.1} = 4.7447 + \log 2$$

$$= 4.7447 + 0.3010 \quad = 5.0457$$

$$pH = 14 - \text{pOH} \qquad = 14 - 5.0457$$

$$= 13.9543 \approx 13.95$$

3.9 Solubility product

Can you recall ?

- What is solubility of a compound ?
- What is saturated solution ?
- What is meant by the sparingly soluble salt ?

Do you know ?

The process of dissolution and precipitation of sparingly soluble ionic compounds are of important in our everyday life, industry and medicine. Kidney stone is developed due to the precipitation of insoluble calcium oxalate, CaC_2O_4. The process of tooth decay occurs due to dissolution of enamel composed of hydroxyapatite, $Ca_5(PO_4)_3OH$ in acidic medium.

3.9.1 Solubility equilibria : Hereafter we confine our attention to sparingly soluble compounds that is, compounds those dissolve only slightly in water.

Suppose some powdered sparingly soluble salt such as AgCl is put into water and stirred vigorously. A very small amount of AgCl dissolves in water to form its saturated solution. Most of the salt remains undissolved. Thus, solid AgCl is in contact with its saturated solution. AgCl is a strong electrolyte. Hence the quantity of AgCl that dissolves in water dissociates completely into its constituent ions, $Ag^{\oplus}$ and $Cl^{\ominus}$. A dynamic equilibrium exists between undissolved solid AgCl and the dissolved ions, $Ag^{\oplus}$ and $Cl^{\ominus}$, in the saturated solution. This equilibrium, called solubility equilibrium, is represented as :

$$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The expression for its equilibrium constant is :

$$K = \frac{[Ag^{\oplus}][Cl^{\ominus}]}{[AgCl]} \quad \text{...........} (3.27)$$

The concentration of undissolved solid AgCl is constant we may write

$$[AgCl] = \text{constant} = K'$$

Substituting in Eq. (3.27) we write

$$K = \frac{[Ag^{\oplus}][Cl^{\ominus}]}{K'}$$

$$K \times K' = [Ag^{\oplus}][Cl^{\ominus}]$$

The product of $K \times K'$ is another constant and is called **solubility product**, that is the product of concentrations of ions in a saturated solution. It is denoted by K_{sp}.

$$K_{sp} = [Ag^{\oplus}][Cl^{\ominus}]$$

For the general salt solubility equilibrium

$$B_xA_y(s) \rightleftharpoons xB^{y\oplus}(aq) + yA^{x\ominus}(aq)$$

The solubility product is

$$K_{sp} = [B^{y\oplus}]^x[A^{x\ominus}]^y \quad \text{...........} (3.28)$$

Thus, in the saturated solution of sparingly soluble salt the product of equilibrium concentrations of the constituent ions raised to the power equal to their respective coefficients in the balanced equilibrium expression at a given temperature is called solubility product. Consider following examples.

i. $BaSO_4(s) \rightleftharpoons Ba^{2\oplus}(aq) + SO_4^{2\ominus}(aq)$

$K_{sp} = [Ba^{2\oplus}][SO_4^{2\ominus}]$

ii. $CaF_2(s) \rightleftharpoons Ca^{2\oplus}(aq) + 2F^{\ominus}(aq)$

$K_{sp} = [Ca^{2\oplus}][F^{\ominus}]^2$

iii. $Bi_2S_3(s) \rightleftharpoons 2Bi^{3\oplus}(aq) + 3S^{2\ominus}(aq)$

$K_{sp} = [Bi^{3\oplus}]^2[S^{2\ominus}]^3$

iv. $Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2\oplus}(aq) + 2PO_4^{3\ominus}(aq)$

$K_{sp} = [Ca^{2\oplus}]^3[PO_4^{3\ominus}]^2$

3.9.2 Relationship between solubility and solubility product : The solubility of a compound is the amount in grams that dissolves per unit volume (which may be 100 mL or 1L of its saturated solution).

Molar solubility : The number of moles of a compound that dissolve to give one litre of saturated solution is called its molar solubility.

$$\text{molar solubility (mol/L)} = \frac{\text{solubility in g/L}}{\text{molar mass in g/mol}}$$

Consider once again the solubility equilibrium for B_xA_y,

$$B_xA_y(s) \rightleftharpoons xB^{y\oplus}(aq) + yA^{x\ominus}(aq)$$

The solubility product is given by Eq. (3.28) :

$$K_{sp} = [B^{y\oplus}]^x[A^{x\ominus}]^y$$

If S is the molar solubility of the compound, the equilibrium concentrations of the ions in the saturated solution will be

$$[B^{y\oplus}] = xS \text{ mol/L}$$

$$[A^{x\ominus}] = xS \text{ mol/L}$$

From Eq. (3.28)

$$K_{sp} = [xS]^x[yS]^y = x^xy^yS^{x+y} \quad \text{...........} (3.29)$$

For example :

i. For AgBr,

$$AgBr(s) \rightleftharpoons Ag^{\oplus}(aq) + Br^{\ominus}(aq)$$

Here, $x = 1, y = 1$

$$\therefore K_{sp} = S \times S = S^2$$

ii. For PbI_2,

$$PbI_2(s) \rightleftharpoons Pb^{2\oplus}(aq) + 2I^{\ominus}(aq)$$

x = 1, y = 2

Therefore, $K_{sp} = (1)^1(2)^2S^{1+2} = 4S^3$

iii. $Al(OH)_3$,

$$Al(OH)_3(s) \rightleftharpoons Al^{3\oplus}(aq) + 3OH^{\ominus}(aq)$$

x = 1, y = 3

$$K_{sp} = (1)^1(3)^3S^{1+3} = 27S^4$$

Use your brain power

What is the relationship between molar solubility and solubility product for salts given below

i. Ag_2CrO_4 ii. $Ca_3(PO_4)_2$ iii. $Cr(OH)_3$.

3.9.3 Condition of precipitation : Ionic product (*IP*) of an electrolyte is defined in the same way as solubility product (K_{sp}). The only difference is that the ionic product expression contains concentration of ions under any condition whereas expression of K_{sp} contains only equilibrium concentrations. If,

a. $IP = K_{sp}$; the solution is saturated and solubility equilibrium exists.

b. $IP > K_{sp}$; the solution is supersaturated and hence precipitation of the compound will occur.

c. If $IP < K_{sp}$, the solution is unsaturated and precipitation will not occur.

Problem 3.11 : A solution is prepared by mixing equal volumes of 0.1M $MgCl_2$ and 0.3M $Na_2C_2O_4$ at 293 K. Would MgC_2O_4 precipitate out ? K_{sp} of MgC_2O_4 at 293 K is 8.56×10^{-5}.

Solution : When solution is prepared by mixing equal volumes, volume gets doubled and hence effective concentration of ions would be half of initial concentration,

$$[Mg^{2+}] = \frac{0.1}{2} = 0.05 \text{ mol/L}$$

$$[C_2O_4^{2-}] = \frac{0.3}{2} \text{ M} = 0.15 \text{ mol/L}$$

These ions would react to form sparingly soluble salt MgC_2O_4 in accordance with reaction

$$Mg^{2\oplus}(aq) + C_2O_4^{2\ominus}(aq) \rightleftharpoons MgC_2O_4(s)$$

Ionic product in the solution is given by

$$[Mg^{2+}][C_2O_4^{2-}(aq)] = 0.05 \times 0.15$$
$$= 0.0075 = 7.5 \times 10^{-3}$$

the K_{sp} value for MgC_2O_4 at 293 K is 8.56×10^{-5}. As ionic product is greater than K_{sp} precipitation will take place.

Problem 3.12 : The solubility product of AgBr is 5.2×10^{-13}. Calculate its solubility in mol dm^{-3} and g dm^{-3}(Molar mass of AgBr = 187.8 g mol^{-1})

Solution : The solubility equilibrium of AgBr is :

$$AgBr(s) \rightleftharpoons Ag^{\oplus}(aq) + Br^{\ominus}(aq)$$

x = 1, y = 1

$$K_{sp} = [Ag^{\oplus}][Br^{\ominus}] = S^2$$

$$S = \sqrt{K_{sp}} = \sqrt{5.2 \times 10^{-13}}$$

$$= 7.2 \times 10^{-7} \text{ mol dm}^{-3}$$

The solubility in g dm^{-3} = molar solubility in mol dm^{-3} × molar mass g mol^{-1}

$$S = 7.2 \times 10^{-7} \text{ mol dm}^{-3} \times 187.8 \text{ g mol}^{-1}$$

$$= 1.35 \times 10^{-4} \text{ g dm}^{-3}$$

Problem 3.13 : If 20.0 cm^3 of 0.050 M $Ba(NO_3)_2$ are mixed with 20.0 cm^3 of 0.020 M NaF, will BaF_2 precipitate ? K_{sp} of BaF_2 is 1.7×10^{-6} at 298 K.

Solution : Final volume of solution is

20 + 20 = 40 cm^3,

$$[Ba(NO_3)_2] = \frac{0.050 \times 20}{40} = 0.025 \text{ M}$$

$$[NaF] = \frac{0.020 \times 20}{40} = 0.010\text{M}$$

Therefore $[Ba^{2\oplus}] = 0.025$ M and

$[F^{\ominus}] = 0.010M$

Hence ionic product of BaF_2 is

$IP = [Ba^{2\oplus}][F^{\ominus}]^2$

$= 0.025 \times (0.01)^2$

$= 2.5 \times 10^{-6}$

K_{sp} $(BaF_2) = 1.7 \times 10^{-6}$ Thus, $K_{sp} < IP$

Ionic product in the solution is greater than K_{sp}. Hence BaF_2 will precipitate from the solution.

3.10 Common ion effect :

Can you recall ?

Which reagents are used to precipitate (i) group II, (ii) group III B, (iii) group III A of basic radicals/ cations ?

Consider a solution of weak acid CH_3COOH and its soluble ionic salt CH_3COONa.

CH_3COOH is weak acid, dissociates only slightly in solution

$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus}(aq) + H^{\oplus}(aq)$$

CH_3COONa being a strong electrolyte dissociates almost completely in solution.

$$CH_3COONa(aq) \longrightarrow CH_3COO^{\ominus} + Na^{\oplus}$$

Both the acid and the salt produce $CH_3COO^{\ominus}$ ions in solution. CH_3COONa dissociates completely. Therefore it provides high concentration of $CH_3COO^{\ominus}$ ions. According to Le-Chatelier principle, the addition of $CH_3COO^{\ominus}$ from CH_3COONa to the solution of CH_3COOH, shifts equilibrium of dissociation of CH_3COOH to left. Thus reverse reaction is favoured in which $CH_3COO^{\ominus}$ combines with $H^{\oplus}$ to form unionised CH_3COOH. Hence dissociation of CH_3COOH is supressed due to presence of CH_3COONa containing a common $CH_3COO^{\ominus}$ ion.

The common ion effect states that the ionisation of a weak electrolyte is supressed in presence of a strong electrolyte containing an ion common to the weak electrolyte.

Remember...

Common ion effect is a special case of Le-Chatelier's principle in which the stress applied to an equilibrium system is an increase in the concentration of one of the product (ions). The effect of this stress is reduced by shifting the equilibrium to the reactant side.

Can you tell ?

How does the ionization of NH_4OH suppressed by addition of NH_4Cl to the solution of NH_4OH ?

3.10.1 Common ion effect and solubility

Do you know ?

The hardness of water is due to presence of $Ca^{2\oplus}$ ions. It is surprising to know that $Ca^{2\oplus}$ ions can be removed by adding more $Ca^{2\oplus}$ ions in the form of lime $Ca(OH)_2$, to the hard water. The $OH^{\ominus}$ ions of lime react with $HCO_3^{\ominus}$ ions present in the hard water to form $CO_3^{2\ominus}$ ions.

$$OH^{\ominus}(aq) + HCO_3^{\ominus}(aq) \longrightarrow CO_3^{2\ominus}(aq) + H_2O(l)$$

Solubility product of $CaCO_3$ is very low ($K_{sp} = 4.5 \times 10^{-9}$). Addition of lime makes $IP >> Ksp$ which results in the precipitation of $CaCO_3$ and thereby removal of hardness.

The presence of a common ion also affects the solubility of a sparingly soluble salt. Consider, the solubility equilibrium of AgCl,

$$AgCl(s) \rightleftharpoons Ag^{\oplus}(aq) + Cl^{\ominus}(aq)$$

The solubility product of AgCl is

$$K_{sp} = [Ag^{\oplus}][Cl^{\ominus}]$$

Suppose $AgNO_3$ is added to the saturated solution of AgCl. The salt $AgNO_3$ being a strong electrolyte dissociates completely in the solution.

$$AgNO_3(aq) \longrightarrow Ag^{\oplus}(aq) + NO_3^{\ominus}(aq)$$

The dissociation of AgCl and $AgNO_3$ produce a common $Ag^{\oplus}$ ion. The concentration of $Ag^{\oplus}$ ion in the solution increases owing to complete dissociation of $AgNO_3$. According to Le-chatelier's principle the addition of $Ag^{\oplus}$ ions from $AgNO_3$ to the solution of AgCl shifts the solubility equilibrium of AgCl from right to left. The reverse reaction in which AgCl precipitates, is favoured until the solubility equilibrium is re-established. The value of K_{sp} however, remains the same since it is an equilibrium constant. The solubility of a sparingly soluble compound, thus decreases with the presence of a common ion in solution.

Exercises

1. Choose the most correct answer :

i. The *pH* of 10^{-8} M of HCl is

   a. 8　　b. 7

   c. less than 7　　d. greater than 7

ii. Which of the following solution will have pH value equal to 1.0 ?

   a. 50 mL of 0.1M HCl + 50mL of 0.1M NaOH

   b. 60 mL of 0.1M HCl + 40mL of 0.1M NaOH

   c. 20 mL of 0.1M HCl + 80mL of 0.1M NaOH

   d. 75 mL of 0.2M HCl + 25mLof 0.2M NaOH

iii. Which of the following is a buffer solution ?

   a. $CH_3COONa + NaCl$ in water

   b. $CH_3COOH + HCl$ in water

   c. $CH_3COOH+CH_3COONa$ in water

   d. $HCl + NH_4Cl$ in water

iv. The solubility product of a sparingly soluble salt AX is 5.2×10^{-13}. Its solubility in mol dm^{-3} is

   a. 7.2×10^{-7}　　b. 1.35×10^{-4}

   c. 7.2×10^{-8}　　d. 13.5×10^{-8}

v. Blood in human body is highly buffered at *pH* of

   a. 7.4　　b. 7.0

   c. 6.9　　d. 8.1

vi. The conjugate base of $[Zn(H_2O)_4]^{2\oplus}$ is

   a. $[Zn(H_2O)_4]^{2\ominus}NH_3$

   b. $[Zn(H_2O)_3]^{2\ominus}$

   c. $[Zn(H_2O)_3OH]^{\oplus}$

   d. $[Zn(H_2O)H]^{3\oplus}$

vii. For $pH > 7$ the hydronium ion concentration would be

   a. 10^{-7}M　　b. $< 10^{-7}$M

   c. $> 10^{-7}$M　　d. $\geq 10^{-7}$M

2. Answer the following in one sentence :

i. Why cations are Lewis acids ?

ii. Why is KCl solution neutral to litmus?

iii. How are basic buffer solutions prepared?

iv. Dissociation constant of acetic acid is 1.8×10^{-5}. Calculate percent dissociation of acetic acid in 0.01 M solution.

v. Write one property of a buffer solution.

vi. The *pH* of a solution is 6.06. Calculate its $H^{\oplus}$ ion concentration.

vii. Calculate the *pH* of 0.01 M sulphuric acid.

viii. The dissociation of H_2S is suppressed in the presence of HCl. Name the phenomenon.

ix. Why is it necessary to add H_2SO_4 while preparing the solution of $CuSO_4$?

x. Classify the following buffers into different types :

a. $CH_3COOH + CH_3COONa$

b. $NH_4OH + NH_4Cl$

c. Sodium benzoate + benzoic acid

d. $Cu(OH)_2 + CuCl_2$

3. Answer the following in brief :

i. What are acids and bases according to Arrhenius theory ?

ii. What is meant by conjugate acid-base pair?

iii. Label the conjugate acid-base pair in the following reactions

a. $HCl + H_2O \rightleftharpoons H_3O^{\oplus} + Cl^{\ominus}$

b. $CO_3^{2\ominus} + H_2O \rightleftharpoons OH^{\ominus} + HCO_3^{\ominus}$

iv. Write a reaction in which water acts as a base.

v. Ammonia serves as a Lewis base whereas $AlCl_3$ is Lewis acid. Explain.

vi. Acetic acid is 5% ionised in its decimolar solution. Calculate the dissociation constant of acid

(Ans : 2.63×10^{-4})

vii. Derive the relation $pH + pOH = 14$.

viii. Aqueous solution of sodium carbonate is alkaline whereas aqueous solution of ammonium chloride is acidic. Explain.

ix. pH of a weak monobasic acid is 3.2 in its 0.02 M solution. Calculate its dissociation constant.

x. In NaOH solution $[OH^{\ominus}]$ is 2.87×10^{-4}. Calculate the pH of solution.

4. Answer the following :

i. Define degree of dissociation. Derive Ostwald's dilution law for the CH_3COOH.

ii. Define pH and pOH. Derive relationship between pH and pOH.

iii. What is meant by hydrolysis ? A solution of CH_3COONH_4 is neutral. why ?

iv. Dissociation of HCN is suppressed by the addition of HCl. Explain.

vi. Derive the relationship between degree of dissociation and dissociation constant in weak electrolytes.

vii. Sulfides of cation of group II are precipitated in acidic solution (H_2S + HCl) whereas sulfides of cations of group IIIB are precipitated in ammoniacal solution of H_2S. Comment on the relative values of solubility product of sulfides of these.

viii. Solubility of a sparingly soluble salt get affected in presence of a soluble salt having one common ion. Explain.

ix. The pH of rain water collected in a certain region of Maharashtra on particular day was 5.1. Calculate the $H^{\oplus}$ ion concentration of the rain water and its percent dissociation.

x. Explain the relation between ionic product and solubility product to predict whether a precipitate will form when two solutions are mixed?

Activity :

Take two test tubes and label them as A and B. Add Zinc filings in both the test tubes. In the test tube labelled A add 5 mL of 1M HCl and in test B 5 mL of acetic acid. Keep the test tubes on the stand. Note down your observations.

a. Do you see any effervescence coming from the two test tubes ?

b. Which gas is evolved ?

c. How do you identify the gas ?

d. What is the relative rate at which the gas is evolved in the two test tubes

e. Based on your observations comment on the strength of acids used.

4. CHEMICAL THERMODYNAMICS

Can you recall ?

1. How do you define energy?
2. What are the different forms of energy?

4.1 Introduction : You know transformation of liquid water into vapour, solid ice into liquid water or burning of carbon forming carbon dioxide, CO_2, are accompanied by a change in energy. In dry cell, the chemical energy is converted into electrical energy. On the other hand, in electroplating of metals electrical energy is converted into chemical energy. Thus it may be realized that the energy can be transformed from one form into another.

Do you know ?

At the top of dam, water is stored in a reservoir. It has certain potential energy due to its height from ground level and its kinetic energy is negligible as it is not in motion. As the water starts to fall down through an outlet its potential energy decreases and kinetic energy increases due to the downward velocity. It means that potential energy of falling water is converted into kinetic energy.

Thermodynamics is concerned with the energy changes in physical and chemical transformations. Thermodynamics, however gives no information on the rates of physical or chemical processes or underlying mechanisms involved in these.

4.2 Terms used in thermodynamics

4.2.1 System and surrounding : Consider a gas enclosed in a cylinder equipped with a movable piston as shown in Fig. 4.1. Suppose we undertake study of change in volume of a gas and the amount of energy released or gained by a gas when the pressure is varied by putting certain mass on the piston. In this case, a gas under study is called the system.

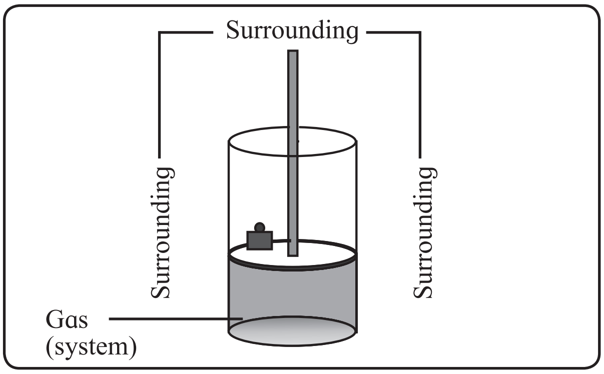


Fig. 4.1 : System and surroundings

A part of the universe under thermodynamic investigation is called the system.All other parts of the universe outside the system such as cylinder, room and others, are surroundings. The universe is made of system plus surroundings.

4.2.2 Types of system :

Observe and discuss...

Observe Fig. 4.2 and discuss with reference to transaction of energy and matter.

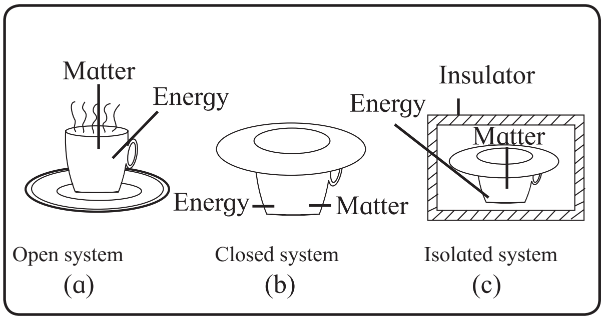


Fig. 4.2 : Kinds of systems

Three types of systems are shown in Fig. 4.2.

i. Open system : Fig. 4.2(a) shows an open cup containing hot coffee placed in a room. You observe coffee cools down releasing heat to the surroundings. The water vapour from coffee simultaneously passes into surroundings. Such a system (coffee) which exchanges both energy and matter with the surroundings is called an open system.

ii. Closed system : In Fig. 4.2(b), a cup containing hot coffee is covered with a saucer. Coffee cools down by giving away heat to the surroundings. The water vapour from coffee now does not pass into surroundings. Such a system that exchanges energy and not the matter with the surroundings is called a closed system.

iii. Isolated system : As you see in Fig. 4.2(c), a cup containing hot coffee covered with a saucer is insulated from the surroundings. Coffee does not cool down. Moreover, there is no escape of water vapour into the surroundings. Such a system that does not allow exchange of either energy or matter with the surroundings is an isolated system.

4.2.3 Properties of system

i. Extensive property :

A property which depends on the amount of matter present in a system is called an extensive property.

Examples : Mass, volume, internal energy, heat capacity, number of moles.

ii. Intensive property :

A property which is independent of the amount of matter in a system is called intensive property.

Examples : Pressure, temperature, surface tension, viscosity, melting point, boiling point, specific heat.

4.2.4 State functions : As shown in Fig. 4.1, certain amount of a gas is enclosed in a cylinder fitted with a movable piston. Suppose the pressure of the gas is 1 bar (P_1), volume is 1 dm^3 (V_1) and temperature is 300 K (T_1) in the beginning. This initial state of the system is fully defined by specifying the values of these properties. Such properties defining the state of a system, are **state functions**.

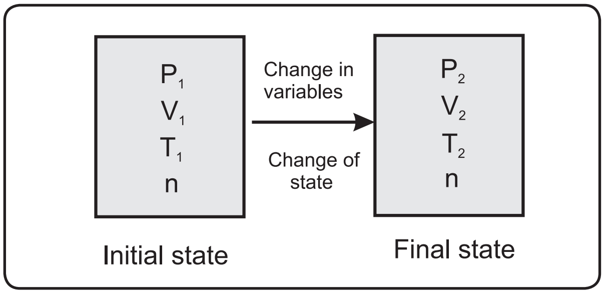


Fig. 4.3 : Change of state

Suppose the pressure of the system is increased to 2 bar, (P_2) volume changes to 0.5 dm^3 (V_2) and the temperature is maintained at 300 K (T_1). This is the final state of the system which is different from the initial state. A change in state functions of the system brings forth a change of its state. This is shown in Fig. 4.3.

The final state of the system in Fig. 4.3. is described by pressure 2 bar (P_2), volume 0.5 dm^3(V_2) and temperature 300 K(T_1). A system continues to be in such state as long as the state functions are unchanged. How the pressure 2 bar is attained whether by increasing from 1 bar to 2 bar or decreasing from 5 bar to 2 bar, would not matter.

The property which depends on the state of a system and independent of a path followed to attain it, is called the **state function.**

The term process means a physical or chemical change in a system on going from one state to another. This can be achieved by a number of paths by some operation. A path here refers to a sequence of situations the system undergoes during the accomplishment of the change. In other words the process in general may not necessarily determine the change in unique way. Only isothermal and adiabatic reversible processes follow the unique path to bring about the change of state of the system.

4.2.5 Path Functions : The properties which depend on the path are called path functions. For example, work *(W)* and heat *(Q)*.

4.2.6 Thermodynamic equilibrium : Consider a gas enclosed in a cylinder fitted with a movable piston shown in Fig. 4.1. The gas has temperature T_1, pressure P_1 and volume V_1. These state functions continue to be constant as long as piston is motionless, and no heat exchange takes place. This is an equilibrium state.

Now move the piston in upward direction so that the gas expands. It passes through states for which pressure, volume and temperature are not specified and vary continuously during the movement of the piston. The gas would then be in nonequilibrium state.

Stop the movement of the piston. Suppose at this stage the pressure and volume of the gas are respectively P_2 and V_2 and the temperature is constant at T_1. The state functions are constant since the piston is motionless. The gas is then in another equilibrium state.

A system is said to be in thermodynamic equilibrium when its state functions do not vary with time. Thermodynamics considered here is limited to equilibrium states.

4.2.7 Process and its types : A transition from one equilibrium state to another is called a process. They are of different types.

i. Isothermal process : It is the process in which temperature of the system remains constant throughout the transformation.

In such process heat flows from the system to surroundings and vice versa so as to keep the temperature constant. For a given temperature the internal energy *(U)* of the system remains constant. Thus, $\Delta T = 0$ and $\Delta U = 0$.

ii. Isobaric process : In isobaric process the pressure remains constant during the transformation. In the laboratory chemical reactions are carried out in open containers at constant atmospheric pressure or $\Delta P = 0$

iii. Isochoric process : It is a process during which volume of the system remains constant during the transformation. A chemical reaction carried out in a closed container is isochoric. For isochoric process $\Delta V = 0$.

iv. Adiabatic process : A process in which there is no exchange of heat between system and surroundings is an adiabatic process. ($Q = 0$). In adiabatic process the system is completely insulated from the surroundings. For an exothermic process the heat is released which rises temperature of the system. If the process is endothermic the temperature falls. This results in either increase or decrease of internal energy.

v. Reversible process : Consider a gas enclosed in a cylinder fitted with a movable piston. Let the external pressure be P_{ext} on the outer surface of the piston be set equal to pressure P of the gas. Neither expansion nor compression of the gas occurs. A system is then said to be in mechanical equilibrium with surroundings.

Consider P_{ext} is reduced by an infinitesimal amount. Now it the P_{ext} is infinitesimally smaller than P the piston moves out slowly allowing gas to expand.

If P_{ext} is slightly increased so that it becomes infinitesimally greater than P, the piston moves inward with a compression of the gas.

For the system in mechanical equilibrium with its surroundings, infinitesimal change may cause the process to occur in the reverse direction. The process is then said to be thermodynamically reversible. A process conducted in such a way so that at every stage the driving force due to pressure *(P)* is infinitesimally greater than the opposing force due to external pressure (P_{ext}) and which can be reversed by a slight change of the opposing force is reversible process.

Features of reversible process

i. The driving and opposing forces differ by an infinitesimal amount.

ii. The process can be reversed by an infinitesimal change in conditions.

iii. A reversible process proceeds infinitely slowly and takes place in infinite number of steps.

iv. At the end of every step of the process, the system attains mechanical equilibrium with the surroundings.

4.3 Nature of heat and work

4.3.1 Nature of work *(W)* : In mechanics the work is defined as the energy by which body is displaced through a distance d with an application of force. Thus,

$$W = f \times d$$

In thermodynamics the type of work involved is pressure-volume or *PV* work, that is, work is done when the system (gas) expands or contracts against the external opposing force.

It may be realized that the product of pressure and volume is equal to work. Pressure is defined as force per unit area. If d is the distance, area $A = d^2$ and volume $V = d^3$. Then

$$PV = \frac{f}{A} \times V = \frac{f}{d^2} \times d^3 = f\,d = W$$

Now let us explore the *PV* work with two chemical reactions in a cylinder equipped with frictionless movable piston attached with a certain mass on its outer surface.

i. Decomposition of H_2O_2

Consider $2\ H_2O_2(l) \longrightarrow 2\ H_2O(l) + O_2(g)$

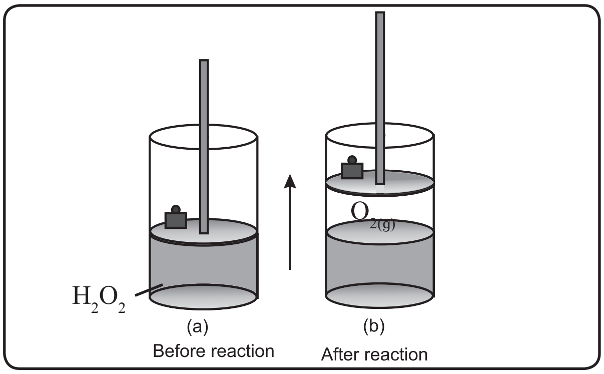


Fig. 4.4 : Decomposition of H_2O_2

The gas produced in above reaction pushes the piston upwards so that the mass in the surroundings is raised as shown in Fig. 4.4. In lifting the mass the system loses energy to the surroundings or it performs work on the surroundings. With no heat being transferred a loss of energy by the system is equal to work done by the system on the surroundings. This is *PV* expansion.

ii. Reaction between NH_3 gas and HCl gas

Now, consider

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

As the reaction progresses the gases are consumed resulting in a decrease of volume. The piston moves down. A decrease in the height of the mass is shown in Fig. 4.5.

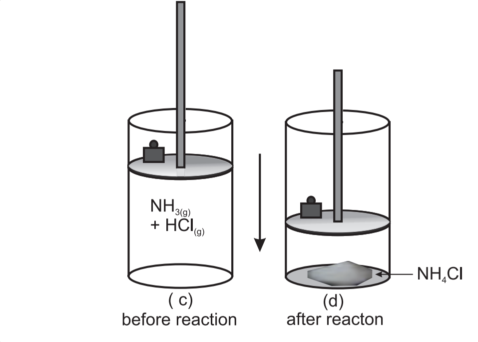


Fig. 4.5 : Reaction between $NH_3(g)$ and HCl(g)

In the process the surroundings lose energy to the system and perform work on the system. If no heat transfer occurs work done by the surroundings is equal to gain in energy by the system. This is *PV* work.

Thus the work refers to a way by which a system exchanges energy with surroundings.

4.3.2 Nature of heat *(Q)* : Like heat is a form of energy by which the system exchanges energy with its surroundings. When the system and its surroundings are at different temperatures heat either flows in or let out of the system.

4.3.3 Sign conventions of *W* and *Q* : The energy changes for the system are considered hereafter.

The energy entering the system from the surroundings has positive value. While the energy leaving the system and flowing into the surroundings is negative. This is shown in Fig. 4.6.

$+Q$: Heat is absorbed by the system from the surroundings.

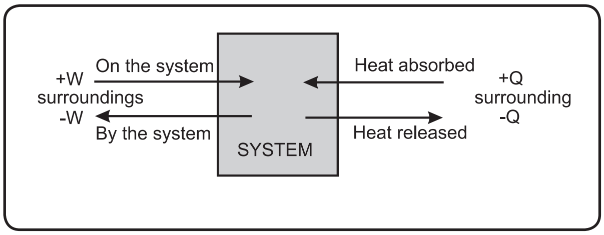


Fig. 4.6 : Sign conventions

-Q : Heat is released by the system to the surroundings.

+W : Work is done on the system by the surroundings.

-W : Work is done by the system on the surroundings.

Note W and Q are path functions.

4.4 Expression for pressure-volume *(PV)* work : Consider a certain amount of gas at constant pressure P is enclosed in a cylinder fitted with frictionless, rigid movable piston of area A. This is shown in Fig. 4.7.

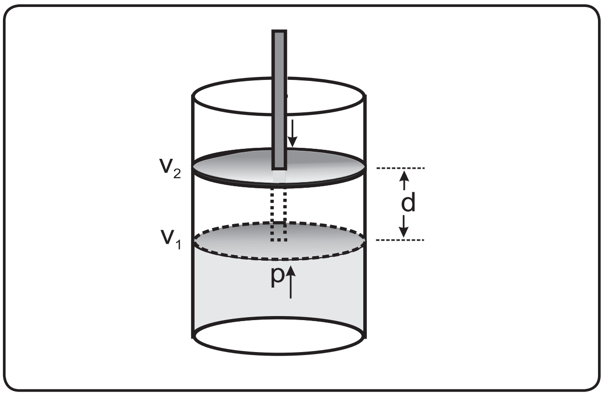


Fig. 4.7 : Pressure-volume work

Let volume of the gas be V_1 at temperature T.

On expansion the force exerted by a gas is equal to area of the piston multiplied by pressure with which the gas pushes against piston. This pressure is equal in magnitude and opposite in sign to the external atmospheric pressure that opposes the movement and has its value -P_{ext}. Thus,

$$f = -P_{ext} \times A \qquad \text{.......} (4.1)$$

where P_{ext} is the external atmospheric pressure.

If the piston moves out a distance d, then the amount of work done is equal to the force multiplied by distance.

$$W = f \times d \qquad \text{.......} (4.2)$$

Substitution from Eq. (4.1) gives

$$W = -P_{ext} \times A \times d \qquad \text{.......} (4.3)$$

The product of area of the piston and distance it moves is the volume change *(ΔV)* in the system.

$$\Delta V = A \times d \qquad \text{.......} (4.4)$$

Combining equations (4.3) and (4.4) we write

$$W = -P_{ex}\,\Delta V \qquad \text{.......} (4.5)$$

$$W = -P_{ex}(V_2 - V_1)$$

where V_2 is final volume of the gas.

When the gas expands, work is done by the system on the surroundings. Since $V_2 > V_1$, W is negative. When the gas is compressed, work is done on the system by surroundings. In this case $V_1 < V_2$, and $-P_{ext}\,\Delta V$ or W is positive.

Eq. (4.5) shows the external pressure determines the work during expansion (or compression) of the gas. A volume change does no work unless the system is linked to the surroundings by external pressure.

Remember...

Remember during expansion of a gas, work is done by the system on the surroundings and during compression work is done on the system by the surroundings.

4.4.1 Free expansion : A free expansion means expansion against zero opposing force. Such expansion occurs in vacuum. The work done by a system during such expansion is given by Eq. (4.5), W = - $P_{ext}\,\Delta V$. When the gas expands in vacuum, there is no opposing force that is P_{ext} and hence, $W = 0$. In other words no work is done when the gas expands freely in vacuum.

4.4.2 Units of energy and work

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ Pa m}^3$$

$$1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$$

From to Eq. (4.5), $W = - P_{ext} \Delta V$, if pressure is expressed in bar and ΔV in dm^3, then the work has the units of bar dm^3.

$$1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$1 \text{ dm}^3 \text{ bar} = \text{dm}^3 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$= \text{m}^3 \times 10^{-3} \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$= 100 \text{ kg m}^2 \text{ s}^{-2} = 100 \text{ J}$$

Problem 4.1 : Three moles of an ideal gas are expanded isothermally from 15 dm^3 to 20 dm^3 at constant external pressure of 1.2 bar. Estimate the amount of work in dm^3 bar and J.

Solution :

$W = - P_{ext} \Delta V = - P_{ext} (V_2 - V_1)$

$P_{ext} = 1.2$ bar, $V_1 = 15$ dm^3, $V_2 = 20$ dm^3

Substitution of these quantities into the equation gives

$$W = -1.2 \text{ bar } (20 \text{ dm}^3 - 15 \text{ dm}^3)$$

$$= -1.2 \text{ bar} \times 5\text{dm}^3 = -6 \text{ dm}^3 \text{ bar}$$

$$1 \text{ dm}^3 \text{ bar} = 100 \text{ J}$$

Hence, $W = -6$ dm^3 bar × 100 J/dm^3 bar $= -600$ J

Problem 4.2 : Calculate the constant external pressure required to compress 2 moles of an ideal gas from volume of 25 dm^3 to 13 dm^3 when the work obtained is 4862.4 J.

Solution :

$W = - P_{ext} \Delta V = - P_{ext} (V_2 - V_1)$

$V_1 = 25$ dm^3, $V_2 = 13$ dm^3, $W = 4862.4$ J

$$W = 4862.4 \text{ J} \times \frac{\text{dm}^3 \text{ bar}}{100 \text{ J}} = 48.62 \text{ dm}^3 \text{ bar}$$

Substitution of these into the equation gives

$$48.62 \text{ dm}^3 \text{ bar} = - P_{ext} (13 \text{ dm}^3 - 25 \text{ dm}^3)$$

$$= - P_{ext} \times 12 \text{ dm}^3$$

$$\text{Hence, } P_{ext} = \frac{48.62 \text{ dm}^3 \text{ bar}}{12 \text{ dm}^3} = 4.052 \text{ bar}$$

Problem 4.3 : 200 mL ethylene gas and 150 mL of HCl gas were allowed to react at 1 bar pressure according to the reaction

$$C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g)$$

Calculate the PV work in joules.

Solution :

$W = - P_{ext} \Delta V = - P_{ext} (V_2 - V_1)$

According to the equation of reaction 1 mole of C_2H_4 reacts with 1 mole of HCl to produce 1 mole of C_2H_5Cl. Hence, 150 mL of HCl would react with only 150 mL of C_2H_4 to produce 150 mL of C_2H_5Cl.

$V_1 = 150$ mL + 150 mL = 300 mL = 0.3 dm^3

$V_2 = 150$ mL = 0.15 L, $P_{ext} = 1$ bar

Substitution of these quantities in above

$$W = -1 \text{ bar } (0.15 \text{ dm}^3 - 0.3 \text{ dm}^3)$$

$$= 0.15 \text{ dm}^3 \text{ bar}$$

$$= 0.15 \text{ dm}^3 \text{ bar} \times 100 \frac{\text{J}}{\text{dm}^3 \text{ bar}}$$

$$= 15.0 \text{ J}$$

4.5 Concept of maximum work : Eq. (4.5) shows the amount of work performed by a system is governed by the opposing force (P_{ext}). Larger the opposing force more work is done by the system to overcome it.

If the opposing force is zero no work is involved. With an increase of the opposing force from zero, more work will be needed by the system. When the opposing force reaches its maximum the system performs maximum work. With an opposing force being greatest more effort would be needed to overcome it.

Thus when the opposing force (P_{ext}) becomes greater than the driving force (P) the process gets reversed. Since the opposing force cannot be greater than the driving force it should be the maximum.

If the pressure P of the gas differs from P_{ext} by a quantity ΔP then $P - P_{ext} = \Delta P$ and $P_{ext} = P - \Delta P$. The eq. (4.5) then becomes

$$W = -(P - \Delta P) \Delta V$$

The work *(W)* would be maximum when ΔP is smallest. This means the opposing force (P_{ex}) must be infinitesimally smaller than the driving force *(P)* for the work to be maximum. This is required for the process to be reversible. The maximum work is obtained from the change which is thermodynamically reversible.

4.5.1 Expression for the maximum work :

Consider n moles of an ideal gas enclosed in a cylinder fitted with frictionless movable rigid piston. It expands isothermally and reversibly from the initial volume V_1 to final volume V_2 at temperature *T*. The expansion takes place in a number of steps illustrated in Fig. 4.8.

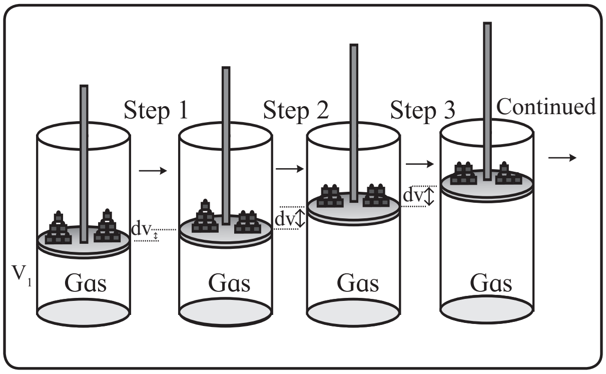


Fig. 4.8 : Reversible expansion

During each step the external pressure P_{ext} is made infinitesimally smaller than the pressure P of the gas, with a gradual removal of masses from the piston. The gas expand slowly and its pressure *P* would decrease. The expansion continues until the pressure of the gas falls to P_{ext}. Beyond this no further expansion occurs and the system attains mechanical equilibrium with its surroundings. The volume of a gas is increased by an infinitesimal quantity dv in each single step.

The process is repeated in such a way that every time P_{ext} is lowered infinitesimally the gas undergoes a series of infinitesimal increments in volume until the volume V_2 is attained.

When the volume of a gas increases by an infinitesimal amount *dV* in a single step, the small quantity of work done

$$dW = -P_{ext}\,dV \qquad \text{....... (4.6)}$$

As the expansion is reversible, *P* is greater by a very small quantity dp than p_{ex}. Thus,

$$P - P_{ext} = dP \text{ or } P_{ext} = P - dP \qquad \text{....... (4.7)}$$

Combining equations (4.6) and (4.7),

$$dW = -(P - dP)dV = -PdV + dP\,dV$$

Neglecting the product *dpdV* which is very small, we get

$$dW = -PdV \qquad \text{....... (4.8)}$$

The total amount of work done during entire expansion from volume V_1 to V_2 would be the sum of infinitesimal contributions of all the steps. The total work is obtained by integration of Eq. (4.8) between the limits of initial and final states. This is the maximum work, the expansion being reversible. Thus,

$$\int_{\text{initial}}^{\text{final}} dW = -\int_{V_1}^{V_2} PdV$$

$$\text{Hence } W_{max} = -\int_{V_1}^{V_2} PdV \qquad \text{....... (4.9)}$$

Using the ideal gas law

$$PV = nRT$$

$$W_{max} = -\int_{V_1}^{V_2} nRT\frac{dV}{V}$$

$$= -nRT\int_{V_1}^{V_2}\frac{dV}{V} \text{ because } T \text{ is constant.}$$

$$= -nRT \ln(V)_{V_1}^{V_2}$$

$$= -nRT(\ln V_2 - \ln V_1)$$

$$= -nRT \ln\frac{V_2}{V_1}$$

$$= -2.303\, nRT \log_{10}\frac{V_2}{V_1} \qquad \text{....... (4.10)}$$

At tconstant temperature, $P_1V_1 = P_2V_2$ or

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Replacing V_2/V_1 in Eq. (4.10) by P_1/P_2, We have

$$W_{max} = -2.303\ nRT \log \frac{P_1}{P_2} \quad \text{.......} (4.11)$$

Problem 4.4 : 2 moles of an ideal gas are expanded isothermally and reversibly from 20 L to 30 L at 300 K. Calculate the work done (R= 8.314 J K^{-1} mol^{-1})

Solution : $W_{max} = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$

n = 2 mol, T = 300 K, V_1 = 20 L, V_2 = 30 L, R = 8.314 J/K mol

Substitution of these quantities into the equation gives

$$W_{max} = -2.303 \times 2 \text{ mol} \times 8.314 \text{ J/K mol} \times 300\text{K} \times \log_{10} \frac{30 \text{ L}}{20 \text{ L}}$$

$$= -2.303 \times 2 \times 8.314 \text{ J} \times 300 \times \log_{10} 1.5$$

$$= -2.303 \times 2 \times 8.314 \text{ J} \times 300 \times 0.1761$$

$$= -2023 \text{ J} = -2.023 \text{ kJ}$$

Problem 4.5 : 22 g of CO_2 are compressed isothermally and reversibly at 298 K from initial pressure of 100 kPa when the work obtained is 1.2 kJ. Find the final pressure.

Solution :

$$W = -2.303\ nRT \log_{10} \frac{P_1}{P_2}$$

$n = \frac{22 \text{ g}}{44 \text{ g mol}^{-1}}$ =0.5 mol, T = 298 K,

P_1= 100 kPa, W = 1.2 kJ = 1200 J

Hence, 1200 J = -2.303 × 0.5 mol ×8.314 J K^{-1} mol^{-1} × 298K × $\log_{10} \frac{100 \text{ kPa}}{P_2}$

or $\log_{10} \frac{100 \text{ kPa}}{P_2} = \frac{-1200}{2.303 \times 0.5 \times 8.314 \times 298}$

$$= -0.4206$$

$$\frac{100 \text{ kPa}}{P_2} = \text{antilog } (-0.4206) = 0.3797$$

Therefore, $P_2 = \frac{100 \text{ kPa}}{0.3797} = 263.4 \text{ kPa}$

Problem 4.6 : 300 mmol of an ideal gas occupies 13.7 dm^3 at 300 K. Calculate the work done when the gas is expanded until its volume has increased by 2.3 dm^3 (a) isothermally against a constant external pressure of 0.3 bar (b) isothermally and reversibly (c) into vacuum.

Solution :

a. $W = -P_{ex}\ \Delta V$

P_{ext} = 0.3 bar, ΔV = 2.3 dm^3

$$W = -0.3 \text{ bar} \times 2.3 \text{ dm}^3$$

$$= -0.69 \text{ dm}^3 \text{ bar}$$

$$= -0.69 \text{ dm}^3 \text{ bar} \times \frac{100 \text{ J}}{\text{dm}^3 \text{ bar}}$$

$$= -69 \text{ J}$$

b. $W_{max} = -2.303\ nRT \log_{10} \frac{V_2}{V_1}$

n = 300 mmol = 300 × 10^{-3} mol = 0.3 mol, T = 300 K

$$W_{max} = -2.303 \times 0.3 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 300\text{K} \times \log_{10} \frac{16}{13.7}$$

$$= -2.303 \times 0.3 \times 8.314 \text{ J} \times 300 \times 0.0674$$

$$= -116.1 \text{ J}$$

c. $W = -P_{ex}\ \Delta V$

When gas is expanded to vaccum, P_{ext} = 0 and W = 0

4.6 Internal energy (U) : Every substance is associated with a definite amount of energy. This energy stored in a substance is internal energy denoted by U.

The internal energy of a system is made up of kinetic and potential energies of individual particles of the system.

$$\Delta U = U_2 - U_1$$

where U_1 and U_2 are internal energies of initial and final states, respectively. U is a state function and extensive property.

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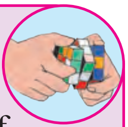


25 kJ of work is done on the system and it releases 10 kJ of heat. What is ΔU?

A transfer of energy (as heat or work) from the system would change its internal energy. To know ΔU the energy supplied to or removed from the system need to be monitored.

i. The energy transferred to the system by heating it or performing work on it is added to the system.

ii. The energy transferred from the system by cooling or by performing work on the surroundings is removed from the system.

The following examples illustrate how to determine ΔU.

i. 30 kJ of heat supplied to the system. It would be added to internal energy of the system and $\Delta U = +30$ kJ.

ii. If 20 kJ of work is done on the system, it is added to internal energy of the system. Consequently, $\Delta U = +\ 20$ kJ.

iii. Suppose a system releases 10 kJ of heat and performs 15 kJ of work on the surroundings. These quantities are removed from internal energy of the system and $\Delta U = -\ 25$ kJ

4.7 First law of thermodynamics :

First law of thermodynamics is simply the conservation of energy. According to this law the total energy of a system and surroundings remains constant when the system changes from an initial state to final state. The law is stated in different ways as follows.

i. Energy of the universe remains constant

ii. The total internal energy of an isolated system is constant

iii. Energy is neither created nor destroyed and can only be converted from one form to another.

All above statements are equivalent.

4.7.1 Formulation of first law of thermodynamics :

A system exchange energy with its surroundings either by transfer of heat or by doing work. An energy supplied to the system increases its internal energy. On the other hand, removal of heat or work from the system decreases its internal energy.

Suppose (Q) is heat supplied to the system and W work done on the system by the surroundings. The internal energy of the system would increase.

Increase in internal energy of the system is equal to sum of the quantity of heat supplied to the system and amount of work done on the system or

$$\Delta U = Q + W \qquad \text{.......(4.12)}$$

where $\Delta \mathrm{U}$ is an increase in internal energy of the system. Eq. (4.12) is the first law of thermodynamics. For infinitesimal changes.

$$dU = dQ + dW \qquad \text{.......(4.13)}$$

4.7.2 First law of thermodynamics for various processes

i. Isothermal process : Temperature is constant in such process, internal energy is constant. Hence, $\Delta U = 0$
For isothermal process

$$0 = Q + W \text{ or } W = -Q \qquad \text{.......(4.14)}$$

The above equation implies that heat absorbed by the system is entirely used for doing work on the surroundings. When work is done on the system by the surroundings it results in release of heat.

ii. Adiabatic process : In adiabatic process, there is no exchange of heat between system and its surroundings that is, $Q = 0$. then

$$-\Delta U = -W \qquad \text{.......(4.15)}$$

Thus an increase in internal energy of the system is the work done on it. If the work is done by the system on the surroundings at the expense of its internal energy, the internal energy accompanying the adiabatic process would decrease.

iii. Isochoric process : Substitution of $W = -P_{ext}\,\Delta V$ into Eq. (4.12)

$$\Delta U = Q - P_{ext}\,\Delta V \qquad \text{....... (4.16)}$$

As the reaction is carried out in a closed container, volume of the system is constant or $\Delta V = 0$ and

$$\Delta U = Q_v \qquad \text{....... (4.17)}$$

Equation (4.17) shows a change in internal energy of the system is due to heat transfer at constant volume. The subscript 'V' indicates that heat is transferred at the constant volume. Further U being a state function, Q_v is also a state function.

iv. Isobaric process : Usually chemical reactions are carried out in the open containers under constant atmospheric pressure. In such reactions, $\Delta V \neq 0$

Replacing Q by Q_p and ΔU by $Q_p - P_{ext}\,\Delta V$ in equation (4.16) gives

$$Q_p = \Delta U + P_{ext}\,\Delta V \qquad \text{....... (4.18)}$$

The reactions carried out in open containers under constant atmospheric pressure are common in chemistry, a special symbol ΔH, the enthalpy change, is given to indicate heat changes occurring at constant pressure.

> **Remember...**
> q is not a state function.
> Whereas Q_v and Q_p are state functions.

4.8 Enthalpy (H) : Enthalpy of a system is sum of internal energy of a system and the energy equivalent to PV work.

$$H = U + PV \qquad \text{....... (4.19)}$$

Change in enthalpy, ΔH, is also state function given by

$$\Delta H = H_2 - H_1 \qquad \text{....... (4.20)}$$

where H_1 and H_2 are the enthalpies of initial and final states, respectively.

From Eq. (4.19), we write

$$H_1 = U_1 + P_1V_1 \text{ and } H_2 = U_2 + P_2V_2$$

With these

$$\begin{aligned}\Delta H &= U_2 + P_2V_2 - U_1 + P_1V_1\\ &= (U_2 - U_1) + (P_2V_2 - P_1V_1)\\ &= \Delta U + \Delta(PV) \qquad \text{.......(4.21)}\end{aligned}$$

For constant pressure, $P_1 = P_2 = P$ and

$$\Delta H = \Delta U + P\Delta V \qquad \text{....... (4.22)}$$

If the pressure inside and outside is the same or $P_{ext} = P$, Eq. (4.18) gives

$$Q_p = \Delta U + P\,\Delta V \qquad \text{....... (4.23)}$$

From equations (4.22) and (4.23)

$$\Delta H = Q_p \qquad \text{.......(4.24)}$$

Thus change in enthalpy of a system is equal to heat transferred from it at the constant pressure. H and Q_p are state functions.

4.8.1 Relationship between ΔH and ΔU for chemical reactions : At constant pressure, ΔH and ΔU are related as

$$\Delta H = \Delta U + P\Delta V$$

i. For reactions involving solids and liquids, ΔV usually is very small (solids or liquids do not show volume change with change of pressure) and $\Delta H = \Delta U$

ii. For reactions involving gases, ΔV cannot be neglected and

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V\\ &= \Delta H + P(V_2 - V_1)\\ \Delta H &= \Delta U + PV_2 - PV_1 \qquad \text{.......(4.25)}\end{aligned}$$

where V_1 is the volume of gas phase reactants and V_2 that of the gaseous products.

We assume reactant and product behave ideally. Applying ideal gas equation $PV = nRT$. When n_1 moles of gaseous reactants produce n_2 moles of gaseous products. The ideal gas equation give,

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT \qquad \text{.......(4.26)}$$

Substitution of Eq. (4.26) into Eq. (4.25) yields

$$\Delta H = \Delta U + n_2RT - n_1RT$$

$$= \Delta U + (n_2 - n_1)\, RT$$

$$= \Delta U + \Delta n_g RT \qquad \text{....... (4.27)}$$

where Δn_g is difference between the number of moles of products and those of reactants.

Problem 4.7 : ΔH for the reaction,

$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$ is -84.4 kJ at 25 ^{0}C. Calculate ΔU for the reaction at 25 ^{0}C. ($R = 8.314$ J K^{-1} mol^{-1})

Solution :

$$\Delta H = \Delta U + \Delta n_g RT$$

Δn_g = (moles of product gases) - (moles of reactant gases)

$$\Delta n_g = 1 - 3 = -2 \text{ mol}$$

$\Delta H = -84.4$ kJ, $R = 8.314$ J K^{-1} mol^{-1}

$= 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}

Substitution of these in above

-84.4 kJ $= \Delta U + 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1} × 298 K × (-2 mol)

$$= \Delta U - 4.96 \text{ kJ}$$

Hence, $\Delta U = -84.4$ kJ $+ 4.96$ kJ $= - 79.44$ kJ

Under what conditions $\Delta H = \Delta U$?

Problem 4.8 : In a particular reaction 2 kJ of heat is released by the system and 6 kJ of work is done on the system. Determine of ΔH and ΔU?

Solution : According to the first law of thermodynamics

$$\Delta U = Q + W$$

$$Q = -2 \text{ kJ}, \qquad W = +6 \text{ kJ}$$

$$\Delta U = -2 \text{ kJ} + 6 \text{ kJ} = + 4 \text{ kJ}$$

$Q_p = \Delta H = - 2$kJ

Problem 4.9 : Calculate the work done in oxidation of 4 moles of SO_2 at 25^{0}C if

$2\, SO_2(g) + O_2(g) \longrightarrow 2\, SO_3(g)$

$R = 8.314$ J K^{-1}mol^{-1}

State whether work is done on the system or by the system.

Solution :

For oxidation of 4 moles of SO_2, the reaction is

$4\, SO_2(g) + 2\, O_2(g) \longrightarrow 4\, SO_3(g)$

$$W = -\Delta n_g RT$$

$\Delta n_g = 4 - 6 = - 2$ mol, $T = 298$ K

Hence,

$W = -2$ mol × -8.314 J K^{-1} mol^{-1} × 298 K

$= 4955$ J $= 4.955$ J

Work is done on the system (since $W > 0$).

4.8.2 Work done in chemical reaction :

The work done by a system at constant temperature and pressure is given by

$W = P_{ext}\, \Delta V$. Assuming $P_{ext} = P$,

$$W = - P\Delta V$$

$$= - P\, (V_2 - V_1)$$

$$= - PV_2 + PV_1$$

II the gases were ideal, using Eq. (4.26)

$PV_1 = n_1RT$ and $PV_2 = n_2RT$

At constant temperature and pressure.

$$W = - n_2RT + n_1RT$$

$$= - (n_2 - n_1)\, RT$$

$$= - \Delta n_g RT \qquad \text{....... (4.28)}$$

The above equation gives the work done by the system in chemical reactions. The sign of W depends on ΔV. We consider the following cases:

i. If $n_2 > n_1$, Δn_g is positive and $W < 0$ or work is done by the system.

ii. If $n_1 > n_2$, Δn_g is negative and $W > 0$ or work is done on the system.

iii. If $n_1 = n_2$, $\Delta n_g = 0$ and $W = 0$, or

No PV work is done when number of moles of reactants and products are equal.

4.9 Enthalpies of physical transformations

4.9.1 Enthalpy of phase transition : In phase transition, one phase of a substance is converted into another at constant temperature and pressure without change in chemical composition.

i. Enthalpy of fusion ($\Delta_{fus}H$) : Enthalpy change that occurs when one mole of a solid is converted into liquid without change in temperature at constant pressure is enthalpy of fusion. For example,

$H_2O\ (s) \longrightarrow H_2O\ (l)$

$\Delta_{fus}H = +6.01$ kJ mol^{-1} at 0 ^{0}C

When 1 mole of solid ice melts at 0 ^{0}C and 1 atm pressure, change in enthalpy is 6.01 kJ. The same amount of heat is absorbed by ice during the melting. A reverse of fusion is freezing of solid.

$H_2O\ (l) \longrightarrow H_2O\ (s)$, $\Delta_{freez}H = -6.01$ kJ mol^{-1} at 0 ^{0}C

Thus, when one mole of liquid water freezes at 0 ^{0}C, heat is evolved.

ii. Enthalpy of vaporization ($\Delta_{vap}H$) : It is the enthalpy change accompanying the vaporization of one mole of liquid without changing its temperature at constant pressure.

For example,

$H_2O(l) \longrightarrow H_2O(g)$ $\Delta_{vap}H = +40$ kJ mol^{-1} at 100 ^{0}C

$H_2O(l) \longrightarrow H_2O(g)$ $\Delta_{vap}H = +44$ kJ mol^{-1} at 25 ^{0}C

Thus, when one mole of water is vaporised at 1 atm presure, the enthalpy change is + 40 kJ at 100 ^{0}C and +44 kJ at 25 ^{0}C.

On the other hand, the condensation to vapour is accompanied with a release of heat.

$H_2O(g) \longrightarrow H_2O(l)$, $\Delta_{con}H = -40.7$ kJ mol^{-1} at 100 ^{0}C

iii. Enthalpy of sublimation ($\Delta_{sub}H$) : It is the enthalpy change for the conversion of one mole of solid directly into vapour at constant temperature and pressure. Consider

$H_2O(s) \longrightarrow H_2O(g)$, $\Delta_{sub}H = 51.08$ kJ mol^{-1}, at 0 ^{0}C

The conversion of solid to vapour occurs in one or two steps, first melting of solid into liquid and second its vaporization; the enthalpy change is the same since enthalpy is the state function. At 0 ^{0}C

$$\begin{array}{lll} H_2O(s) \longrightarrow H_2O(l) & \Delta_{fus}H = 6.01 \text{ kJ mol}^{-1} \\ H_2O(l) \longrightarrow H_2O(g) & \Delta_{vap}H = 45.07 \text{ kJ mol}^{-1} \\ \hline H_2O(s) \longrightarrow H_2O(g) & \Delta_{sub}H = 51.08 \text{ kJ mol}^{-1} \end{array}$$

It follows that

$\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$. (See Fig. 4.9)

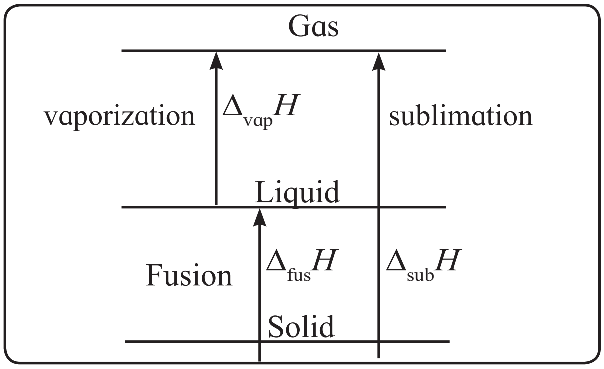


Fig. 4.10 Representing $\Delta_{fus}H$, $\Delta_{vap}H$ and $\Delta_{sub}H$

4.9.2 Enthalpy for the atomic / molecular change

i. Enthalpy of ionization ($\Delta_{ion}H$) : It is the enthalpy change accompanying the removal of an electron from one mole of gaseous atom. For example,

$Na(g) \longrightarrow Na^{\oplus}(g) + e^{\ominus}$ $\Delta_{ion}H = 494$ kJ mol^{-1}

The equation signifies when one mole of gas-phase atomic sodium is ionized to gas phase $Na^{\oplus}$ ions, the enthalpy change is 494 kJ. The same amount of heat would be required to ionize one mole of Na atoms.

The electron gain enthalpy on the other hand, gives the enthalpy change when one mole of gas-phase atoms of an element accept electron to form gaseous anion.

For example,

$Cl(g) + e^{\ominus} \longrightarrow Cl^{\ominus}(g)\ \Delta_{eg}H = -349\ kJ\ mol^{-1}$

Electron gain enthalpy of Cl is -349 kJmol^{-1}

ii. Enthalpy of atomization ($\Delta_{atom}H$) : The enthalpy change accompanying the dissociation of one mole of gaseous substance into atoms is the enthalpy of atomization. Consider,

$Cl_2(g) \longrightarrow Cl(g) + Cl(g);\ \Delta_{atom}H = 242\ kJ\ mol^{-1}$

$CH_4(g) \longrightarrow C(g) + 4H(g);\ \Delta_{ato}H = 1660\ kJ\ mol^{-1}$

iii. Enthalpy of solution ($\Delta_{soln}H$) : Enthalpy of solution is the enthalpy change in a process when one mole of a substance is dissolved in specified amount of solvent.

$NaCl(s) + aq \rightleftharpoons NaCl(aq)\ \Delta_{soln}H = 4\ kJ\ mol^{-1}$

Enthalpy of solution at infinite dilution is the enthalpy change when one mole of substance is dissolved in infinite amount of solvent.

An ionic compound dissolves in water in two steps:

1. The ions are separated from the molecule

$MX(s) \longrightarrow M^{\oplus}(g) + X^{\ominus}(g)$

Enthalpy change for this step is crystal lattice enthalpy, $\Delta_L H$ which is always positive.

2. The ions are hydrated with water molecules surrounding them.

$M^{\oplus}(g) + x\ H_2O \longrightarrow [M(H_2O)_x]^{\oplus}$

$X^{\ominus}(g) + y\ H_2O \longrightarrow [\ x(H_2O)_y]^{\ominus}$

The enthalpy change for this step is always negative and called enthalpy of hydration, $\Delta_{hyd}H$.

The enthalpy of solution is the sum of crystal lattice enthalpy and enthalpy of hydration.

$$\Delta_{soln}H = \Delta_L H + \Delta_{hyd}H$$

For NaCl, $\Delta_L H = +790$ kJ/mol and

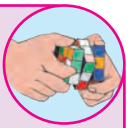
$\Delta_{hyd}H = -786\ kJ/mol^{-1}$

The enthalpy of solution of NaCl is

$\Delta_{soln}H\ (NaCl) = (+790 - 786)\ kJ/mol^{-1}$

$= +4\ kJ/mol^{-1}$

Try this...



For KCl, $\Delta_L H = 699\ kJ/mol^{-1}$ and $\Delta_{hyd}H = -681.8\ kJ/mol^{-1}$. What will be its enthalpy of solution?

4.10 Thermochemistry : Thermochemistry deals with enthalpy changes in chemical reactions

4.10.1 Enthalpy of chemical reaction ($\Delta_r H$)

Consider, $aA + bB \longrightarrow cC + dD$

The enthalpy change for the reaction is

$$\Delta_r H = (cH_C + d\ H_D) - (a\ H_A + bH_B)$$

where H_A, H_B, H_C and H_D are molar enthalpies of A, B, C and D, respectively. We write

$$\Delta_r H = \sum H_{products} - \sum H_{reactants} \quad ....(4.29)$$

Thus, **enthalpy of a chemical reaction is the difference between the sum of enthalpies of products and that of reactants with each substance in definite physical state and their amounts (moles) being represented by the coefficients in the balanced equation of the reaction.**

4.10.2 Exothermic and endothermic reactions : The enthalpy of a reaction can be positive or negative depending on $\sum H_{products}$ and $\sum H_{reactants}$.

Thus $\sum H_{products} > \sum H_{reactants}$, $\Delta_r H$ is positive signifies the reaction is endothermic.

On the other hand, if

$$\sum H_{\text{products}} < \sum H_{\text{reactants}},\ \Delta_r H \text{ is negative}$$

which means that heat is released and the reaction is exothermic.

For example,

$N_2(g) + O_2(g) \longrightarrow 2\ NO_2(g)$,

$\Delta_r H = 66.4$ kJ (endothermic)

$2\ KClO_3(s) \longrightarrow 2\ KCl(s) + 3O_2(g)$,

$\Delta_r H = -78$ kJ (exothermic)

4.10.3 Standard enthalpy of reaction($\Delta_r H^0$)

To compare enthalpy changes of different reactions they have to be reported under similar set of conditions.

Thermodynamic standard state : The standard state of a substance is the form in which the substance is most stable at a pressure of 1 bar and at temperature 298 K. If the reaction involves species in solution its standard state refers to 1 M concentration.

Standard states of certain elements and compounds are $H_2(g)$, $Hg(g)$, $Na(s)$ or C(graphite), $C_2H_5OH(l)$, $CaCO_3(s)$, $CO_2(g)$ $C_2H_5OH(l)$, $H_2O(l)$, $CaCO_3(s)$, $CO_2(g)$ refer to 1 bar and 25 ^{0}C.

The standard enthalpy ($\Delta_r H^0$) of reaction is the enthalpy change accompanying the reaction when the reactants and products involved are in their standard states.

4.10.4 Thermochemical equation : It is the balanced chemical equation in which the enthalpy change, physical states and the number of moles of reactants and products, have been specified. Here follow the guidelines for writing thermochemical equations :

i. Consider the balanced equation for reactants and products.

ii. The value and appropriate sign of enthalpy change is given on the right hand side. This value is $\Delta_r H^0$.

iii. The physical states of reactants and products are specified by letter, s (solid), *l* (liquid), g (gas) and aq (aqueous). $\Delta_r H^0$ value refers to physical states of substances those appear in the equation.

iv. The given value of $\Delta_r H^0$ assumes that the reaction occurs in a given direction. $\Delta_r H^0$ for the reverse reaction equals in magnitude and opposite in the sign to that of the forward reaction. A exothermic reaction on reversal becomes endothermic and vice versa.

v. When the coefficients indicating the number of moles of all substances in thermochemical equation are multiplied or divided by a certain numerical factor, the corresponding $\Delta_r H^0$ need to be multiplied or divided by the same.

Example of thermochemical equation

$$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2H_2O(l),\quad \Delta_r H^0 = -890 \text{ kJ}$$

The equation signifies that when 1 mole of gaseous CH_4 and 2 moles of O_2 in their standard states produce 1 mole of CO_2 gas and 2 moles of liquid water also in their standard states the enthalpy change would be -890 kJ.

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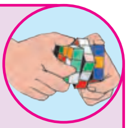


Given the thermochemical equation,

$$C_2H_2(g) + 5/2\ O_2(g) \longrightarrow 2CO_2(g) + H_2O(l),\quad \Delta_r H^0 = -1300 \text{ kJ}$$

Write thermochemical equations when

i. Coefficients of substances are multiplied by 2.

ii. equation is reversed.

4.10.5 Standard enthalpy of formation ($\Delta_f H^0$)

Consider

$$H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(l),\ \Delta_r H^0 = -286 \text{ kJ}$$

For the reaction where one mole of liquid water in standard state is formed from H_2 and O_2 gases in their standard states, the enthalpy changes for the reaction would be the standard enthalpy of formation of water. $\Delta_f H$ of water is -286 kJmol$^{-1.}$

The standard enthalpy of formation of a compound is the enthalpy change that accompanies a reaction in which one mole of pure compound in its standard state is formed from its elements in their standard states.

The formation of one mole of CH_4 in its standard state from the elements carbon and hydrogen in their standard states is represented by

$$C_{(graphite)} + 2H_2(g) \longrightarrow CH_4(g),\ \Delta_r H^0 = -74.8\ kJ$$

or $\Delta_f H^0\ (CH_4) = -74.8\ kJ\ mol^{-1}$

> **Do you know ?**
>
> The reaction to form a substance from its constituent elements is hypothetical. It is not possible to combine C and H_2 in the laboratory to prepare CH_4. The enthalpy of reaction for the formation of CH_4 can be obtained indirectly by knowing the standard enthalpy change for system. The value $-74.8\ kJ\ mol^{-1}$ corresponds to the hypothetical reaction.

4.10.6 Standard enthalpy of reaction from standard enthalpies of formation

The standard enthalpies of formation of compounds are used to determine standard enthalpies of reactions.

Calculations of $\Delta_r H^0$ from $\Delta_f H^0$ of compounds are based on the following.

i. Standard enthalpies of formation of an element is zero.

$$\Delta_f H^0(H_2) = \Delta_f H^0(Cl_2) = \Delta_f H^0(C) = 0$$

ii. Standard enthalpy of formation of a compound is equal to its standard enthalpy

$$\Delta_f H^0(\text{compound}) = H^0(\text{compound})$$

Consider the reaction

$$aA + bB \longrightarrow cC + dD$$

Standard enthalpy of the reaction is given by

$$\Delta_f H^0 = (cH^0_C + dH^0_D) - (aH^0_A + bH^0_B)$$

$$= [c\ \Delta_f H^0(C) + d\ \Delta_f H^0(D)] - [a\ \Delta_f H^0(A) + b\ \Delta_f H^0(B)]$$

$$= \sum \Delta_f H^0\ (\text{products}) - \sum \Delta_f H^0\ (\text{reactants}) \quad \text{.......}\ (4.30)$$

> **Problem 4.10**
>
> Calculate standard enthalpy of reaction,
>
> $2C_2H_6(g) + 7O_2(g) \longrightarrow 4\ CO_2(g) + 6\ H_2O(l)$
>
> Given that
>
> $\Delta_f H^0\ (CO_2) = -393.5\ kJ\ mol^{-1}$,
>
> $\Delta_f H^0\ (H_2O) = -285.8\ kJ\ mol^{-1}$ and
>
> $\Delta_f H^0(C_2H_6) = -84.9\ kJ\ mol^{-1}$
>
> **Solution -**
>
> $\Delta_r H^0 = \sum \Delta_f H^0(\text{products}) - \sum \Delta_f H^0(\text{reactants})$
>
> $= [4\ \Delta_f H^0(CO_2) + 6\ \Delta_f H^0(H_2O)]$
>
> $- [2\ \Delta_f H^0(C_2H_6) + 7\ \Delta_f H^0(O_2)]$
>
> $= [4\ mol \times (-393.5\ kJ\ mol^{-1}) + 6\ mol \times (-285.8\ kJ\ mol^{-1})]$
>
> $- [2\ mol \times (-84.9\ kJ\ mol^{-1}) + 0]$
>
> $= -1574\ kJ - 1714.8\ kJ + 169.8\ kJ$
>
> $= -3119\ kJ$

4.10.7 Standard enthalpy of combustion ($\Delta_c H^0$)

Consider the reaction

$$C_2H_2(g) + \frac{5}{2}\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(l),\quad \Delta_r H^0 = -1300\ kJ$$

In the above reaction, the standard enthalpy change of the oxidation reaction, -1300 kJ is the standard enthalpy of combustion of $C_2H_2(g)$.

The standard enthalpy of combustion of a substnce is the standard enthalpy change accompanying a reaction in which one mole of the substance in its standard state is completely oxidised.

Try this...

Write thermochemical equation for complete oxidation of one mole of $H_2(g)$. Standard enthalpy change of the reaction is -286 kJ.

Is the value -286 kJ, enthalpy of formation or enthalpy of combustion or both? Explain.

Problem 4.11: Estimate the standard enthalpy of combustion of $CH_4(g)$ if $\Delta_f H^0(CH_4) = -74.8$ kJ mol^{-1}, $\Delta_f H^0(CO_2) = -393.5$ kJ mol^{-1} and $\Delta_f H^0(H_2O) = -285.8$ kJ mol^{-1}

Solution : The equation for the combustion of CH_4 is

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l), \quad \Delta_r H^0 = ?$$

$$\Delta_r H^0 = [\Delta_f H^0(CO_2) + 2\,\Delta_f H^0(H_2O)] - [\Delta_f H^0(CH_4) + 2\,\Delta_f H^0(O_2)]$$

$$= [1 \times (-393.5) + 2 \times (-285.8)] - [1 \times (-74.8) + 2 \times 0]$$

$$\Delta_c H^0(CH_4) = -890.3 \text{ kJ}$$

4.10.8 Bond enthalpy

Consider the reaction

$$H_2(g) \longrightarrow H(g) + H(g), \ \Delta_r H^0 = 436.4 \text{ kJ}$$

It shows that H-H bond in one mole of $H_2(g)$ is decomposed producing gaseous H atoms. The enthalpy change of the reaction, 436.4 kJ is bond enthalpy of the H-H bond. **The enthalpy change required to break particular covalent bond in one mole of gaseous molecule to produce gaseous atoms and/or radicals, is called bond enthalpy.**

Try this...

Write equation for bond enthalpy of Cl-Cl bond in Cl_2 molecule $\Delta_r H^0$ for dissociation of Cl_2 molecule is 242.7 kJ

Remember...

For diatomic molecules the bond enthalpy is the same as enthalpy of atomization.

HCl molecule dissociates as

$$HCl(g) \longrightarrow H(g) + Cl(g), \ \Delta_r H^0 = 431.9 \text{ kJ}$$

$$\Delta H^0 \text{(H-Cl bond)} = 431.9 \text{ kJ mol}^{-1}$$

Average bond enthalpy in polyatomic molecules : Each covalent bond in polyatomic molecules is associated with its own specific bond enthalpy. The thermochemical equation for dissociation of H_2O molecules is

$$H_2O(g) \longrightarrow 2\,H(g) + O(g), \ \Delta_r H^0 = 927 \text{ kJ}$$

The above equation implies that the enthalpy change for breaking of two O-H bonds in one mole of gaseous H_2O molecules is 927 kJ. Two O-H bonds in H_2O are identical the energies needed to break individual O-H bonds are different.

The bonds in H_2O are broken in successive steps as shown

i. $H_2O(g) \longrightarrow OH(g) + H(g) \quad \Delta_r H^0 = 499$ kJ

ii. $OH(g) \longrightarrow O(g) + H(g) \quad \Delta_r H^0 = 428$ kJ

$H_2O(g) \longrightarrow 2\,H(g) + O(g) \quad \Delta_r H^0 = 927$ kJ

The total enthalpy change, 927 kJ, not twice as large of the O-H bond enthalpy. What is the enthalpy of O-H bond in H_2O molecule?

For polyatomic molecules the average bond enthalpy of a particular bond would be considered. Thus, the average bond enthalpy of the O-H bond = 927 2 = 463.5 kJ or ΔH^0 (O-H) = 463.5 kJ mol^{-1}

Do you know ?

In CH_4 molecule there are four identical C-H bonds. The bond enthalpy of all the 4 C-H bonds are different. The breaking of C-H bonds in CH_4 occurs in four steps as follows:

$CH_4(g) \rightarrow CH_3(g) + H(g),\ \Delta_r H^0 = 427$ kJ

$CH_3(g) \rightarrow CH_2(g) + H(g),\ \Delta_r H^0 = 439$ kJ

$CH_2(g) \rightarrow CH(g) + H(g),\ \Delta_r H^0 = 452$ kJ

$CH(g) \rightarrow C(g) + H(g),\ \Delta_r H^0 = 347$ kJ

$CH_4(g) \rightarrow C(g) + 4\,H(g),\ \Delta_r H^0 = 1665$ kJ

Average C-H bond enthalpy

= 1665 kJ/4 = 416 kJ

Hence, $\Delta_r H^0$(C-H) = 416 kJ mol^{-1}

Reaction and bond enthalpies : In a chemical reaction bonds are broken and formed. The enthalpies of reactions involving substances having covalent bonds are calculated by knowing the bond enthalpies of reactants and those in products. The calculations assume all the bonds of a given type are identical.

Enthalpy change of a reaction

$$\Delta_r H^0 = \sum \Delta H^0 \text{(reactant)} - \sum \Delta H^0 \text{(product)} \quad \ldots\ldots. \ (4.31)$$

Consider the reaction

$H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$

The enthalpy is given by

$\Delta_r H^0 = [\Delta H^0(H\text{-}H) + \Delta H^0(I\text{-}I)] - [2\Delta H^0(H\text{-}I)]$

Remember...

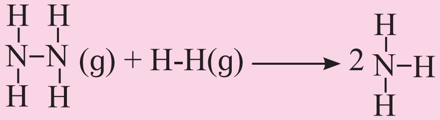
If reactants and products are diatomic molecules the Eq. (4.31) gives accurate results. The bond enthalpies are known accurately. For reactions involving polyatomic molecules the reaction enthalpies calculated via. Eq. (4.31) would be approximate and refer to averag bond enthalpies.

Examples 4.12 : Calculate the standard enthalpy of :

$N_2H_4(g) + H_2(g) \longrightarrow 2\,NH_3(g)$

if ΔH^0(N-H) = 389 kJ mol^{-1}, ΔH^0(H-H) = 435 kJ mol^{-1}, ΔH^0 (N-N) = 159 kJ mol^{-1}

Solution :



$$\underset{H\ \ H}{\overset{H\ \ H}{N{-}N}}\,(g) + H{-}H(g) \longrightarrow 2\ \underset{H}{\overset{H}{N{-}H}}$$

$\Delta_r H^0 = \sum \Delta H^0$ (reactant) -

$\sum \Delta H^0$ (product)

= [4ΔH^0(N-H) + ΔH^0(N-N) + ΔH^0(H-H)] - [6 ΔH^0(N-H)]

= ΔH^0 (N-N) + ΔH^0(H-H) - 2 ΔH^0(N-H)

= 1 × 159 + 1 mol × 435 - 2 × 389

= -184 kJ

Example 4.13 : The enthalpy change of the following reaction

$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$, $\Delta_r H^0$ = -104 kJ. Calculate C-Cl bond enthalpy. The bond enthalpies are

Bond	C-H	Cl-Cl	H-Cl
ΔH^0/kJ mol^{-1}	414	243	431

Solution

$\Delta_r H^0 = \sum \Delta H^0$ (reactant) - $\sum \Delta H^0$ (product)

= [4ΔH^0(C-H) + ΔH^0(Cl-Cl)] - [3ΔH^0(C-H)+ΔH^0(C-Cl) +ΔH^0(H-Cl)]

= ΔH^0(C-H) + ΔH^0(Cl-Cl) - ΔH^0(C-Cl) - ΔH^0(H-Cl)

-104 kJ = 1 × 414 + 1× 243 -1 × ΔH^0(C-Cl) - 1 × 431

= 226 - 1 × ΔH^0(C-Cl)

1 × ΔH^0(C-Cl) = 226 + 104

ΔH^0(C-Cl) = 330 kJ mol^{-1}

4.10.9 Hess's law of constant heat summation

The law states that, "**Overall the enthalpy change for a reaction is equal to sum of enthalpy changes of individual steps in the reaction**".

The enthalpy change for a chemical reaction is the same regardless of the path by which the reaction occurs. Hess's law is a direct consequence of the fact that enthalpy is state function. The enthalpy change of a reaction depends only on the initial and final states and not on the path by which the reaction occurs.

To determine the overall equation of reaction, reactants and products in the individual steps are added or subtracted like algebraic entities.

Consider the synthesis of NH_3

i. $2H_2(g) + N_2(g) \longrightarrow N_2H_4(g)$, $\Delta_r H_1^0 = +95.4$ kJ

ii. $N_2H_4(g) + H_2(g) \longrightarrow 2\ NH_3(g)$, $\Delta_r H_2^0 = -187.6$ kJ

$3\ H_2(g) + N_2(g) \longrightarrow 2\ NH_3(g)$, $\Delta_r H^0 = -92.2$ kJ

The sum of the enthalpy changes for steps (i) and (ii) is equal to enthalpy change for the overall reaction.

Application of Hess's law

The Hess's law has been useful to calculate the enthalpy changes for the reactions with their enthalpies being not known experimentally.

Example 4.14 : Calculate the standard enthalpy of the reaction,

$$2Fe(s) + 3/2\ O_2(g) \longrightarrow Fe_2O_3(s)$$

Given :

i. $2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$, $\Delta_r H^0 = -847.6$ kJ

ii. $2\ Al(s) + 3/2\ O_2(g) \longrightarrow Al_2O_3(s)$, $\Delta_r H^0 = -1670$ kJ

Solution :

Reverse Eq.(i) and then add to Eq. (ii)

$2Fe(s) + Al_2O_3(s) \longrightarrow 2\ Al(s) + Fe_2O_3(s)$, $\Delta_r H^0 = +847.6$ kJ

$2\ Al(s) + 3/2\ O_2(g) \longrightarrow Al_2O_3(s)$, $\Delta_r H^0 = -1670$ kJ

$2Fe(s) + 3/2\ O_2(g) \longrightarrow Fe_2O_3(s)$, $\Delta_r H^0 = -822.4$ kJ

Example 4.15 : Calculate the standard enthalpy of the reaction,

$SiO_2(s) + 3C(graphite) \longrightarrow SiC(s) + 2\ CO(g)$

from the following reactions,

i. $Si(s) + O_2(g) \longrightarrow SiO_2(s)$, $\Delta_r H^0 = -911$ kJ

ii. $2\ C(graphite) + O_2(g) \longrightarrow 2CO(g)$, $\Delta_r H^0 = -221$ kJ

iii. $Si(s) + C(graphite) \longrightarrow SiC(s)$, $\Delta_r H^0 = -65.3$kJ

Solution : Reverse the Eq. (i)

iv. $SiO_2(s) \longrightarrow Si(s) + O_2(g)$, $\Delta_r H^0 = -911$ kJ

Add equations (ii), (iii) and (iv)

ii. $2\ C(graphite) + O_2(g) \longrightarrow 2\ CO(g)$, $\Delta_r H^0 = -221$ kJ

iii. $Si(s) + C(graphite) \longrightarrow SiC(s)$, $\Delta_r H^0 = -65.3$ kJ

iv. $SiO_2(s) \longrightarrow Si(s) + O_2(g)$, $\Delta_r H^0 = +911$ kJ

$SiO_2(s) + 3\ C(graphite) \longrightarrow SiC(s) + 2\ CO(g)$, $\Delta_r H^0 = +624$ kJ

4.11 Spontaneous (irreversible) process :

Spontaneous processes have a natural tendency to occur and do not require any external influence for their occurrence.

Do you know ?

i. The aqueous NaOH and HCl solutions mixed together. NaOH immediately combines with HCl to form NaCl and water.

$$NaOH(aq)+HCl(aq) \longrightarrow NaCl(aq)+ H_2O(l), \quad \Delta_r H^0 = -57 \text{ kJ}$$

No external force or energy is required for the reaction to occur. This is spontaneous. The process stops when HCl or NaOH is consumed.

NaCl is dissolved in water, it does not react with water to produce NaOH and HCl.

ii. Water flows from higher level to lower level. It is not necessary to apply external force. It is a spontaneous process. The flow ceases when two levels become equal or when the equilibrium is reached.

iii. Ice melts spontaneously above 0 °C.

iv. Hot coffee in a cup placed in a room cools down releasing heat to the surroundings. This is spontaneous.

Key points of spontaneous process

i. It occurs of its own and does not require any external agency to occur.

ii. It proceeds in one direction and cannot take place in the opposite direction unless the external stimulant is present.

iii. The spontaneous processes can be rapid or slow or spontaneity is not concerned with the rate of the reaction.

iv. The processes continues till equilibrium is reached. **The spontaneous (natural) processes tend to occur in a direction that leads to equilibrium.**

4.11.1 Energy and spontaneity :

The spontaneous reaction takes place in a direction in which energy of the system is lowered. It is accompanied by release of energy. The reaction between NaOH and HCl is exothermic ($\Delta_r H^\circ$ = -57 kJ) and is spontaneous.

On the other hand :

i. Ice melts spontanoeusly above 0 °C by absorbing heat from the surroundings. It is endothermic.

ii. Likewise, NaCl dissolves spontaneously in water with the absorbtion of heat from the surroundings.

$$NaCl(s) + aq \longrightarrow Na^{\oplus}(aq) + Cl^{\ominus}(aq) \quad \Delta H^0 = +3.9 \text{ kJ mol}^{-1}$$

These are endothermic and spontaneous. It is therefore, clear that the exothermicity is not the sufficient criterion for deciding of spontaneity. There needs to be an another factor to describe spontaneity.

4.11.2 Entropy :

To know what entropy consider the following processes:

i. In solid state water molecules in ice are arranged in a definite order.

ii. When ice melts, this highly crystalline arrangements of water molecules collapse. The molecules become free in liquid state. An ordered state thus tends to become more disordered.

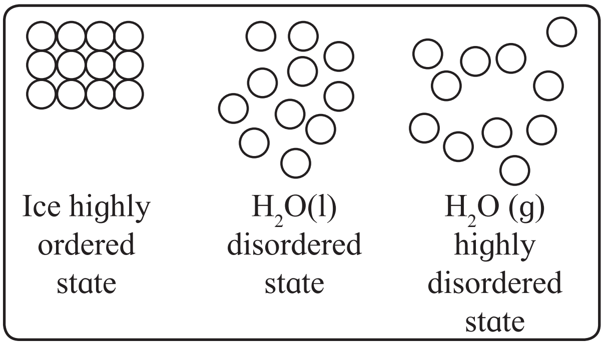


Fig. 4.10 Increasing disorder

iii. When liquid water vaporises, gaseous water molecules move freely and randomly in the available space. A less disordered state becomes highly disordered as shown in Fig. 4.10.

During melting of ice or the vaporisation of liquid water the disorder or randomness increases. The disorder or randomness is measured by **entropy,** denoted by S. Greater the disorder of a system larger is its entropy. The melting of ice and vaporisation of liquid water show that disorder and hence, entropy of substance increases as it passes from solid to liquid to gas.

In both processes entropy change $\Delta S > 0$. Look at the following processes :

i. Dissolution of solid I_2 in water :

$I_2(s) + aq. \longrightarrow I_2\,(aq)$ (ΔS is positive)

ordered state disordered state

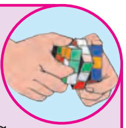
When solid iodine dissolves in water I_2 molecules move randomly. Thus disorder and hence, entropy of the system increases or ΔS is positive for the dissolution process.

ii. Dissociation of H_2 molecule into atoms

$H_2(g) \longrightarrow 2H(g)$ (ΔS is positive)

One mole of H_2 gas is converted into two H atoms. Larger disorder is associated with separated H atoms than with H_2 molecule. Thus, disorder and hence entropy increases or ΔS is positive.

Try this...



State whether ΔS is positive, negative or zero for the following reactions.

i. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

ii. $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$

Quantitative definition of entropy

Entropy is a measure of molecular disorder or randomness. An entropy change of a system is equal to the amount of heat transferred (Q_{rev}) to it in a reversible manner divided by the temperature in kelvin T at which the transfer takes place. Thus

$$\Delta S = \frac{Q_{rev}}{T} \quad \text{....... (4.32)}$$

the ΔS is thus expressed in J K^{-1}.

Entropy or its change ΔS is a state function and depends on the initial and final states of the system and not on the path connecting two states.

i. When heat is added to a system the molecular motions increase owing to increase of their kinetic energies. This results in increased molecular disorder and thus entropy of the system. ΔS is proportional to Q_{rev}.

ii. The effectiveness of the addition of heat to increase randomness depends on temperature.

If a certain amount of heat is added to system at the higher temperature then the disorder caused is lesser than that caused by adding the same amount of heat is added to system at the lower temperature Thus, ΔS relates reciprocally to temperature at which the of heat is added.

4.11.3 Entropy and spontaneity (Second law of Thermodynamics)

Look at the following examples :

i. The entropy increases when ice melts above 0 °C and water vaporizes at 100 °C. Both are spontaneous.

ii. Consider the spontaneous reaction at room temperature

$2H_2O_2\,(l) \longrightarrow 2H_2O\,(l) + O_2\,(g),$

$\Delta S = +126$ J K^{-1}

Entropy increases due to the formation of O_2 gas.

From above examples, it is clear that the entropy of the system increases in the spontaneous processes. Consider the reaction.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l),$$

$$\Delta S = -327 \text{ J K}^{-1}.$$

The entropy of the system decreases. Note the reaction is spontaneous.

4.11.4 Second law of thermodynamics :

The second law of thermodynamics states that total entropy of a system and its surroundings increases in a spontaneous process. For the process to be spontaneous

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0 \qquad (4.33)$$

Consider

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

ΔS = -327 J K^{-1}, and ΔH = -572 kJ (both at 298 K)

To find ΔS_{total}, we need to know ΔS_{surr}. ΔH for the reaction is -572 kJ. When 2 moles of H_2 and 1 mole of O_2 gas combine to form 2 moles of liquid water, 527 kJ of heat is released which is received by surroundings at constant pressure (and 298 K). The entropy change of surroundings is

$$\Delta S_{surr} = \frac{Q_{rev}}{T} = \frac{572 \times 10^3 \text{ J}}{298 \text{ K}} = 1919 \text{ J K}^{-1}$$

$$\begin{aligned} \Delta S_{total} &= \Delta S_{sys} + \Delta S_{surr} \\ &= -327 \text{ J K}^{-1} + 1919 \text{ J K}^{-1} \\ &= +1592 \text{ J K}^{-1} \end{aligned}$$

$$\Delta S_{total} > 0.$$

The reaction is thus spontaneous. It follows that to decide spontaneity of reactions, we need to consider the entropy of system and its surroundings.

The total entropy increases during a spontaneous process that finally reaches equilibrium. The equilibrium corresponds to maximum total entropy. The total entropy change, ΔS_{total} must be zero for a process at equilibrium.

From above,

i. $\Delta S_{total} > 0$, the process is spontaneous

ii. $\Delta S_{total} < 0$, the process is nonspontaneous

iii. $\Delta S_{total} = 0$, the process is at equilibrium

4.11.5 Gibbs energy

As pointed out in the preceding section, it is necessary to determine, ΔS_{sys} and ΔS_{surr}, for predicting the spontaneity of a reaction. We are more interested in the system (reaction mixture) . It. is, therefore convenient to consider the criterion of spontaneity in terms of the thermodynamic properties of a system. This problem was solved by American theoretician J. W. Gibbs. He introduced a new thermodynamic property called Gibbs energy usually denoted by G.

The Gibbs energy is defined as

$$G = H - TS \qquad \text{.......} (4.34)$$

where H is enthalpy and S entropy of the system. Since H, T and S are state functions, G is state function. A change in Gibbs energy depends on initial and final states of the system and not on a path connecting the two states.

The change in Gibbs energy at constant temperature and constant pressure is given by

$$\Delta G = \Delta H - T\,\Delta S \qquad \text{.......} (4.35)$$

4.11.6 Gibbs energy and spontaneity

The total entropy change that accompanies a process is given by

$$\begin{aligned} \Delta S_{total} &= \Delta S_{sys} + \Delta S_{surr} \\ &= \Delta S + \Delta S_{surr} \qquad \text{.......} (4.36) \end{aligned}$$

The subscript sys that refers to the system is dropped hereafter.

Relation between ΔG and ΔS_{total}

According to second law of thermodynamics for a process to be spontaneous, $\Delta S_{total} > 0$

If ΔH is the enthalpy change accompanying a reaction (system) the enthalpy change of the surroundings is $-\Delta H$. With

$$\Delta S_{surr} = -\frac{\Delta H}{T} \qquad .... (4.37)$$

Substituting above into Eq. (4.36),

$$\Delta S_{total} = \Delta S - \frac{\Delta H}{T} \qquad .... (4.38)$$

Thus ΔS_{total} is expressed in terms of the properties of the system only. Rearranging

$$T\,\Delta S_{total} = \Delta H - T\,\Delta S \qquad .... (4.39)$$

Substituting in Eq. (4.35)

$$\Delta G = -T\,\Delta S_{total} \qquad .... (4.40)$$

For a spontaneous reaction $S_{total} > 0$ and hence, $\Delta G < 0$. At constant temperature and pressure Gibbs energy of the system decreases in a spontaneous process.

The second law leads to the conditions of spontaneity which are summarised here.

i. $\Delta S_{total} > 0$ and $\Delta G < 0$, the process is spontaneous.

ii. $\Delta S_{total} < 0$ and $\Delta G > 0$, the process is nonspontaneous.

iii. $\Delta S_{total} = 0$ and $\Delta G = 0$, the process is at equilibrium.

4.11.7 Sponaneity and ΔH or ΔS

From $\Delta G = \Delta H - T\,\Delta S$ (at constant T and P).

The temperature term determines relative contributions of ΔH and ΔS to ΔG.

1. ΔH and ΔS are both negative then ΔG will be negative only when ΔH is more negative than $T\Delta S$. This is possible at **low temperatures** only**.**

2. ΔH amd ΔS both positive ΔG will be negative only if $T\Delta S > \Delta H$. This is possible only at high temperatures.

3. For ΔH negative and ΔS is positive it follows that ΔG is negative regardless of temperature.

4. For ΔH positive and ΔS is negative then

ΔG is positive regardless of temperature. Such reactions are nonspontaneous at all temperatures.

4.11.8 Temperature of equilibrium

For equilibrium

$$\Delta G = \Delta H - T\Delta S \text{ gives}$$

$$\therefore\ T = \frac{\Delta H}{\Delta S} \qquad .... (4.41)$$

T is the temperature at which the change over from spontaneous to nonspontaneous behavior occurs. ΔH and ΔS are assumed to be independent of temperature in Eq. (4.41). Introducing of temperature dependence of ΔH or ΔS would not cause significant error for the moderate temperature range.

4.11.9 Gibbs function and equilibrium constant : Gibbs energy change for a chemical reaction is given by

$$\Delta G = \Delta G^0 + RT \ln Q \qquad ....(4.42)$$

where ΔG^0 is standard Gibbs energy change that is, the Gibbs energy change when the reactants and products in a reaction are in their standard states. Q is called reaction quotient Q is analogus to that of the equilibrium constant. and involves nonequilibrium concentrations or partial pressures in case of gaseous reaction.

Consider

$$\mathrm{aA + bB \longrightarrow cC + dD}$$

$$\Delta G = \Delta G^0 + RT \ln Q_c$$

$$= \Delta G^0 + RT \ln \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b} \qquad ....(4.43)$$

or $\quad \Delta G = \Delta G^0 + RT \ln Q_p$

$$= \Delta G^0 + RT \ln \frac{P_C^{\,c} \times P_D^{\,d}}{P_A^{\,a} \times P_B^{\,b}} \qquad ....(4.44)$$

When the reaction reaches equilibrium, $\Delta G^0 = 0$ and Q_c and Q_p become K_c and K_p, respectively. Thus,

$$0 = \Delta G^0 + RT \ln K_c \text{ and } 0 = \Delta G^0 + RT \ln K_p$$

or

$$\Delta G^0 = -RT \ln K_c \text{ and } \Delta G^0 = -RT \ln K_p \qquad \text{.......(4.45)}$$

or $\Delta G^0 = -2.303\ RT \log_{10} K_c$

and

$$\Delta G^0 = -2.303\ RT \log_{10} K_p \qquad \text{....... (4.46)}$$

Problem 4.16 : State whether following reactions are spontaneous or not. Further state whether they are exothermic or endothermic.

a. $\Delta H = -110$ kJ and $\Delta S = +40$ JK^{-1} at 400 K

b. $\Delta H = +50$ kJ and $\Delta S = -130$ JK^{-1} at 250 K

Solution :

a. $\Delta G = \Delta H - T\Delta S$

$\Delta H = -110$ kJ, $\Delta S = +40$ J K^{-1}

$= +40 \times 10^{-3}$ kJ K^{-1}, T = 400 K

Therefore, $\Delta G = -110 \text{ kJ} - 400 \text{ K} \times 40 \times 10^{-3} \text{ kJ K}^{-1}$

$= -110 \text{ kJ} - 16 \text{ kJ} = -126 \text{ kJ}$

Since ΔG is negative, the reaction is spontaneous. It is exothermic since ΔH is negative

b. $\Delta H = +50$ kJ, $\Delta S = -130 \times$J K^{-1}

$= -130 \times 10^{-3}$ kJ K^{-1} $T = 250$ K

$\Delta G = +50 \text{ kJ} - 250 \text{ K} \times (-130 \times 10^{-3} \text{ kJ K}^{-1})$

$= 50 \text{ kJ} + 32.5 \text{ kJ} = +82.5 \text{ kJ}$

As ΔG is positive, the reaction is nonspontaneous. It is endothermic since ΔH is positive.

Problem 4.17

For a certain reaction ΔH^0 is -224 kJ and ΔS^0 is -153 J K^{-1}. At what temperature the change over from spontaneous to nonspontaneous will occur?

Solution -

$$T = \frac{\Delta H^0}{\Delta S^0}$$

$\Delta H^0 = -224$ kJ, $\Delta S^0 = -153$ JK^{-1} $= -0.153$ kJ K^{-1}

Therefore, $T = \dfrac{-224 \text{ kJ}}{-0.153 \text{ J K}^{-1}} = +1464 \text{ K}$

Since ΔH^0 and ΔS^0 are both negative, the reaction is spontaneous at low temperatures. A change over will occur at 1464 K. The reaction is spontaneous below 1464 K .

Problem 4.18

For the reaction,

$CH_4(g) + H_2(g) \longrightarrow C_2H_6(g)$,

$K_p = 3.356 \times 10^{17}$

Calculate ΔG^0 for the reaction at 25 ^{0}C.

Solution :

$\Delta G^0 = -2.303\ RT \log_{10} K_p$

$R = 8.314$ J K^{-1}mol^{-1}, $T = 298$ K,

$K_p = 3.356 \times 10^{17}$

$\Delta G^0 = -2.303 \times 8.314 \times 298 \times \log_{10}(3.356 \times 10^{17})$

$= -2.303 \times 8.314 \text{ J mol}^{-1} \times 298 \times 17.526$

$= -100{,}000 \text{ J mol}^{-1}$

$= -100 \text{ kJ mol}^{-1}$

Problem 4.19 : Calculate ΔS_{total} and state whether the reaction is spontaneous or nonspontaneous at 25 ^{0}C.

$HgS(s) + O_2(g) \longrightarrow Hg(l) + SO_2(g)$,

$\Delta H^0 = -238.6$ kJ, $\Delta S^0 = +36.7$ J K^{-1}

Solution :

$$\Delta S_{surr} = -\frac{\Delta H^0}{T}$$

$$= \frac{(-238.6 \text{ kJ})}{298 \text{ K}}$$

$$= +0.8007 \text{ kJ K}^{-1} = +800.7 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$= +36.7 \text{ JK}^{-1} + 800.7 \text{ JK}^{-1}$$

$$= +837.4 \text{ J K}^{-1}$$

$\Delta S_{total} > 0$, the reaction is spontaneous at 25 ^{0}C.

Problem 4.20 : Calculate ΔG for the reaction at 25 ^{0}C

$CO(g) + 2\ H_2(g) \longrightarrow CH_3OH(g)$, $\Delta G^0 = -24.8$ kJ mol^{-1} The partial pressures of gases are $P_{CO} = 4$ bar, $P_{H_2} = 2$ bar and $P_{CH_3OH} = 2$ bar

Solution : $\Delta G = \Delta G^0 + RT \ln Q_p$

$$= \Delta G^0 + 2.303\, RT \log_{10} \frac{P_{CH_3OH}}{P_{CO} \times P^2_{H_2}}$$

$\Delta G^0 = -24.8$ kJ mol^{-1}, $R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}, $T = 298$ K

Calculate Q_p,

$$Q_p = \frac{P_{CH_3OH}}{P_{Co} \times P^2_{H_2}} = \frac{2}{4 \times 4} = \frac{1}{8} = 0.125$$

$\Delta G = -24.8$ kJ mol^{-1} $+ 2.303 \times 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1} $\times$ 298 K $\times \log_{10} 0.125$

$= -24.8$ kJ mol^{-1} $+ 5.706 \times (-0.903)$ kJ mol^{-1}

$= -24.8$ kJ mol^{-1} $- 5.153$ kJ mol^{-1}

$= -29.953$ kJ mol^{-1}

Exercises

1. Select the most apropriate option.

i. The correct thermodynamic conditions for the spontaneous reaction at all temperatures are

a. $\Delta H < 0$ and $\Delta S > 0$

b. $\Delta H > 0$ and $\Delta S < 0$

c. $\Delta H < 0$ and $\Delta S < 0$

d. $\Delta H < 0$ and $\Delta S = 0$

ii. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 bar from an initial volume of 2.5 L to a final volume of 4.5 L. The change in internal energy, ΔU of the gas will be

a. -500 J b. + 500 J

c. -1013 J d. + 1013 J

iii. In which of the following, entropy of the system decreases?

a. Crystallization of liquid into solid

b. Temperature of crystalline solid is increased from 0 K to 115 K

c. $H_2(g) \longrightarrow 2H(g)$

d. $2\ NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

iv. The enthalpy of formation for all elements in their standard states is

a. unity

b. zero

c. less than zero

d. different elements

v. Which of the following reactions is exothermic?

a. $H_2(g) \longrightarrow 2H(g)$

b. $C(s) \longrightarrow C(g)$

c. $2\,Cl(g) \longrightarrow Cl_2(g)$

d. $H_2O(s) \longrightarrow H_2O(l)$

vi. 6.24 g of ethanol are vaporized by supplying 5.89 kJ of heat. Enthalpy of vaporization of ethanol will be

a. 43.4 kJ mol^{-1}

b. 60.2 kJ mol^{-1}

c. 38.9 kJ mol^{-1}

d. 20.4 kJ mol^{-1}

vii. If the standard enthalpy of formation of methanol is -238.9 kJ mol^{-1} then entropy change of the surroundings will be

a. -801.7 J K^{-1} b. 801.7 J K^{-1}

c. 0.8017 J K^{-1} d. -0.8017 J K^{-1}

viii. Which of the following are not state functions?

1. $Q + W$ 2. Q 3. W 4. $H\text{-}TS$

a. 1,2 and 3 b. 2 and 3

c. 1 and 4 d. 2,3 and 4

ix. For vaporization of water at 1 bar, $\Delta H = 40.63$ kJ mol^{-1} and $\Delta S = 108.8$ J K^{-1} mol^{-1}. At what temperature, $\Delta G = 0$?

a. 273.4 K b. 393.4 K

c. 373.4 K d. 293.4 K

x. Bond enthalpies of H-H, Cl-Cl and H-Cl bonds are 434 kJ mol^{-1}, 242 kJ mol^{-1} and 431 kJ mol^{-1}, respectively. Enthalpy of formation of HCl is

a. 245 kJ mol^{-1} b. -93 kJmol^{-1}

c. -245 kJ mol^{-1} d. 93 kJ mol^{-1}

2. Answer the following in one or two sentences.

i. Comment on the statement: no work is involved in an expansion of gas in vacuum.

ii. State the first law of thermodynamics.

iii. What is enthalpy of fusion?

iv. What is standard state of a substance?

v. State whether ΔS is positive, negative or zero for the reaction $2H(g) \longrightarrow H_2(g)$. Explain.

vi. State second law of thermodynamics in terms of entropy.

vii. If the enthalpy change of a reaction is ΔH how will you calculate entropy of surroundings?

viii. Comment on spontaneity of reactions for which ΔH is positive and ΔS is negative.

3. Answer in brief.

i. Obtain the relationship between ΔG^0 of a reaction and the equilibrium constant.

ii. What is entropy? Give its units.

iii. How will you calculate reaction enthalpy from data on bond enthalpies?

iv. What is the standard enthalpy of combustion ? Give an example.

v. What is the enthalpy of atomization? Give an example.

vi. Obtain the expression for work done in chemical reaction.

vii. Derive the expression for *PV* work

viii. What are intensive properties? Explain why density is intensive property.

ix. How much heat is evolved when 12 g of CO reacts with NO_2 ? The reaction is :

$$4\ CO(g) + 2\ NO_2(g) \longrightarrow 4\ CO_2(g) + N_2(g),\ \Delta_r H^0 = -1200\ kJ$$

4. Answer the following questions.

i. Derive the expression for the maximum work.

ii. Obtain the relatioship between ΔH and ΔU for gas phase reactions.

iii. State Hess's law of constant heat summation. Illustrate with an example. State its applications.

iv. Although ΔS for the formation of two moles of water from H_2 and O_2 is $-327 JK^{-1}$, it is spontaneous. Explain. (Given ΔH for the reaction is -572 kJ).

v. Obtain the relation between ΔG and ΔS_{total} Comment on spontaneity of the reaction.

vi. One mole of an ideal gas is compressed from 500 cm^3 against a constant external pressure of 1.2×10^5 Pa. The work involved in the process is 36.0 J. Calculate the final volume. (200 cm^3)

vii. Calculate the maximum work when 24 g of O_2 are expanded isothermally and reversibly from the pressure of 1.6 bar to 1 bar at 298 K.

Ans. : (-873.4 J)

viii. Calculate the work done in the decomposition of 132 g of NH_4NO_3 at 100 ^0C.

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2\ H_2O(g)$$

State whether work is done on the system or by the system.

Ans. : (-18.6 kJ)

ix. Calculate standard enthalpy of reaction,

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2\ Fe(s) + 3CO_2(g)$, from the following data.

$\Delta_f H^0(Fe_2O_3) = -824$ kJ/mol,

$\Delta_f H^0(CO) = -110$ kJ/mol,

$\Delta_f H^0(CO_2) = -393$ kJ/mol

Ans. : (-25 kJ)

x. For a certain reaction $\Delta H^0 = 219$ kJ and $\Delta S^0 = -21$ J/K. Determine whether the reaction is spontaneous or nonspontaneous.

xi. Determine whether the following reaction is spontaneous under standard state conditions.

$$2\ H_2O(l) + O_2(g) \longrightarrow 2H_2O_2(l)$$

if $\Delta H^0 = 196$ kJ, $\Delta S^0 = -126$ J/K

Does it have a cross-over temperature?

(Nonspontaneous, No)

xii. Calculate ΔU at 298 K for the reaction,

$$C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g),\quad \Delta H = -72.3\ kJ$$

How much PV work is done?

Ans. : (-69.8 kJ, 2.48 kJ)

xiii. Calculate the work done during synthesis of NH_3 in which volume changes from 8.0 dm^3 to 4.0 dm^3 at a constant external pressure of 43 bar. In what direction the work energy flows?

Ans. : (17.2 kJ, work energy flows into system)

xiv. Calculate the amount of work done in the (a) oxidation of 1 mole HCl(g) at 200 ^0C according to reaction.

$$4HCl(g) + O_2(g) \longrightarrow 2\ Cl_2(g) + 2\ H_2O(g)$$

(b) decomposition of one mole of NO at 300 ^0C for the reaction

$$2\ NO(g) \longrightarrow N_2(g) + O_2$$

Ans. : (a = + 983 kJ ; b = 0 kJ)

xv. When 6.0 g of O_2 reacts with CIF as per

$2Cl\,F(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g)$

The enthalpy change is 38.55 kJ. What is standard enthalpy of the reaction ?

$(\Delta_r H^0 = 205.6 \text{ kJ})$

xvi. Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data

i. $CH_3OH(l) + \frac{3}{2} O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$,

$\Delta H^0 = -726 \text{ kJ mol}^{-1}$

ii. $C \text{ (Graphite)} + O_2(g) \longrightarrow CO_2(g)$,

$\Delta_c H^0 = -393 \text{ kJ mol}^{-1}$

iii. $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$,

$\Delta_f H^0 = -286 \text{ kJ mol}^{-1}$

Ans. : ($-$ 239 kJ mol^{-1})

xvii. Calculate ΔH^0 for the following reaction at 298 K

$H_2B_4O_7(s) + H_2O(l) \longrightarrow 4HBO_2(aq)$

i. $2H_3BO_3(aq) \longrightarrow B_2O_3(s) + 3H_2O(l)$,

$\Delta H^0 = 14.4 \text{ kJ mol}^{-1}$

ii. $H_3BO_3(aq) \longrightarrow HBO_2(aq) + H_2O,(l)$

$\Delta H^0 = -0.02 \text{ kJ mol}^{-1}$

iii. $H_2B_4O_7(s) \longrightarrow 2P_2O_3(s) + H_2O(l)$,

$\Delta H^0 = 17.3 \text{ kJ mol}^{-1}$

Ans. : ($-$ 11.58 kJ)

xviii. Calculate the total heat required (a) to melt 180 g of ice at 0 ^{0}C, (b) heat it to 100 ^{0}C and then (c) vapourise it at that temperature. Given $\Delta_{fus} H^0(\text{ice}) = 6.01$ kJ mol^{-1} at 0 ^{0}C, $\Delta_{vap} H^0(H_2O) = 40.7$ kJ mol^{-1} at 100 ^{0}C specific heat of water is 4.18 J g^{-1} K^{-1}

Ans. : (542.3 kJ)

xix. The enthalpy change for the reaction,

$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$

is -620 J when 100 ml of ethylene and 100 mL of H_2 react at 1 bar pressure. Calculate the pressure volume type of work and ΔU for the reaction.

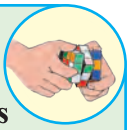
Ans.: ($W = +10.13$ J; $\Delta U = -609.9$ J)

xx. Calculate the work done and comment on whether work is done on or by the system for the decomposition of 2 moles of NH_4NO_3 at 100 ^{0}C

$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(g)$

Ans. (-18.61 kJ, work is done by the system)

Activity :



Following are some processes occurrring in nature.

- **River originates in a mountain and flows towards sea.**
- **After proper incubations for 21 days a chicken egg hatches and baby chick comes out.**
- **List out some more processes you come across in nature.**
- **Identify the processes that are in accordance with the second law of thermodynamics and those which are against it.**

5. ELECTROCHEMISTRY

Can you recall ?

- What is a redox reaction ?
- Which form of energy is converted into electrical energy in dry cells ?

- How is NaOH manufactured from NaCl ?

5.1 Introduction : Dry cell is used to power our electrical and electronic equipments because it generates electricity. Do you know how does a dry cell generate electricity ? A chemical reaction occurs in it which generates electricity. Thus in a dry cell chemical energy is converted into electrical energy.

You are familiar with the electrolysis of solutions of ions. Electrolysis is breaking down of an ionic compound by the passage of eletricity. Breaking down of an electrolyte during electrolysis is a chemical reaction that takes place by the passage of electricity. Electrical energy is, thus, converted into chemical energy.

Electrochemistry is the area of chemistry which is concerned with interconversion of chemical and electrical energy.

It also deals with the resistance and conductance of aqueous electrolytic solutions. The determination of conductivities of aqueous electrolytic solutions provide an information on the extent of ionization of electrolytes in water. (Refer to Chapter 3).

The study of electrochemical cells is important in science and technology. It makes possible the manufacture of essential chemicals. You have learnt preparation of NaOH, widely used in the manufacture of soaps, detergents and paper, by electrolysis of NaCl. Electrolysis is possibly the only means to produce fluorine. The processes such as electro-refining (for purification of metals), electroplating (for coating one metal is on the surface of another) are also electrochemical processes.

In standard XI, you learnt redox reactions. Redox reaction forms the basis for the generation of electricity by chemical reactions and also for chemical reactions brought out by means of electricity. These processes are carried out in an **electrochemical cell**. Electrochemistry deals with the design and operation of such cells.

The current research in electrochemistry is focused on the design of fuel cells. The fuel cells are being explored as convenient and compact source of electricity.

5.2 Electric conduction : We know that the electric current represents a charge transfer. A charge transfer or flow of electricity occurs through substances called conductors. There are two types of conductors which give rise to two types of conduction of electricity.

5.2.1 Metallic conduction :

Can you recall ?

- What is the origin of electrical conductivity of metals ?

Electrical conduction through metals involves a direct flow of electrons from one point to the other. The outermost electrons of metals form conduction bond. The electrons in conduction band are free to move and hence flow under the influence of applied electrical potential (Chapter 1). Metallic conductors are, thus, electronic conductors.

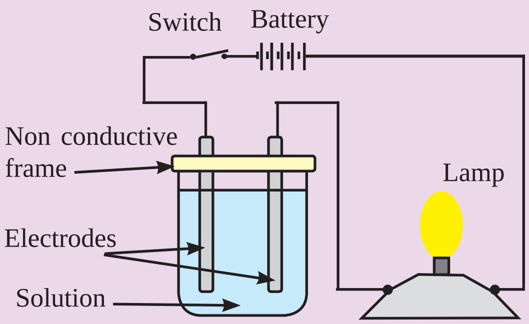
5.2.2 Electrolytic or ionic conduction :

Electrolytic conduction involves conduction of electric current by the movement of ions of the electrolytes. In this type of conduction the charge transfer occurs in the form of movement of ions through molten electrolytes or the aqueous solutions of electrolytes. Substances such as ionic salts, strong or weak acids and bases are the electrolytes. These dissociate into ions when dissolved in polar solvents such as water. Ionic solids dissociate into ions in molten state as well.

Conduction through electrolytic conductors involves transfer of matter from one part of the conductor to the other. It means that the current flowing through an electrolytic conductor is accompanied by a chemical change.

5.2.3 Information provided by measurement of conductivities of solutions :

Try this...



- Arrange a simple set up as shown in the diagram above.
- The lamp will glow when circuit is complete.
- Prepare 5 % (mass/volume) solutions of cane sugar, acetic acid, sodium chloride and urea in distilled water.
- Check the electrical conductivity of these solutions using the above assembly. Compare these with that observed with distilled water.

i. The conducting and nonconducting nature of solutions can be identified by measurement of their conductivity. Sucrose and urea do not dissociate in their aqueous solutions. The conductivities of these solutions are nearly the same as that of water. These substances are called **nonelectrolytes**.

On the other hand, substances like potassium chloride, acetic acid, sodium hydroxide, HCl dissociate in their aqueous solutions. The conductivities of their aqueous solutions are higher than that of water. These are called **electrolytes**. Electrolytes conduct electricity in molten state or when dissolved in water.

ii. On the basis of high or low electrical conductivity electrolytes are classified into strong and weak electrolytes. The substances such as ionic salts, strong acids or bases are almost completely dissociated in aqueous solutions. These are strong electrolytes. The solutions of **strong electrolytes** exhibit high conductivities.

The weak acids and weak bases are **weak electrolytes**. They dissociate to a very small extent in aqueous solutions and show lower conductivities than those of strong electrolytes.

Remember...

Electrolyte is a compound that conducts electricity when molten or in aqueous solution and breaks down into ions during electrolysis.

5.3 Electrical conductance of solution :

According to Ohm's law, the electrical resistance R of a conductor is equal to the electric potential difference V divided by the electric current, I :

$$R = \frac{V}{I} \qquad \text{............ (5.1)}$$

The SI unit of potential is volt (V) and that of current is ampere (A). The unit of electrical resistance is ohm denoted by the symbol Ω (omega). Thus, $\Omega = VA^{-1}$.

The electrical conductance, G, of a solution is reciprocal of resistance.

$$G = \frac{1}{R} \qquad \text{........... (5.2)}$$

The SI unit of G is siemens, denoted by S, which is equal to Ω^{-1}. Therefore, we write $S = \Omega^{-1} = AV^{-1} = CV^{-1}s^{-1}$ where C represents coulomb, the unit of electricity related to current strength in ampere and time in seconds as C = A s.

The electrical resistance of a conductor is proportional to length l and inversely proportional to cross sectional area a. Thus,

$$R \propto \frac{l}{a} \text{ or } R = \rho\frac{l}{a} \qquad \text{........... (5.3)}$$

where ρ, the proportionality constant is called resistivity of the conductor. It is the resistance of conductor of unit length and unit cross sectional area.

Can you recall ?

What is the SI unit of resistivity ?

5.3.1 Conductivity (k) : We have seen that $G = 1/R$ and R is directly proportional to length and inversely proportional to its cross sectional area. It, therefore, follows that G is directly proportional to a and inversely proportional to the length l. Thus

$$G \propto \frac{a}{l} \quad \text{or} \quad G = k\frac{a}{l} \qquad \text{........... (5.4)}$$

The proportionality constant k is called conductivity. $G = k$ if length and cross sectional area of conductor are unity.

Thus, conductivity is the electrical conductance of a conductor of unit length and unit area of cross section. In other words, the conductivity is the electrical conductance of unit cube of material. Conductivity of solution of an electrolyte is called electrolytic conductivity which refers to the electrical conductance of unit volume ($1\ m^3$ or $1\ cm^3$) of solution.

From Eq. (5.2) and Eq. (5.4), we write

$$k = G\frac{l}{a} = \frac{1}{R}\ \frac{l}{a} \qquad \text{........... (5.5)}$$

Combination of Eq. (5.3) and Eq. (5.5) shows that $k = 1/\rho$.

Units of electrolytic conductivity

Quantity	SI unit	Common unit
Length	m	cm
Area	m^2	cm^2
Resistance	Ω	Ω
Conductivity	$\Omega^{-1}\ m^{-1}$ or $S\ m^{-1}$	$\Omega^{-1}\ cm^{-1}$

5.3.2 Molar conductivity (∧) : The electrolytic conductivity is not suitable for comparing conductivities of different solutions. The conductivity of a solution depends on number of ions present in unit volume of solution. The solution of higher concentration contains more ions and exhibits higher conductivity than the solution of lower concentration. To compare conductivities of different solutions, they must have the same concentration.

In 1880, the German physicist F.W.G. Kohlrausch introduced the term molar conductivity denoted by ∧ (lambda).

The molar conductivity of an electrolytic solution is the electrolytic conductivity, k, divided by its molar concentration c.

$$\wedge = \frac{k}{c} \qquad \text{........... (5.6)}$$

SI units of k are $S\ m^{-1}$ and that of c are $mol\ m^{-3}$. Hence SI units of ∧ are $S\ m^2\ mol^{-1}$. Common units employed for molar conductivity are $\Omega^{-1}\ cm^2\ mol^{-1}$.

Significance of molar conductivity : To understand the significance of ∧, consider volume of a solution containing 1 mole of dissolved electrolyte. Suppose the solution is placed between two parallel electrodes 1 cm apart and large enough to accommodate it. The electrical conductance exhibited by this solution is the molar conductivity. The molar conductivity is the electrical conductance generated by all the ions in 1 mole of the electrolyte.

Remember...

Conductivity is electrical conductance due to all the ions in 1 cm^3 of given solution. Molar conductivity is the electrical conductance due to the ions obtained from 1 mole of an electrolyte in a given volume of solution.

5.3.3 Relation between *k* and $\wedge$: Conductivity *k* is the electrical conductance of 1 cm^3 of solution. If *V* is volume of solution in cm^3 containing 1 mole of dissolved electrolyte, its electrical conductance is $\wedge$. Each 1 cm^3 portion in the volume *V* has conductance *k*. Hence, total conductance of *V* cm^3 is *kV* which is molar conductivity.

Thus, we have $\wedge = k\ V$ ……….. (5.7)

Concentration of solution

$$= c \text{ mol } L^{-1}$$

$$= \frac{c \text{ mol } L^{-1}}{1000 \text{ cm}^3 L^{-1}} = \frac{c}{1000} \text{ mol cm}^{-3}$$

Volume, *V* of solution in cm^3 containing 1 mole of an electrolyte is reciprocal of concentration. Therefore,

$$V = \frac{1}{\text{concentraion}} = \frac{1000}{c} \text{ cm}^3 \text{ mol}^{-1} \quad \text{……….. (5.8)}$$

Substitution for *V* in Eq. (5.7) yields

$$\wedge = \frac{1000k}{c} \quad \text{……….. (5.9)}$$

Try this...

What must be the concentration of a solution of silver nitrate to have the molar conductivity of 121.4 Ω^{-1} cm^2 mol^{-1} and the conductivity of 2.428 × 10^{-3} Ω^{-1} cm^{-1} at 25 ^{0}C ?

Problem 5.1 : The molar conductivity of 0.05 M $BaCl_2$ solution at 25^{0}C is 223 Ω^{-1} cm^2 mol^{-1}. What is its conductivity ?

Solution :

$$\wedge = \frac{1000k}{c} \text{ or } k = \frac{\wedge\ c}{1000}$$

$\wedge = 223\ \Omega^{-1}\ cm^2\ mol^{-1}$, $c = 0.05$ mol L^{-1}

Hence

$$k = \frac{223\ \Omega^{-1}\ cm^2\ mol^{-1} \times 0.05\ mol\ L^{-1}}{1000\ cm^3 L^{-1}}$$

$$= 0.01115\ \Omega^{-1}\ cm^{-1}$$

5.3.4 Variation of conductivity with concentration

i. The electrolytic conductivity is electrical conductance of unit volume (1 cm^3) of solution. It depends on the number of current carrying ions present in unit volume of solution.

ii. On dilution total number of ions increase as a result of increased degree of dissociation.

iii. An increase in total number of ions is not in proportion of dilution. Therefore, the number of ions per unit volume of solution decreases. This results in decrease of conductivity with decrease in concentration of solution.

Suppose 100 cm^3 of solution of an electrolyte contains 8 × 10^{20} ions. The number of ions per cm^3 is 8 × 10^{18}.

If the solution is diluted to 1000 cm^3 the total number of ions will increase but not by a factor of 10. Assume that the number of ions increases from 8 × 10^{20} to 64 × 10^{20} on dilution. After dilution the number of ions per cm^3 is 6.8 × 10^{18}.

It is evident that the number of ions per cm^3 decreases from 8 × 10^{18} to 6.8 × 10^{18} on dilution from 100 cm^3 to 1000 cm^3 and in turn, the conductivity decreases.

5.3.5 Variation of molar conductivity with concentration

i. The molar conductivity is the electrical conductance of 1 mole of an electrolyte in a given volume of solution.

ii. The increasing number of ions produced in solution by 1 mole of the electrolyte lead to increased molar conductivity.

5.3.6 Variation of molar conductivity with concentration : The variation of molar conductivity with concentration in case of strong and weak electrolytes is qualitatively different.

i. Strong electrolytes : The molar conductivity of solution of strong electrolyte increases rapidly with dilution. It approaches the limiting value for 0.001 M or 0.0001 M solution. The dilution has no effect on molar conductivity thereafter. The maximum limiting value of molar conductivity is the molar conductivity at zero concentration or at infinite dilution. It is denoted by $\wedge_0$. The zero concentration or infinite dilution means the solution is so dilute that further dilution does not increase the molar conductivity.

During nineteenth century F. Kohlrausch with repeated experiments showed that the molar conductivity of strong electrolytes varies linearly with square root of concentration as :

$$\wedge = \wedge_0 - \boldsymbol{a}\sqrt{c} \qquad \text{........... (5.10)}$$

where $\boldsymbol{a}$ is constant. For strong electrolytes a plot of $\wedge$ versus $\sqrt{c}$ is linear as shown in Fig. 5.1.

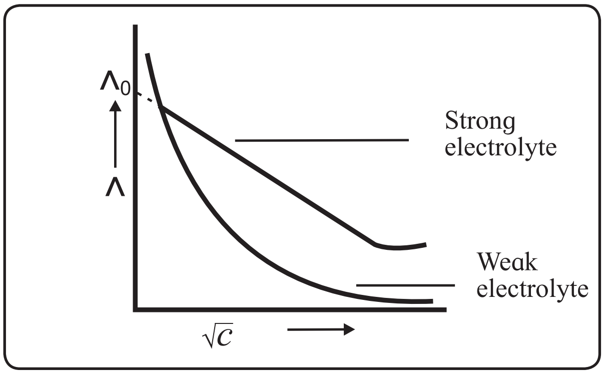


Fig. 5.1 : Variation of $\wedge$ with $\sqrt{c}$

ii. Weak electrolytes : The molar conductivity of weak electrolytes increases rapidly on dilution. For concentrations of 0.001M or 0.0001 M, the $\wedge$ value is lower than $\wedge_0$ the molar conductivity at zero concentration.

For weak electrolytes the variation of $\wedge$ with $\sqrt{c}$ shown in Fig. 5.1 is not linear.

Molar conductivity of strong electrolytes at zero concentration can be determined by extrapolation of linear part of $\wedge$ versus $\sqrt{c}$ curve as shown in Fig. 5.1. This method cannot be used for weak electrolytes since $\wedge$ versus $\sqrt{c}$ curve does not approach linearity. Kohlrausch law is useful for calculating $\wedge_0$ of weak electrolytes.

5.3.7 Kohlrausch law of independent migration of ions : The law states that at infinite dilution each ion migrates independent of co-ion and contributes to total molar conductivity of an elctrolyte irrespective of the nature of other ion to which it is associated.

Both cation and anion contribute to molar conductivity of the electrolyte at zero concentration and thus $\wedge_0$ is sum of molar conductivity of cation and that of the anion at zero concentration. Thus,

$$\wedge_0 = n_\oplus \lambda^0_\oplus + n_\ominus \lambda^0_\ominus \qquad \text{........... (5.11)}$$

where $\lambda_\oplus$ and $\lambda_\ominus$ are molar conductivities of cation and anion, respectively, and $n_\oplus$ and $n_\ominus$ are the number of moles of cation and anion, specified in the chemical formula of the electrolyte.

Applications of Kohlrausch theory

1. The theory can be used to calculate the molar conductivity of an electrolyte at the zero concentration. For example,

   $\wedge_0 \text{(KCl)} = \lambda^0_{K^\oplus} + \lambda^0_{Cl^\ominus}$

   $\wedge_0 [Ba(OH)_2] = \lambda^0_{Ba^{2\oplus}} + 2\,\lambda^0_{OH^\ominus}$

   Knowing the molar conductivites of ions at infinite dilution, $\wedge_0$ values of electrolyte can be obtained.

2. The theory is particularly useful in calculating $\wedge_0$ values of weak electrolytes from those of strong electrolytes. For example, $\wedge_0$ of acetic acid can be calculated by knowing those of HCl, NaCl and CH_3COONa as described below :

$$\wedge_0 \text{(HCl)} + \wedge_0 (CH_3COONa) - \wedge_0 \text{(NaCl)}$$

$$= \lambda^0_{H^\oplus} + \lambda^0_{Cl^\ominus} + \lambda^0_{CH_3COO^\ominus} + \lambda^0_{Na^\oplus} - \lambda^0_{Na^\oplus} - \lambda^0_{Cl^\ominus}$$

$= \lambda^0_{H^\oplus} + \lambda^0_{CH_3COO^\ominus} = \wedge_0 (CH_3COOH)$

Thus,

$$\wedge_0 (CH_3COOH) = \wedge_0 (HCl) + \wedge_0 (CH_3COONa) - \wedge_0 (NaCl)$$

Because $\wedge_0$ values of strong electrolytes, HCl, CH_3COONa and NaCl, can be determined by extrapolation method, the $\wedge_0$ of acetic acid can be obtained.

Problem 5.2 : Calculate the molar conductivity of AgI at zero concentration if the molar conductivities of NaI, $AgNO_3$ and $NaNO_3$ at zero concentration are respectively, 126.9, 133.4 and 121.5 Ω^{-1} $cm^2\, mol^{-1}$.

Solution :

According to Kohrausch law,

i. $\wedge_0 (NaI) = \lambda^0_{Na^\oplus} + \lambda^0_{I^\ominus}$

$= 126.9\ \Omega^{-1}\ cm^2\, mol^{-1}$

ii. $\wedge_0 (AgNO_3) = \lambda^0_{Ag^\oplus} + \lambda^0_{NO_3^\ominus}$

$= 133.4\ \Omega^{-1}\ cm^2\, mol^{-1}$

iii. $\wedge_0 (NaNO_3) = \lambda^0_{Na^\oplus} + \lambda^0_{NO_3^\ominus}$

$= 121.5\ \Omega^{-1}\ cm^2\, mol^{-1}$

Eq. (i) + eq. (ii) - eq. (iii) gives

$\wedge_0 (NaI) + \wedge_0 (AgNO_3) - \wedge_0 (NaNO_3)$

$= \lambda^0_{Na^\oplus} + \lambda^0_{I^\ominus} + \lambda^0_{Ag^\oplus} + \lambda^0_{NO_3^\ominus} - \lambda^0_{Na^\oplus} - \lambda^0_{NO_3^\ominus}$

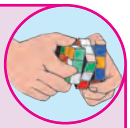
$= \lambda^0_{Ag^\oplus} + \lambda^0_{I^\ominus}$

$= \wedge_0 (AgI)$

$= 126.9\ \Omega^{-1}\ cm^2\, mol^{-1} + 133.4\ \Omega^{-1}\ cm^2\, mol^{-1} - 121.5\ \Omega^{-1}\ cm^2\, mol^{-1}$

$= 138.8\ \Omega^{-1}\ cm^2\, mol^{-1}$

Try this...



Calculate $\wedge_0$ (CH_2ClOOH) if $\wedge_0$ values for HCl, KCl and $CH_2ClCOOK$ are repectively, 4.261, 1.499 and 1.132 Ω^{-1} $cm^2\, mol^{-1}$.

Problem 5.3 : Calculate molar conductivities at zero concentration for $CaCl_2$ and Na_2SO_4. Given : molar ionic conductivitis of $Ca^{2\oplus}$, $Cl^\ominus$, $Na^\oplus$ and $SO_4^{2\ominus}$ ions are respectively, 104, 76.4, 50.1 and 159.6 $\Omega^{-1}\ cm^2\, mol^{-1}$.

Solution :

According to Kohrausch law,

i. $\wedge_0 (CaCl_2) = \lambda^0_{Ca^{2\oplus}} + 2\lambda^0_{Cl^\ominus}$

$= 104\ \Omega^{-1}\ cm^2\, mol^{-1} + 2 \times 76.4\ \Omega^{-1}\ cm^2\, mol^{-1}$

$= 256.8\ \Omega^{-1}\ cm^2\, mol^{-1}$

ii. $\wedge_0 (Na_2SO_4) = 2\lambda^0_{Na^\oplus} + \lambda^0_{SO_4^{2\ominus}}$

$= 2 \times 50.1\ \Omega^{-1}\ cm^2\, mol^{-1} + 159.6\ \Omega^{-1}\ cm^2\, mol^{-1}$

$= 259.8\ \Omega^{-1}\ cm^2\, mol^{-1}$

Problem 5.4 : The molar conductivity of 0.01M acetic acid at 25 ^{0}C is 16.5 Ω^{-1} cm^2 mol^{-1}. Calculate its degree of dissociation in 0.01 M solution and dissociation constant if molar conductivity of acetic acid at zero concentration is 390.7 $\Omega^{-1}\ cm^2\, mol^{-1}$.

Solution :

The degree of dissociation,

$$\propto = \frac{\wedge_c}{\wedge_0}$$

$$= \frac{16.6\ \Omega^{-1}\ cm^2\, mol^{-1}}{390.7\ \Omega^{-1}\ cm^2\, mol^{-1}} = 0.0422$$

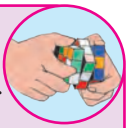
$$Ka = \frac{\propto^2 c}{1 - \propto} = \frac{(0.0422)^2 \times 0.01}{(1 - 0.0422)} = 1.85 \times 10^{-5}$$

5.3.8 Molar conductivity and degree of dissociation of weak electrolytes : The degree of dissociation ($\propto$) of weak electrolyte is related to its molar conductivity at a given concentration c by the equation,

$$\propto = \frac{\wedge_c}{\wedge_0} \qquad \text{...........} (5.12)$$

where $\wedge_c$ is the molar conductivity of weak electrolyte at concentration c ; $\wedge_0$ is molar conductivity at zero concentration.

Try this...



Obtain the expression for dissociation constant in terms of $\wedge_c$ and $\wedge_0$ using Ostwald's dilution law.

5.3.9 Measurement of conductivity

5.3.9 Measurement of conductivity : The conductivity of a solution can be determined from the resistance measurements by Wheatstone bridge.

Conductivity Cell : The conductivity cell consists of a glass tube with two platinum plates coated with a thin layer of finely divided platinium black. This is achieved by the electrolysis of solution of chloroplatinic acid. The cell is dipped in a solution whose resistance is to be measured as shown in Fig. 5.2.

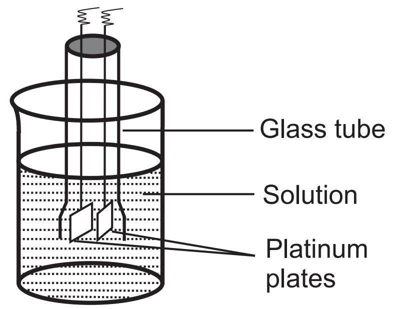


Fig. 5.2 : Conductivity cell

Cell constant : The conductivity of an electrolytic solution is given by Eq. (5.5),

$$k = \frac{1}{R}\;\frac{l}{a}$$

For a given cell, the ratio of separation (l) between the two electrodes divided by the area of cross section (a) of the electrode is called the cell constant. Thus,

$$\text{Cell constant} = \frac{l}{a} \qquad \text{........... (5.13)}$$

SI unit of cell constant is m^{-1} which is conveniently expressed in cm^{-1}. The Eq. (5.5) then becomes

$$k = \frac{\text{cell constant}}{R} \qquad \text{........... (5.14)}$$

The determination of conductivity consists of three steps :

1. Determination of cell constant : The cell constant is determined using the 1 M, 0.1 M or 0.01 M KCl solutions. The conductivity of KCl solution is well tabulated at various temperatures. The resistance of KCl solution is measured by Wheatstone bridge. (Refer to standard XII Physics Textbook Chapter 9)

In Fig. 5.3 AB is the uniform wire. R_x is the variable known resistance placed in one arm of Wheatstone bridge.

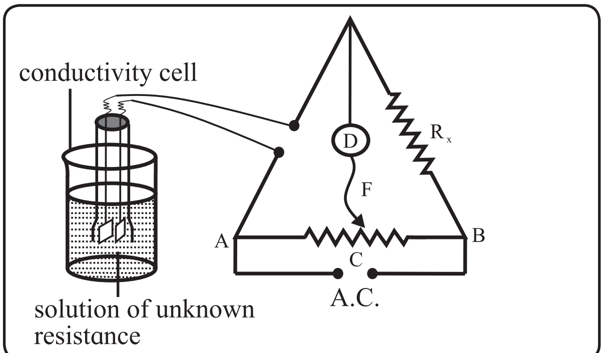


Fig. 5.3 : Measurement of resistance

The conductivity cell containing KCl solution of unknown resistance is placed in the other arm of Wheatstone bridge. D is a current detector. F is the sliding contact that moves along AB. A.C. represents the source of alternating current.

The sliding contact is moved along AB until no current flows. The detector D shows no deflection. The null point is, thus, obtained at C.

According to Wheatstone bridge principle,

$$\frac{R_{solution}}{l\ (AC)} = \frac{R_x}{l\ (BC)}$$

$$\text{Hence, } R_{solution} = \frac{l(AC)}{l(BC)} \times R_x \text{........... (5.15)}$$

By measuring lengths AC and BC and knowing R_x, resistance of KCl solution can be calculated. The cell constant is given by Eq. (5.13).

$$\text{Cell constant} = k_{KCl} \times R_{solution}$$

The conductivity of KCl solution is known. The cell constant, thus, can be calculated.

2. Determination of conductivity of given solution : KCl solution in the conductivity cell in step (1) is replaced by the given solution whose conductivity is to be measured. Its resistance is measured by the process described in step (1). The conductivity of given solution is then calculated as :

$$k = \frac{\text{Cell constant}}{R_{solution}}$$

3. Calculation of molar conductivity : The molar conductivity of the given solution is then calculated using Eq. (5.9).

$$\wedge = \frac{1000\ k}{c}$$

Problem 5.5 : A conductivity cell containing 0.01M KCl gives at 25^{0}C the resistance of 604 ohms. The same cell containing 0.001M $AgNO_3$ gives resistance of 6530 ohms. Calculate the molar conductivity of 0.001M $AgNO_3$. [Conductivity of 0.01M KCl at 25 ^{0}C is 0.00141 Ω^{-1} cm^{-1}]

Solution :

i. Calculation of cell constant

$$\text{Cell constant} = k_{KCl} \times R_{KCl}$$

$$= 0.00141\ \Omega^{-}\ \text{cm}^{-} \times 604\ \Omega$$

$$= 0.852\ \text{cm}^{-1}$$

ii. Calculation of conductiviy of $AgNO_{3'}$

$$k = \frac{\text{Cell constant}}{R} \quad \text{where } R = 6530\ \Omega$$

$$= \frac{0.852\ \text{cm}^{-1}}{6530\ \Omega}$$

$$= 1.3 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$$

iii. Calculation of molar conductivity of $AgNO_3$

$$\wedge = \frac{1000\text{k}}{c} \quad \text{where} \quad c = 0.001\ \text{M}$$

$$= \frac{1000\ \text{cm}^3\ \text{L}^{-1} \times 1.3 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}}{0.001\ \text{mol L}^{-1}}$$

$$= 130\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

5.4 Electrochemical cells : An electrochemical cell consists of two metal plates or carbon (graphite) rods. These electronic conductors are dipped into an electrolytic or ionic conductor.

5.4.1 Electrochemical reactions :

Can you recall ?

What is the reaction involving transfer of electrons from one chemical species to another called?

The chemical reaction occuring in electrochemical cells involves transfer of electrons from one species to the other. It is a redox reaction, we learnt in (Std. XI, Chapter 6).

Electrochemical reactions, are made of oxidation and reduction half reactions. The oxidation half reaction occurs at one electrode and the reduction half reaction occurs at the other electrode. The net cell reaction is the sum of these half reactions.

5.4.2 Electrodes : Electrodes are the surfaces on which oxidation and reduction half reactions take place. Electrodes may or may not participate in the reactions. The electrodes which do not take part in reactions are inert electrodes.

Cathode : It is an electrode at which the reduction takes place. At this electrode the species undergoing reduction gains electrons.

Anode : It is an electrode at which oxidation takes place. At this electrode, the species undergoing oxidation loses electrons.

5.4.3 Types of electrochemical cells : There are two types of electrochemical cells.

1. **Electrolytic cell :** In this type of cell, a nonspontaneous reaction, known as electrolysis, is forced to occur by passing a direct current from an external source into the solution. In such cells electrical energy is converted into chemcial energy. The anode of electrolytic cell is positive and cathode is negative.

2. **Galvanic or voltaic cell :** In galvanic (voltaic) cell a spontaneous chemical reaction produces electricity. In these cells chemical energy is converted into electrical energy. The anode of galvanic cell is negative and cathode is positive.

Use your brain power

Distinguish between electrolytic and galvanic cells.

5.5 Electrolytic cell

Do you know ?

Michael Faraday was the first person to explain electrolysis nearly 200 years ago.

Electrolytic cell consists of a container in which electrolyte is placed. Two electrodes are immersed in the electrolyte and connected to a source of direct current.

At anode (+) a species oxidises with the removal of electrons. These electrons are pulled from anode and pushed to cathode through an external circuit. The electrons are supplied to species at cathode which are reduced.

Remember...

Electrolysis is the process of breaking down of an ionic compound in molten state or in aqueous solution by the passage of electricity.

5.5.1 Electrolysis of molten NaCl

Construction of cell : The electrolytic cell consists of a container in which fused NaCl is placed. Two graphite electrodes are immersed in it. They are connected by metallic wires to a source of direct current that is battery. This is shown in Fig. 5.4.

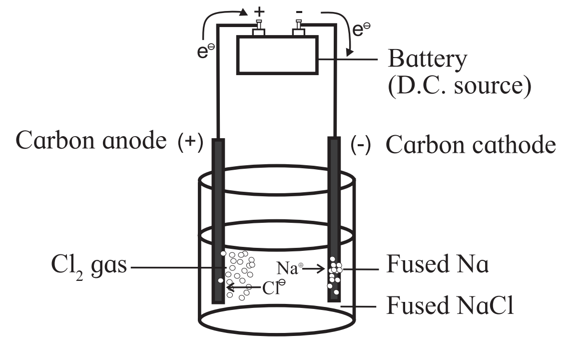


Fig. 5.4 : Electrolysis of fused NaCl

The carbon electrode connected to terminal electrode of the battery is anode and that connected to negative terminal of the battery is cathode.

Remember...

In electrolysis the electrodes are usually inert, Pt or graphite.

Reactions occuring in the cell : Fused NaCl contains $Na^{\oplus}$ and $Cl^{\ominus}$ ions which are freely mobile. When potential is applied, cathode attracts $Na^{\oplus}$ ions and anode attracts $Cl^{\ominus}$ ions. As these are charged particles, their migration results in an electric current. When these ions reach the respective electrodes, they are discharged according to the following reactions.

Oxidation half reaction at anode :

$Cl^{\ominus}$ ions migrate to anode. Each $Cl^{\ominus}$ ion, that reaches anode, gives one electron to anode. It oxidises to neutral Cl atom in the primary process. Two Cl atoms then combine to form chlorine gas in the secondary process.

$$2\,Cl^{\ominus}\,(l) \longrightarrow Cl\,(g) + Cl\,(g) + 2e^{\ominus}$$

(primary process)

$$Cl\,(g) + Cl\,(g) \longrightarrow Cl_2\,(g)$$

(secondary process)

$$2Cl^{\ominus}\,(l) \longrightarrow Cl_2\,(g) + 2e^{\ominus}$$

(overall oxidation)

The battery sucks electrons so produced at the anode and pushes them to cathode through a wire in an external circuit. The battery thus serves as an electron pump. The electrons from the battery enter into solution through cathode and leave the solution through anode.

Reduction half reaction at cathode : The electrons supplied by the battery are used in cathodic reduction. Each $Na^{\oplus}$ ion, that reaches cathode accepts an electron from the cathode and reduces to metallic sodium.

$$Na^{\oplus}\,(l) + e^{\ominus} \longrightarrow Na\,(l)$$

Net cell reaction

The net cell reaction is the sum of two electrode reactions.

$$2\ Cl^{\ominus}\ (l) \longrightarrow Cl_2\ (g) + 2e^{\ominus}$$
(oxidation half reaction)

$$2\ Na^{\oplus}\ (l) + 2e^{\ominus} \longrightarrow 2\ Na\ (l)$$
(reduction half reaction)

$$2\ Na^{\oplus}\ (l) + 2\ Cl^{\ominus}\ (l) \longrightarrow 2\ Na\ (l) + Cl_2(g)$$
(overall cell reaction)

Results of electrolysis of molten NaCl

i. A pale green Cl_2 gas is released at anode.

ii. A molten silvery-white sodium is formed at cathode.

Decomposition of NaCl into metallic sodium and $Cl_2(g)$ is nonspontaneous. The electrical energy supplied by the battery forces the reaction to occur.

Remember...

When molten ionic compound is electrolysed, a metal is formed at the negative electrode and a nonmetal at the positive electrode.

5.5.2 Electrolysis of aqueous NaCl :

Electrolysis of an aqueous NaCl can be carried out in the cell used for the electrolysis of molten NaCl using inert electrodes shown in Fig. 5.4. The fused NaCl is replaced by moderately concentrated aqueous solution of NaCl. The water involved in electrolysis of aqueous NaCl, leads to electrode reactions that differ from electrolysis of molten NaCl.

Reduction half reaction at cathode : At cathode, two reduction reactions compete. One is the reduction of $Na^{\oplus}$ ions as in case of molten NaCl.

i. $Na^{\oplus}\ (aq) + e^{\ominus} \longrightarrow Na\ (s),\ E^0 = -2.71\ V$

The other is the reduction of water to hydrogen gas.

ii. $2\ H_2O\ (l) + 2e^{\ominus} \longrightarrow H_2\ (g) + 2\ OH^{\ominus}(aq),$
$E^0 = -\ 0.83\ V$

The standard potential (section 5.7.1) for the reduction of water is higher than that for reduction of $Na^{\oplus}$. This implies that water has much greater tendency to get reduced than the $Na^{\oplus}$ ion. Hence reaction (ii), that is, reduction of water is the cathode reaction when the aqueous NaCl is electrolysed.

Oxidation half reaction at anode : At anode there will be competition between oxidation of $Cl^{\ominus}$ ion to Cl_2 gas as in case of molten NaCl and the oxidation of water to O_2 gas.

i. $2\ Cl^{\ominus}\ (aq) \longrightarrow Cl_2\ (g) + 2e^{\ominus}, E^0_{oxi} = -\ 1.36\ V$

ii. $2H_2O\ (l) \longrightarrow O_2\ (g) + 4H^{\oplus}\ (aq) + 2e^{\ominus}$
$E^0_{oxi} = -\ 0.4\ V$

Standard electrode potential for the oxidation of water is greater than that of $Cl^{\ominus}$ ion or water has greater tendency to undergo oxidation. It is, therefore, expected that anode half reaction would be oxidation of water. The experiments have shown, however, that the gas produced at the anode is Cl_2 and not O_2. This suggests that anode reaction is oxidation of $Cl^{\ominus}$ to Cl_2 gas. This is because of the overvoltage, discussion of which is beyond the scope of the present book.

It has been found experimentally that the actual voltage required for electrolysis is greater than that calculated using standard potentials. This additional voltage required is the overpotential.

Do you know ?

Refining of metal and electroplating are achieved by electrolysis.

Overall cell reaction

It is the sum of electrode reactions.

$$2\,Cl^{\ominus}\,(aq) \longrightarrow Cl_2\,(g) + 2e^{\ominus}$$
(oxidation at anode)

$$2\,H_2O\,(l) + 2e^{\ominus} \longrightarrow H_2\,(g) + 2\,OH^{\ominus}\,(aq)$$
(reduction at cathode)

$$2\,Cl^{\ominus}\,(aq) + 2\,H_2O\,(l) \longrightarrow Cl_2\,(g) + H_2(g) + 2\,OH^{\ominus}\,(aq)$$
(overall cell reaction)

Results of electrolysis of aqueous NaCl

i. H_2 gas is liberated at cathode.

ii. Cl_2 gas is released at anode.

iii. Because $Na^{\oplus}$ ions remain unreacted and $OH^{\ominus}$ ions are formed at cathode, NaCl solution is converted to NaOH solution.

Do you know ?

Sea water is the source of 300000 tones of Mg produced every year by electrolysis.

Electrochemical art : Al, Cr and Sn can be coloured by an electrochemical process called anodizing. In this process metal anode oxidizes to give metal oxide coat. When an organic dye is added to the electrolyte, dye molecules soak forming spongy surface of coating and become trapped with the hardening of the metal oxide surface.

5.5.3 Quantitative aspects of electrolysis :

a. The mass of reactant consumed or the mass of product formed at an electrode during electrolysis can be calculated by knowing stoichiometry of the half reaction at the electrode.

i. Calculation of quantity of electricity passed : To calculate the quantity of eletricity (Q) passed during electrolysis, the amount of current, I, passed through the cell is measured. The time for which the current is passed is noted.

$$Q\,(C) = I\,(A) \times t\,(s) \qquad \text{..........} (5.16)$$

ii. Calculation of moles of electrons passed

Total charge passed is Q(C). The charge of one mole electrons is 96500 coulombs (C). It is referred to as one faraday (IF). Hence,

Moles of electrons actually passed

$$= \frac{Q(C)}{96500\,(C/mol\;e^{\ominus})} \qquad \text{..........} (5.17)$$

iii. Calculation of moles of product formed

The balanced equation for the half reaction occuring at the electrode is devised. The stoichiometry of half reaction indicates the moles of electrons passed and moles of the product formed. For the reaction,

$Cu^{2\oplus}\,(aq) + 2e^{\ominus} \longrightarrow Cu\,(s)$, two moles of electrons are required for the production of one mole of Cu. So we can calculate the moles of product formed. The moles of electrons actually passed are given by Eq. (5.16).

To simplify further we introduce the entity mole ratio given by

$$\text{Mole ratio} = \frac{\text{moles of product formed in the half reaction}}{\text{moles of electrons required in the half reaction}}$$

For the reaction of Cu, mole ratio = $\frac{1}{2}$

Therefore,

Moles of product formed

= moles of electrons actually passed × mole ratio

$$= \frac{Q(C)}{96500\,(C/mol\;e^{\ominus})} \times \text{mole ratio} \qquad \text{..........} (5.18)$$

$$= \frac{I\,(A) \times t\,(s)}{96500\,(C/mol\;e^{\ominus})} \times \text{mole ratio} \qquad \text{..........} (5.19)$$

iv. Calculation of mass of product :

Mass of product

W = moles of product × molar mass of product

$$= \frac{I\,(A) \times t\,(s)}{96500\,(C/mol\;e^{\ominus})} \times \text{mole ratio} \times \text{molar mass of product}$$

.... (5.20)

b. Suppose two cells containing different electrolytes are connected in series. The same quantity of electricity is passed through them. The masses of the substances liberated at the electrodes of the two cells are related as given below :

The mass of the substance produced at the electrode of first cell is given by

$$W_1 = \frac{Q(\text{C})}{96500\ (\text{C/mol e}^{\ominus})} \times (\text{mole ratio})_1 \times \text{M}_1$$

Hence, $\dfrac{Q(\text{C})}{96500\ (\text{C/mol e}^{\ominus})}$

$$= \frac{W_1}{(\text{mole ratio})_1 \times M_1}$$

Similarly mass of substance liberated at the electrode of second cell is W_2 in the equation,

$$\frac{Q(\text{C})}{96500\ (\text{C/mol e}^{\ominus})} = \frac{W_2}{(\text{mole ratio})_2 \times M_2}$$

M_1 and M_2 are the molar masses of substances produced at the electrodes of cells 1 and 2.

Because $\dfrac{Q(\text{C})}{96500\ (\text{C/mol e}^{\ominus})}$ is the same for both,

We have

$$\frac{W_1}{(\text{mole ratio})_1 \times M_1} = \frac{W_2}{(\text{mole ratio})_2 \times M_2} \qquad \text{.........… (5.21)}$$

Problem 5.6 : What is the mass of Cu metal produced at the cathode during the passage of 5 ampere current through $CuSO_4$ solution for 100 minutes. Molar mass of Cu is 63.5 g mol^{-1}.

Solution :

i. Stoichiometry for the formation of Cu is

$Cu^{2\oplus}\ (aq) + 2\ e^{\ominus} = Cu\ (s)$

Hence,

$$\text{mole ratio} = \frac{1\ \text{mol}}{2\ \text{mol e}^{\ominus}}$$

ii. Mass of Cu formed,

$$W = \frac{I\ (\text{A}) \times t\ (\text{s})}{96500\ (\text{C/mol e}^{\ominus})} \times \text{mole ratio} \times \underset{\text{of Cu}}{\text{molar mass}}$$

$$= \frac{5\ \cancel{\text{A}} \times 100 \times 60\ \cancel{\text{s}}}{96500\ (\cancel{\text{C}}/\cancel{\text{mol e}^{-}})} \times \frac{1\ \cancel{\text{mol}}}{2\ \cancel{\text{mol}}\ \text{e}^{-}} \times 63.5\ \text{g}\ \cancel{\text{mol}^{-1}}$$

$= 9.87$ g

Problem 5.7 : How long will it take to produce 2.415 g of Ag metal from its salt solution by passing a current of 3 ampere ? Molar mass of Ag is 107.9 g mol^{-1}.

Solution :

i. Stoichiometry :

$$Ag^{\oplus}\ (aq) + e^{\ominus} \longrightarrow Ag\ (s)$$

$$\text{mole ratio} = \frac{1\ \text{mol}}{1\ \text{mol e}^{\ominus}}$$

ii. W =

$$\frac{I\ (\text{A}) \times t\ (\text{s})}{96500\ (\text{C/mol e}^{\ominus})} \times \text{mole ratio} \times \underset{\text{of Ag}}{\text{molar mass}}$$

$$2.415\ \cancel{\text{g}} = \frac{3\ \text{A} \times t}{96500\ (\text{C}/\cancel{\text{mol e}^{\ominus}})} \times \frac{1\ \cancel{\text{mol}}}{1\ \cancel{\text{mol}}\ \text{e}^{\ominus}} \times 107.9\ \ \text{g}\ \cancel{\text{mol}^{-1}}$$

$$t = \frac{2.415 \times 96500\ (\text{C} = \cancel{\text{A}}\text{s})}{3\ \cancel{\text{A}} \times 107.9}$$

$= 720$ s $= 12$ min.

Do you know ?

Names, galvanic or voltaic are given in honour of Italian scientists L. Galvani and A. Volta for their work in electrochemistry.

Problem 5.8 : How many moles of electrons are required for reduction of 3 moles of $Zn^{2\oplus}$ to Zn ? How many Faradays of electricity will be required ?

Solution :

i. The balanced equation for the reduction of $Zn^{2\oplus}$ to Zn is

$$Zn^{2\oplus}\ (aq) + 2e^{\ominus} \longrightarrow Zn\ (s)$$

The equation shows that 1 mole of $Zn^{2\oplus}$ is reduced to Zn by 2 moles of electrons. For reduction of 3 moles of $Zn^{2\oplus}$ 6 moles of electrons will be required.
Faraday (96500 Coulombs) is the amount of charge on one mole of electrons. Therefore, for 6 moles of electrons, 6 F electricity will be required.

Problem 5.9 : In a certain electrolysis experiment 4.36 g of Zn are deposited in one cell containing $ZnSO_4$ solution. Calculate the mass of Al deposited in another cell containing $AlCl_3$ solution connected in series with $ZnSO_4$ cell. Molar masses of Zn and Al are 65.4 g mol^{-1} and 27 g mol^{-1}, respectively.

Solution :

Cell 1 :

$$Zn^{2\oplus}\ (aq) + 2e^{\ominus} \longrightarrow Zn\ (s)$$

$$(\text{mole ratio})_1 = \frac{1\ \text{mol}}{2\ \text{mol}\ e^{\ominus}}$$

Cell 2 :

$$Al^{3\oplus}\ (aq) + 3e^{\ominus} \longrightarrow Al\ (s)$$

$$(\text{mole ratio})_2 = \frac{1\ \text{mol}}{3\ \text{mol}\ e^{\ominus}}$$

$$\frac{W_1}{(\text{mole ratio})_1 \times M_1} = \frac{W_2}{(\text{mole ratio})_2 \times M_2}$$

$W_1 = 4.36$ g, $M_1 = 65.4$ g mol^{-1},

$M_2 = 27$ gmol^{-1}

Substitution of the quantities gives

$$\frac{4.36\text{g}}{1\ \cancel{\text{mol}}/2\cancel{\text{mol}}\ \text{e} \times 65.4\ \cancel{\text{g mol}}^{-1}} = \frac{W_2}{1\ \cancel{\text{mol}}/3\cancel{\text{mol}}\ \text{e}^- \times 27\ \cancel{\text{g mol}}^{-1}}$$

or $$\frac{4.36\ \text{g} \times 2}{65.4} = \frac{W_2 \times 3}{27}$$

Hence, $$W_2 = \frac{4.36\ \text{g} \times 2 \times 27}{65.4 \times 3} = 1.2\ \text{g}$$

5.6 Galvanic or voltaic cell : In galvanic or voltaic cells, electricity is generated through the use of spontaneous chemical reactions.

A galvanic (or voltaic) cell is made of two half cells. Each half cell consists of a metal strip immersed in the solution of its own ions of known concentration. For example, a strip of zinc metal immersed in 1 M aqueous solution of zinc ions forms an half cell.

It follows that two metal plates and the solutions of their ions with known concentrations are required for the construction of a galvanic (voltaic) cell. Two half cells are constructed by immersing the two metal plates in solutions of their respective ions placed in separate containers. The two half cells so constructed are combined together to form the galvanic cell. The metal plates called electrodes are connected through voltmeter by a conducting wire for transfer of electrons between them. To complete the circuit the two solutions are connected by conducting medium through which cations and anions move from one compartment to the other. This requirement is fulfilled by a salt bridge.

5.6.1 Salt bridge : In a galvanic cell, the two solutions are connected by a salt bridge. It is an U tube containing a saturated solution of an inert electrolyte such as KCl or NH_4NO_3 and 5 % agar solution. The ions of electrolyte do not react with the ions of electrode solutions or the electrodes.

Salt bridge is prepared by filling a U tube with hot saturated solution of the salt and agar agar solution allowing it to cool. The cooled solution sets into a gel which does not come out on inverting the tube. The salt bridge is kept dipped in distilled water when not in use as shown in Fig. 5.5.

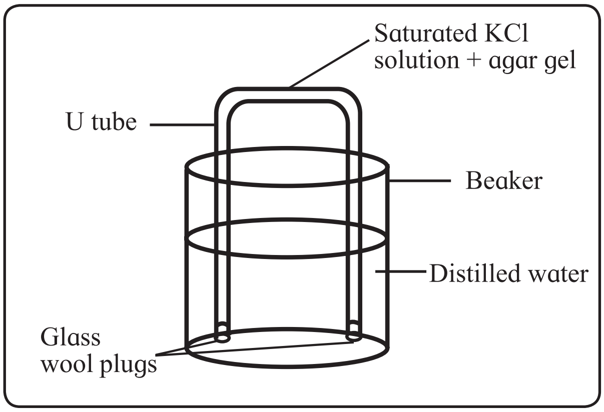


Fig. 5.5 : Salt bridge

Try this...

Salt bridge can be prepared with a laminated long strip of good quality filter paper. Cut the two ends of a laminated strip. Dip the two ends in a saturated solution of KCl for 24 hours. This strip can be used as salt bridge by dipping the two ends in two solutions.

Functions of salt bridge

The salt bridge serves the following functions :

i. It provides an electrical contact between two solutions and thereby completes the electrical circuit.

ii. It prevents mixing of two solutions.

iii. It maintains electrical neutrality in both the solutions by transfer of ions.

5.6.2 Formulation or short notation of galvanic cells :

A galvanic cell is represented by a formula or short notation that includes electrodes, aqueous solutions of ions and other species which may or may not be involved in the cell reaction. The following conventions are used to write the cell notation.

i. The metal electrodes or the inert electrodes are denoted by vertical lines placed at the ends of the formula or the short notation. The anode (-) is written at the extreme left and cathode (+) at extreme right.

ii. The insoluble species if any or gases are placed in the interior position adjacent to the metal electrodes.

iii. The aqueous solutions of ions are placed at the middle of the cell formula.

iv. A single vertical line between two phases indicates the phase boundary. It indicates the direct contact between them.

v. A double vertical line between two solutions indicates that they are connected by salt bridge.

vi. The additional information such as concentration of solutions and gas pressures is also given.

vii. A single half cell is written in the order: aqueous solution of ions first and then the solid electrode.

For example $Zn^{2\oplus}(1M)\ |Zn\ (s)$. This order is reversed when the electrode acts as anode in the cell. The following example illustrates these conventions. The cell composed of Mg (anode) and Ag (cathode) consists of two half cells, $Mg^{2\oplus}\ (1M)\ |Mg\ (s)$ and $Ag^{\oplus}\ (1M)|Ag(s)$. The cell is represented as :

$$Mg\ (s)\ |Mg^{2\oplus}\ (1M)\ ||Ag^{\oplus}(1M)\ |Ag(s).$$

Can you tell ?

You have learnt Daniel cell in XI th standard. Write notations for anode and cathode. Write the cell formula.

5.6.3 Writing of cell reaction :

The cell reaction corresponding to the cell notation is written on the assumption that the right hand side electrode is cathode (+) and left hand side electrode is anode (-).

As mentioned in section 5.4.2, oxidation half reaction occurs at anode and reduction half reaction at cathode. It, therefore, follows that in galvanic cell oxidation half reaction takes place on the left hand side electrode and reduction half reaction on the right hand side electrode.

The following steps are followed to write the cell reaction.

i. Write oxidation half reaction for the left hand side electrode and reduction half reaction for the right hand side electrode.

ii. Add two electrode half reactions to get the overall cell reaction. While adding the electrons must be cancelled. For this purpose, it may be necessary to multiply one or both the half reactions by a suitable numerical factor (s). No electrons should appear in the overall reaction.

iii. It is important to note that the individual half reactions may be written with one or more electrons. For example, half reactions for H_2 gas, whether written as $2H^{\oplus}$ (aq) + $2e^{\ominus} \longrightarrow H_2$ (g) or $H^{\oplus}$(aq) + $e^{\ominus} \longrightarrow 1/2\ H_2$ (g) makes no difference. In writing the overall cell reaction, the electrons must be balanced.

Consider the cell,

$$\overset{e^{\ominus}\ \longrightarrow}{\mathrm{Ni\ (s)} \,|\, \mathrm{Ni^{2\oplus}\ (1M)} \,||\, \mathrm{Al^{3\oplus}\ (1M)} \,|\, \mathrm{Al\ (s)}}$$

The oxidation at anode is

$$\mathrm{Ni\ (s)} \longrightarrow \mathrm{Ni^{2\oplus}\ (1M)} + 2e^{\ominus}$$

The reduction half reaction at cathode is

$$\mathrm{Al^{3\oplus}\ (1M)} + 3\ e^{\ominus} \longrightarrow \mathrm{Al\ (s)}.$$

To balance the electrons, oxidation reaction is multiplied by 3 and reduction reaction by 2. The two half reactions so obtained when added give the overall cell reaction. Thus,

$$3\ \mathrm{Ni\ (s)} \longrightarrow 3\ \mathrm{Ni^{2\oplus}\ (1M)} + 6\ e^{\ominus}$$

(oxidation half reaction)

$$2\ \mathrm{Al^{3\oplus}\ (1M)} + 6\ e^{\ominus} \longrightarrow 2\ \mathrm{Al\ (s)}$$

(reduction half reaction)

$$3\ \mathrm{Ni\,(s)} + 2\mathrm{Al^{3\oplus}\,(1M)} \longrightarrow 3\mathrm{Ni^{2\oplus}\ (1M)} + 2\ \mathrm{Al\ (s)}$$

(overall cell reaction)

Try this...

Write electrode reactions and overall cell reaction for Daniel cell you learnt in standard XI.

5.7 Electrode potential and cell potential

: A galvanic cell is composed of two half cells, each consisting of electronic (metal plates) and electrolytic (solution of ions) conductors in contact. At the surface of separation of solid metal and the solution, there exists difference of electrical potential. This **potential difference established due to electrode half reaction occurring at the electrode surface, is the electrode potential**.

The potential is associated with each of the half reaction, be it oxidation or reduction. The potential associated with oxidation reaction is oxidation potential while that associated with reduction gives the reduction potential. The overall cell potential, also called electromotive force (emf), is made of the contributions from each of the electrodes. In other words, the cell potential is algebraic sum of the electrode potentials,

$$E_{cell} = E_{oxi}\ \text{(anode)} + E_{red}\ \text{(cathode)} \qquad \text{........... (5.22)}$$

where E_{oxi} is the oxidation potential of anode (-) and E_{red} is the reduction potential of cathode (+).

When galvanic cell operates, electrons are generated at the anode. These electrons move through external circuit to the cathode. The cell potential is the force that pushes electrons away from anode (-) and pulls them toward cathode where they are consumed.

5.7.1 Standard potentials

: The electrode potential and the cell potential depend on concentrations of solutions, pressures of gases and the temperature. To facitilate comparison of different galvanic cells, it is necessary to measure the cell voltage under given set of standard conditions of concentration and temperature.

The standard conditions chosen are 1 M concentration of solution, 1 atm pressure for gases, solids and liquids in pure form and 25^{0}C. The voltage measured under these conditions is called standard potential designated as E^0.

The standard cell potential is the algebraic sum of the standard electrode potentials similar to Eq. (5.22).

$$E^0_{cell} = E^0_{oxi}\ (\text{anode}) + E^0_{red}\ (\text{cathode}) \qquad \ldots\ldots\ldots\ (5.23)$$

Here E^0_{oxi} is standard oxidation potential and E^0_{red} is the standard reduction potential.

According to IUPAC convention, standard potential of an electrode is taken as the standard reduction potential.

It must be realised that standard oxidation potential of any electrode is numerically equal to its standard reduction potential with the reversal of sign. For example standard oxidation potential of $Zn^{2\oplus}$ (1M) | Zn electrode is 0.76V. Its standard reduction potential will be -0.76 V. Hereafter the standard reduction potential will be called standard potential, the voltage associated with a reduction reaction.

It follows that the standard cell potential (emf) is written in terms of the standard potentials of the electrodes. In Eq. (5.23), E^0_{oxi}(anode) is replaced by - E^0_{red} (anode). We then write,

$$E^0_{cell} = -E^0_{red}\ (\text{anode}) + E^0_{red}\ (\text{cathode})$$

Omitting the subscript red, we have

$$E^0_{cell} = E^0\ (\text{cathode}, +) - E^0\ (\text{anode}, -) \qquad \ldots\ldots\ldots\ (5.24)$$

Remember...

- While constructing a galvanic cell from two electrodes, the electrode with higher standard potential is cathode (+) and that with lower standard potential is anode (-).
- The difference in electrical potential between anode and cathode is cell voltage.

5.7.2 Dependence of cell potential on concentration (Nernst equation) :

The standard cell potential tells us whether or not the reactants in their standard states form the products in their standard states spontaneously. To predict the spontaneity of reactions for anything other than standard concentration conditions we need to know how voltage of galvanic cell varies with concentration.

Dependence of cell voltage on concentrations is given by Nernst equation. For any general reaction,

$$aA + bB \longrightarrow cC + dD$$

The cell voltage is given by

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$= E^0_{cell} - \frac{2.303RT}{nF}\ \log_{10} \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \ldots\ldots\ldots\ (5.25)$$

where n = moles of electrons used in the reaction, F = Faraday = 96500 C, T = temperature in kelvin, R = gas constant = 8.314 J K^{-1}mol^{-1}

At 25 ^{0}C, $\frac{2.303RT}{F} = 0.0592$ V

Therefore at 25 ^{0}C, eq. (5.24) becomes

$$E_{cell} = E^0_{cell} - \frac{0.0592\text{V}}{n}\ \log_{10} \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \ldots\ldots\ldots\ (5.26)$$

The Eq. (5.25) or Eq. (5.26) is the Nernst equation. The first term on the right hand of Nernst equation represents standard state electrochemical conditions. The second term is the correction for non standard state conditions. The cell potential equals standard potential if the concentrations of reactants and products are 1 M each. Thus, if [A] = [B] = [C] = [D] = 1M,

$$E_{cell} = E^0_{cell}$$

If a gaseous substance is present in the cell reaction its concentration term is replaced by the partial pressure of the gas.

The Nernst equation can be used to calculate cell potential and electrode potential.

i. Calculation of cell potential : Consider the cell

$$Cd(s)|Cd^{2\oplus}(aq)||\ Cu^{2\oplus}(aq)\ |Cu.$$

Let us first write the cell reaction

$$Cd\ (s) \longrightarrow Cd^{2\oplus}\ (aq) + 2\ e^{\ominus}$$

(oxidation at anode)

$$Cu^{2\oplus}\ (aq) + 2\ e^{\ominus} \longrightarrow Cu\ (s)$$

(reduction at cathode)

$$Cd\ (s) + Cu^{2\oplus}\ (aq) \longrightarrow Cd^{2\oplus}\ (aq) + Cu\ (s)$$

(overall cell reaction)

Here $n = 2$

The potential of cell is given by Nernst equation,

$$E_{cell} = E^0_{cell} - \frac{0.0592}{2}\log_{10}\frac{[Cd^{2\oplus}]}{[Cu^{2\oplus}]}$$

at 25 °C.

(Concentration of solids and pure liquids are taken to be unity.)

ii. Calculation of electrode potential

Consider $Zn^{2\oplus}(aq)|Zn(s)$

The reduction reaction for the electrode is

$$Zn^{2\oplus}\ (aq) + 2\ e^{\ominus} \longrightarrow Zn\ (s)$$

Applying Nernst equation, electrode potential is given by

$$E_{Zn} = E^0_{Zn} - \frac{0.0592}{2}\log_{10}\frac{1}{[Zn^{2\oplus}]}$$

$$= E^0_{Zn} + \frac{0.0592}{2}\log_{10}[Zn^{2\oplus}] \text{ at } 25\ ^0C$$

Problem 5.10 : Calculate the voltage of the cell, $Sn\ (s)|Sn^{2\oplus}\ (0.02M)||Ag^{\oplus}\ (0.01M)|Ag\ (s)$ at 25 °C.

$E^0_{Sn} = -\,0.136$ V, $E^0_{Ag} = 0.800$ V.

Solution :

First we write the cell reaction.

$$Sn\ (s) \longrightarrow Sn^{2\oplus}\ (0.02M) + 2\ e^{\ominus}$$

(oxidation at anode)

$$[Ag^{\oplus}\ (0.01M) + e^{\ominus} \longrightarrow Ag\ (s)] \times 2$$

(reduction at cathode)

$$Sn\ (s) + 2\ Ag^{\oplus}\ (0.01M) \longrightarrow Sn^{2\oplus}\ (0.02\ M) + 2\ Ag\ (s)$$

(overall cell reaction)

The cell potential is given by

$$E_{cell} = E^0_{cell} - \frac{0.0592V}{2}\log_{10}\frac{[Sn^{2\oplus}]}{[Ag^{\oplus}]^2}$$

$$E^0_{cell} = E^0_{Ag} - E^0_{Sn} = 0.8\ V + 0.136\ V$$
$$= 0.936\ V$$

Hence,

$$E_{cell} = 0.936V - \frac{0.0592V}{2}\log_{10}\frac{0.02}{(0.01)^2}$$

$$= 0.936V - \frac{0.0592V}{2}\log_{10}200$$

$$= 0.936V - \frac{0.0592V}{2} \times 2.301$$

$$= 0.936\ V - 0.0681V = 0.8679\ V$$

Problem 5.11 : The standard potential of the electrode, $Zn^{2\oplus}\ (0.02\ M)\ |Zn\ (s)$ is - 0.76 V. Calculate its potential.

Solution :

Electrode reaction :

$$Zn^{2\oplus}\ (0.02M) + 2\ e^{\ominus} \longrightarrow Zn\ (s)$$

$$E_{Zn} = E^0_{Zn} - \frac{0.0592V}{n}\log_{10}\frac{1}{[Zn^{2\oplus}]}$$

$$= -\,0.76\ V + \frac{0.0592V}{2}\log_{10}(0.02)$$

$$= -\,0.76\ V + \frac{0.0592V}{2} \times (-1.6990)$$

$$= -\,0.76\ V - 0.0503V = -\,0.81\ V$$

5.8 Thermodynamics of galvanic cells

5.8.1 Gibbs energy of cell reactions and cell potential : The electrical work done in a galvanic cell is the electricity (charge) passed multiplied by the cell potential.

Electrical work
= amount of charge passed × cell potential.

Charge of one mole electrons is F coulombs. For the cell reaction involving n moles of electrons.

charge passed = nF coulombs

Hence, electrical work = nFE_{cell}

W. Gibbs in 1878 concluded that electrical work done in galvanic cell is equal to the decrease in Gibbs energy, - ΔG, of cell reaction. It then follows that

Electrical work = - ΔG

and thus $-\Delta G = nFE_{cell}$

$$\text{or} \qquad \Delta G = -nFE_{cell} \qquad \ldots\ldots (5.27)$$

Under standard state conditions, we write

$$\Delta G^0 = -nFE^0_{cell} \qquad \ldots\ldots\ldots\ldots (5.28)$$

The Eq. (5.28) explains why E^0_{cell} is an intensive property.

We know that ΔG^0 is an extensive property since its value depends on the amount of substance. If the stoichiometric equation of redox reaction is multiplied by 2 that is the amounts of substances oxidised and reduced are doubled, ΔG^0 doubles. The moles of electrons transferred also doubles. The ratio,

$$E^0_{cell} = -\frac{\Delta G^0}{nF} \text{ then becomes}$$

$$E^0_{cell} = -\frac{2\Delta G^0}{2\,nF} = -\frac{\Delta G^0}{nF}$$

Thus, E^0_{cell} remains the same by multiplying the redox reaction by 2. It means E^0_{cell} is independent of the amount of substance and the intensive property.

Remember...

For chemical reaction to be spontaneous, ΔG must be negative. Because $\Delta G = -nFE_{cell}$, E_{cell} must be positive for a cell reaction if it is spontaneous.

5.8.2 Standard cell potential and equilibrium constant : The relation between standard Gibbs energy change of cell reaction and standard cell potential is given by Eq. (5.27).

$$-\Delta G^0 = nFE^0_{cell}$$

The relation between standard Gibbs energy change of a chemical reaction and its equilibrium constant as given in thermodynamics is :

$$\Delta G^0 = -RT \ln K \qquad \ldots\ldots\ldots\ldots (5.29)$$

Combining Eq. (5.28) and Eq. (5.29), we have

$$-nFE^0_{cell} = -RT \ln K$$

$$\text{or} \qquad E^0_{cell} = \frac{RT}{nF} \ln K$$

$$= \frac{2.303\,RT}{nF} \log_{10}K$$

$$= \frac{0.0592}{n} \log_{10}K \quad \text{at } 25\ {}^0\text{C} \qquad \ldots\ldots\ldots\ldots (5.29)$$

Try this...

Write expressions to calculate equilibrium constant from

i. Concentration data

ii. Thermochemical data

iii. Electrochemical data

Problem 5.12 : Calculate standard Gibbs energy change and equilibrium constant at 25^0C for the cell reaction,

$$\mathrm{Cd\ (s) + Sn^{2\oplus}\ (aq) \longrightarrow Cd^{2\oplus}\ (aq) + Sn\ (s)}$$

Given : $E^0_{Cd} = -0.403\text{V}$ and $E^0_{Sn} = -\ 0.136$ V. Write formula of the cell.

Solution :

i. The cell is made of two electrodes, $\mathrm{Cd^{2\oplus}}$ (aq) |Cd (s) and $\mathrm{Sn^{2\oplus}}$ (aq) |Sn (s). E^0 value for $\mathrm{Sn^{2\oplus}}$ (aq) |Sn (s) electrode is higher than that of $\mathrm{Cd^{2\oplus}}$(aq) |Cd (s) electrode. Hence, $\mathrm{Sn^{2\oplus}}$ (aq) |Sn (s) electrode is cathode and $\mathrm{Cd^{2\oplus}}$ (aq) |Cd (s) anode. Cell formula is Cd(s) |$\mathrm{Cd^{2\oplus}}$ (aq) ||$\mathrm{Sn^{2\oplus}}$(aq) |Sn (s)

ii. $\Delta G^0 = -\ n\text{F}\ E^0_{cell}$

$$E^0_{cell} = E^0_{Sn} - E^0_{Cd} = -\ 0.136\ \text{V} - (-0.403\text{V})$$

$$= 0.267\ \text{V.}$$

$n = 2$ mol $\mathrm{e^{\ominus}}$

$$\Delta G^0 = -2\ \cancel{\text{mol e}^{\ominus}}\ 96500\ \text{C}/\cancel{\text{mol e}^{\ominus}} \times 0.267\ \text{V}$$

$$= -\ 51531\ \text{V C} = -\ 51531\ \text{J} = -\ 51.53\ \text{kJ}$$

iii. $E^0_{cell} = \dfrac{0.0592\ \text{V}}{2} \log_{10}K$

$$0.267\ \cancel{\text{V}} = \frac{0.0592\ \cancel{\text{V}}}{2} \log_{10}K$$

$$\log_{10}K = \frac{0.267 \times 2}{0.0592} = 9.0203$$

$K = \text{antilog } 9.0203 = 1.05 \times 10^9$

5.9 Reference electrodes : Every oxidation needs to be accompanied by reduction. The occurrence of only oxidation or only reduction is not possible. (Refer to Std. XI Chemistry Textbook Chapter 6)

In a galvanic cell oxidation and reduction occur simultaneously. The potential associated with the redox reaction can be experimentally measured. For the measurement of potential two electrodes need to be combined together where the redox reaction occurs.

What would happen if potential of one of the electrodes in a galvanic cell is zero ? Can we measure the potential of such a galvanic cell ? There are two electrodes combined together and a redox reaction results. The measured cell potential is algebraic sum of two electrode potentials. One electrode potential is zero. Therefore, the measured cell potential is equal to the potential of other electrode.

From foregoing arguments, it follows that it is necessary to choose an arbitrary standard electrode as a reference point. The chemists have chosen hydrogen gas electrode consisting of H_2 gas at 1 atm pressure in contact with 1 M $\mathrm{H^{\oplus}}$ ion solution as a primary reference electrode. The potential of this electrode has arbitrarily been taken as zero. The electrode is called standard hydrogen electrode (SHE).

We will see later that SHE is not the most convenient electrode. Several other electrodes namely calomel, silver-silver chloride and glass electrodes with known potentials are used as secondary reference electrodes. The potentials of these electrodes are determined using SHE.

A reference electrode is then defined as an electrode whose potential is arbitrarily taken as zero or is exactly known.

5.9.1 Standard hydrogen electrode (SHE) :

Construction : SHE consists of a platinum plate, coated with platinum black used as electrodes. This plate is connected to the external circuit through sealed narrow glass tube containing mercury. It is surrounded by an outer jacket.

The platinum electrode is immersed in 1 M $\mathrm{H^{\oplus}}$ ion solution. The solution is kept saturated with dissolved H_2 by bubbling hydrogen gas under 1 atm pressure through the side tube of the jacket as shown in Fig.5.6. Platinum does not take part in the electrode reaction. It is inert electrode and serves as the site for electron transfer.

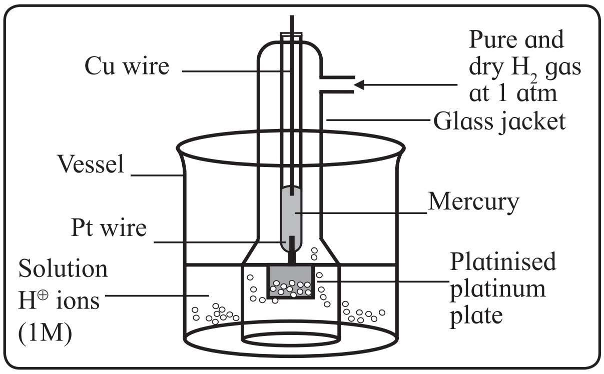


Fig. 5.6 : Standard hydrogen electrode

Formulation : Standard hydrogen electrode is represented as

$$H^\oplus\ (1M)\ |H_2\ (g,\ 1atm)|Pt$$

Electrode reaction : The platinum black capable of adsorbing large quantities of H_2 gas, allows the change from gaseous to ionic form and the reverse process to occur.

The reduction half reaction at the electrode is

$$2H^\oplus\ (1M) + 2e^\ominus \longrightarrow H_2\ (g,\ 1atm) \qquad E^0_{H_2} = 0.000\ V$$

Application of SHE

SHE is used as a primary reference electrode to determine the standard potentials of other electrodes.

To determine the standard potential of $Zn^{2\oplus}(1M)|Zn\ (s)$, it is combined with SHE to form the cell,

$Zn|Zn^{2\oplus}(1M)||H^\oplus\ (1M)|H_2\ (g,\ 1atm)|Pt$
This is shown in Fig. 5.7.

The standard cell potential, E^0_{cell}, is measured.

$E^0_{cell} = E^0_{H_2} - E^0_{Zn} = - E^0_{Zn}$, because $E^0_{H_2}$ is zero.

Thus, the measured emf of the cell is equal to standard potential of $Zn^{2\oplus}(1M)|Zn\ (s)$ electrode.

Difficulties in setting SHE

i. It is difficult to obtain pure and dry hydrogen gas.

ii. The pressure of hydrogen gas cannot be maintained exactly at 1 atm throughout the measurement.

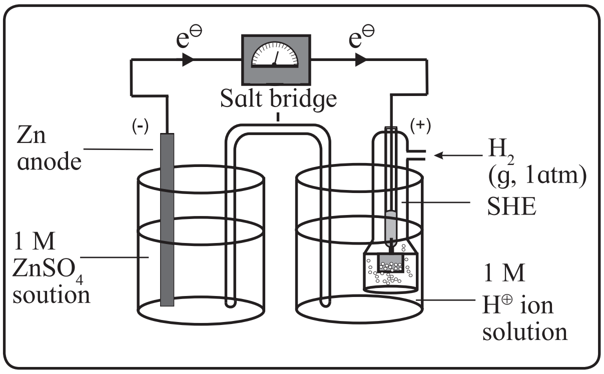


Fig. 5.7 : Determination of standard potential using SHE

iii. The concentration of $H^\oplus$ ion solution cannot be exactly maintained at 1 M. Due to bubbling of gas into the solution, evaporation of water may take place. This results in changing the concentration of solution.

Hydrogen gas electrode

For hydrogen gas electrode, $H^\oplus(aq)|H_2(g,P_{H_2})\ |Pt$, $[H^\oplus]$ and pressure of hydrogen gas differ from unity.

Electrode reaction :

$$2H^\oplus\ (aq) + 2e^\ominus \longrightarrow H_2\ (g,\ P_{H_2})$$

From the Nernst equation

$$E_{H_2} = E^0_{H_2} - \frac{0.0592}{2}\log_{10}\frac{P_{H2}}{[H^\oplus]^2}$$

$$= -\frac{0.0592}{2}\log_{10}\frac{P_{H2}}{[H^\oplus]^2}$$

Because $E^0_{H_2} = 0$

5.10 Galvanic cells useful in day-to-day life

Voltaic (or galvanic) cells in common use can be classified as primary and secondary cells.

i. **Primary voltaic cells :** When a galvanic cell discharges during current generation, the chemicals are consumed. In primary voltaic cell, once the chemicals are completely consumed, cell reaction stops. The cell reaction cannot be reversed even after reversing the direction of current flow or these cells cannot be recharged. The most familiar example is dry cell.

ii. **Secondary voltaic cells :** In secondary voltaic cell, the chemicals consumed during current generation can be regenerated. For this purpose an external potential slightly greater than the cell potential is applied across the electrodes. This results in reversal of the direction of current flow causing the reversal of cell reaction This is recharging of cell. The voltaic cells which can be recharged are called secondary voltaic cells.

It is amazing to see that secondary cells are galvanic cells during discharge and electrolytic cells during recharging. Examples of secondary cells are lead storage battery, mercury cell and nickel-cadmium cell.

5.10.1 Dry cell (Leclanche' cell) : It is a cell without liquid component, but the electrolyte is not completely dry. It is a viscous aqueous paste.

Construction : The container of the cell is made of zinc which serves as anode (-). It is lined from inside with a porous paper to separate it from the other material of the cell.

An inert graphite rod in the centre of the cell immersed in the electrolyte paste serves as cathode. It is surrounded by a paste of manganese dioxide (MnO_2) and carbon black.

The rest of the cell is filled with an electrolyte. It is a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). Some starch is added to the paste to make it thick so that it cannot be leaked out.

The cell is sealed at the top to prevent drying of the paste by evaporation of moisture. See Fig. 5.8.

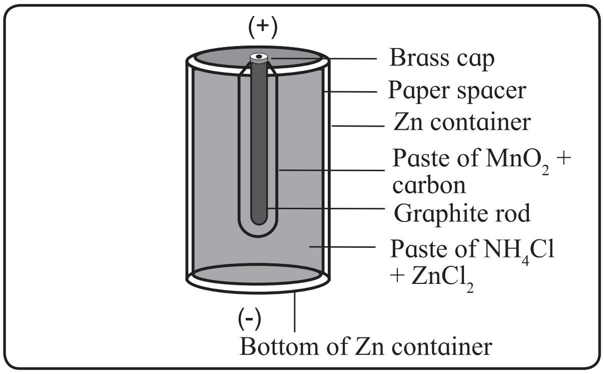


Fig. 5.8 : Dry cell (Leclanche' cell)

Cell reactions:

i. **Oxidation at anode :** When the cell operates the current is drawn from the cell and metallic zinc is oxidised to zinc ions.

$$Zn\ (s) \longrightarrow Zn^{2\oplus}\ (aq) + 2e^{\ominus}$$

ii. **Reduction at cathode :** The electrons liberated in oxidation at anode flow along the container and migrate to cathode. At cathode $NH_4^{\oplus}$ ions are reduced.

$$2NH_4^{\oplus}\ (aq) + 2e^{\ominus} \longrightarrow 2NH_3\ (aq) + H_2\ (g)$$

Hydrogen gas produced in reduction reaction is oxidised by MnO_2 and prevents its collection on cathode.

$$H_2(g)+2MnO_2(s) \longrightarrow Mn_2O_3(s)+H_2O(l)$$

The net reduction reaction at cathode is combination of these two reactions.

$$2NH_4^{\oplus}(aq) + 2\ MnO_2(s) + 2e^{\ominus} \longrightarrow Mn_2O_3\ (s) + 2\ NH_3\ (aq) + H_2O\ (l)$$

iii. **Net cell reaction :** The net cell reaction is sum of oxidation at anode and reduction at cathode.

$$Zn\ (s) + 2\ NH_4^{\oplus}\ (aq) + 2\ MnO_2(s) \longrightarrow Zn^{2\oplus}\ (aq) + Mn_2O_3\ (s) + 2\ NH_3\ (aq) + H_2O(l)$$

The ammonia produced combines with $Zn^{2\oplus}$ to form soluble compound containing complex ion.

$$Zn^{2\oplus}\ (aq) + 4\ NH_3\ (aq) \longrightarrow [Zn\ (NH_3)_4]^{2\oplus}(aq)$$

Do you know ?

Alkaline dry cell : The Leclanche' dry cell works under acidic conditions due to the presence of NH_4Cl. The difficulty with this dry cell is that Zn anode corrodes due to its actions with $H^{\oplus}$ ions from $NH_4^{\oplus}$ ions.

This results in shortening the life of dry cell. To avoid this a modified or of the dry cell called alkaline dry cell has been proposed. In alkaline dry cell NaOH or KOH is used as electrolyte in place of NH_4Cl.

The alkaline dry cell has longer life than acidic dry cell since the Zn corrodes more slowly.

Uses of dry cell : Dry cell is used as a source of power in flashlights, portable radios, tape recorders, clocks and so forth.

5.10.2 Lead storage battery (Lead accumulator) :

Lead accumulator stores electrical energy due to regeneration of original reactants during recharging. It functions as galvanic cell and as electrolytic cell, as well.

Construction : A group of lead plates packed with spongy lead serves as anode (-). Another group of lead plates bearing lead dioxide (PbO_2) serves as cathode (+).

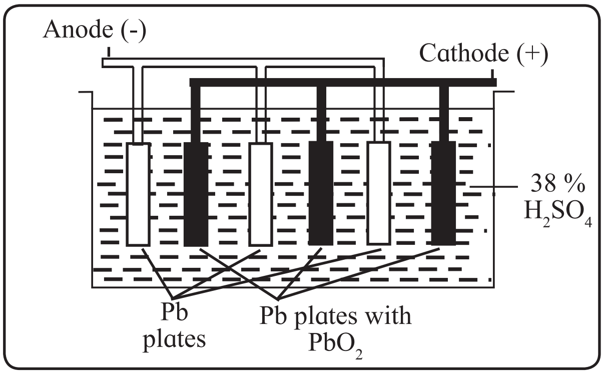


Fig. 5.9 : Lead storage cell

To provide large reacting surface, the cell contains several plates of each type. The two types of plates are alternately arranged as shown in Fig. 5.9.

The electrodes are immersed in an electrolytic aqueous solution of 38 % (by mass) of sulphuric acid of density 1.2 g/mL.

Notation of the cell : The cell is formulated as $Pb(s)|PbSO_4(s)|38\%H_2SO_4(aq)|PbSO_4(s)|PbO_2(s) \,|\, Pb(s)$

a. Cell reactions during discharge

i. **Oxidation at anode (-) :** When the cell provides current, spongy lead is oxidised to $Pb^{2\oplus}$ ions and negative charge accumulates on lead plates. The $Pb^{2\oplus}$ ions so formed combine with $SO_4^{2\ominus}$ ions from H_2SO_4 to form insoluble $PbSO_4$. The net oxidation is the sum of these two processes.

$$Pb\,(s) \longrightarrow Pb^{2\oplus}\,(aq) + 2\,e^{\ominus} \qquad \text{(oxidation)}$$

$$Pb^{2\oplus}\,(aq) + SO_4^{2\ominus}\,(aq) \longrightarrow PbSO_4\,(s) \qquad \text{(precipitation)}$$

$$Pb\,(s) + SO_4^{2\ominus}\,(aq) \longrightarrow PbSO_4\,(s) + 2\,e^{\ominus} \quad ...(i) \qquad \text{(overall oxidation)}$$

ii. **Reduction at cathode (+) :** The electrons produced at anode travel through external circuit and re-enter the cell at cathode. At cathode PbO_2 is reduced to $Pb^{2\oplus}$ ions in presence of $H^{\oplus}$ ions. Subsequently $Pb^{2\oplus}$ ions so formed combine with $SO_4^{2\ominus}$ ions from H_2SO_4 to form insoluble $PbSO_4$ that gets coated on the electrode.

$$PbO_2\,(s) + 4H^{\oplus}\,(aq) + 2\,e^{\ominus} \longrightarrow Pb^{2\oplus}\,(aq) + 2H_2O(l) \qquad \text{(reduction)}$$

$$Pb\,(s) + SO_4^{2\ominus}\,(aq) \longrightarrow PbSO_4\,(s) \qquad \text{(precipitation)}$$

$$PbO_2\,(s) + 4H^{\oplus}\,(aq) + SO_4^{2\ominus}\,(aq) + 2\,e^{\ominus} \longrightarrow PbSO_4\,(s) + 2H_2O\,(l) \quad ...(ii) \qquad \text{(overall reduction)}$$

iii. **Net cell reaction during discharge:** The net cell reaction is the sum of overall oxidation at anode and overall reduction at cathode.

$$Pb\,(s) + PbO_2\,(s) + 4H^{\oplus}\,(aq) + 2SO_4^{2\ominus}\,(aq) \longrightarrow 2PbSO_4\,(s) + 2H_2O\,(l)$$

or

$$Pb\,(s) + PbO_2\,(s) + 2H_2SO_4\,(aq) \longrightarrow 2PbSO_4(s) + 2H_2O\,(l) \quad ...(iii)$$

As the cell operates to generate current, H_2SO_4 is consumed. Its concentration (density) decreases and the cell potential is decreased. The cell potential thus depends on sulphuric acid concentration (density).

b. Cell reactions during recharging : The potential of lead accumulator is 2V. It must be recharged with the falling of the cell potential to 1.8 V. To recharge the cell external potential slightly greater than 2 V needs to be applied across the electrodes.

During recharging the cell functions as electrolytic cell. The anode and cathode are interchanged with PbO_2 electrode being anode (+) and lead electrode cathode (-).

iv. **Oxidation at anode (+) :** It is reverse of reduction reaction (ii) at cathode that occurs during discharge.

$$PbSO_4\,(s) + 2H_2O\,(l) \longrightarrow PbO_2\,(s) + 4H^{\oplus}(aq) + SO_4^{2\ominus}\,(aq) + 2\,e^{\ominus} \quad ...(iv)$$

v. **Reduction at cathode (-) :** It is reverse of oxidation reaction (i) at anode that occurs during discharge.

$$PbSO_4\,(s) + 2\,e^{\ominus} \longrightarrow Pb\,(s) + SO_4^{2\ominus}\,(aq) \quad ...(v)$$

vi. **Net cell reaction :** It is the sum of reaction (iv) and (v) or the reverse of net cell reaction (iii) that occurs during discharge

$$2PbSO_4\,(s) + 2H_2O\,(l) \longrightarrow Pb\,(s) + PbO_2\,(s) + 2\,H_2SO_4\,(aq)$$

The above reaction shows that H_2SO_4 is regenerated. Its concentration (density) and in turn, the cell potential increases.

Applications of lead accumulator

i. It is used as a source of direct current in the laboratory.

ii. A 12 V lead storage battery constructed by connecting six 2 V cells in series is used in automobiles and inverters.

5.10.3 Nickel-Cadmium or NICAD storage cell :

Nickel-cadmium cell is a secondary dry cell. In other words it is a dry cell that can be recharged.

Anode of the NICAD storage cell is cadmium metal. The cathode is nickel (IV) oxide, NiO_2 supported on Ni. The electrolyte solution is basic.

The electrode reactions and overall cell reaction are as follows :

$$Cd\,(s) + 2OH^{\ominus}\,(aq) \longrightarrow Cd(OH)_2\,(s) + 2\,e^{\ominus}$$

(anodic oxidation)

$$NiO_2\,(s) + 2\,H_2O\,(l) + 2\,e^{\ominus} \longrightarrow Ni(OH)_2\,(s) + 2OH^{\ominus}\,(aq)$$

(cathodic reduction)

$$Cd\,(s) + NiO_2\,(s) + 2\,H_2O\,(l) \longrightarrow Cd(OH)_2\,(s) + Ni(OH)_2\,(s)$$

(overall cell reaction)

The reaction product at each electrode is solid that adheres to electrode surface. Therefore the cell can be recharged. The potential of the cell is about 1.4 V. The cell has longer life than other dry cells. It can be used in electronic watches, calculators, photographic equipments, etc.

5.10.4 Mercury battery :

Mercury battery is a secondary dry cell and can be recharged. The mercury battery consists of zinc anode, amalgamated with mercury. The cathode is a paste of Hg and carbon. The electrolyte is strongly alkaline and made of a paste of KOH and ZnO. The electrode ractions and net cell reaction are :

$$Zn(Hg) + 2OH^{\ominus}(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^{\ominus}$$

(anode oxidation)

$$HgO(s) + H_2O(l) + 2e^{\ominus} \longrightarrow Hg(l) + 2\,OH^{\ominus}(aq)$$

(cathode reduction)

$$Zn\,(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

(overall cell reaction)

The overall reaction involves only solid substances. There is no change in electrolyte composition during operation. The mercury battery, therefore, provides more constant voltage (1.35V) than the Leclanche' dry cell. It also has considerably higher capacity and longer life than dry cell.

The mercury dry cell finds use in hearing aids, electric watches, pacemakers, etc.

5.11 Fuel cells :

The functioning of fuel cells is based on the fact that combustion reactions are of redox type and can be used to generate electricity.

The fuel cells differ from ordinary galvanic cells in that the reactants are not placed within the cell. They are continuously supplied to electrodes from a reservoir.

In these cells one of the reactants is a fuel such as hydrogen gas or methanol. The other reactant such as oxygen, is oxidant.

The simplest fuel cell is hydrogen-oxygen fuel cell.

5.11.1 Hydrogen-oxygen fuel cell :

In H_2 - O_2 fuel cell, the fuel is hydrogen gas. Oxygen gas is an oxidising agent. The energy of the combustion of hydrogen is converted into electrical energy.

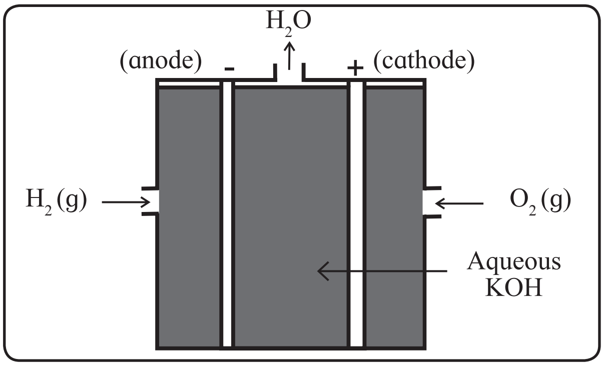


Fig. 5.10 : H_2 - O_2 fuel cell

Construction : The anode and cathode are porous carbon rods containing small amount of finely divided platinum metal that acts as a catalyst. The electrolyte is hot aqueous solution of KOH. The carbon rods immersed into electrolyte are shown in Fig. 5.10.

Hydrogen gas is continuously bubbled, through anode and oxygen gas through cathode into the electrolyte.

Cell reactions

i. **Oxidation at anode (-) :** At anode hydrogen gas is oxidised to H_2O.

$$2H_2\ (g) + 4OH^{\ominus}\ (aq) \longrightarrow 4H_2O\ (l) + 4\ e^{\ominus}$$

ii. **Reduction at cathode (+) :** The electrons released at anode travel, through external circuit to cathode. Here O_2 is reduced to OH^-.

$$O_2\ (g) + 2H_2O\ (aq) + 4\ e^{\ominus} \longrightarrow 4OH^{\ominus}\ (aq)$$

iii. **Net cell reaction :** The overall cell reaction is the sum of electrode reactions (i) and (ii).

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l)$$

The overall cell reaction is combustion of H_2 to form liquid water. Interestingly, the fuel H_2 gas and the oxidant O_2 do not react directly.

The chemical energy released during the formation of O-H bond is directly converted into electrical energy accompanying in above combustion reaction. The cell continues to operate as long as H_2 and O_2 gases are supplied to electrodes.

The cell potential is given by

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0.4V - (-0.83V) = 1.23\ V.$$

Advantages of fuel cells

i. The reacting substances are continuously supplied to the electrodes. Unlike conventional galvanic cells, fuel cells do not have to be discarded on consuming of chemicals.

ii. They are nonpolluting as the only reaction product is water.

iii. Fuel cells provide electricity with an efficiency of about 70 % which is twice as large when compared with efficiency of thermal plants (only 40 %).

Drawbacks of fuel cell

H_2 gas is hazardous to handle and the cost of preparing H_2 is high.

Internet my friend

Fuel cells are also used in cell phones and laptop computers. The cell proposed for use in these products is direct methanol fuel cell (DMFC). Collect information of this cell.

Applications of fuel cells

i. The fuel cells are used on experimental basis in automobiles.

ii. The fuel cell are used for electrical power in the space programme.

iii. In space crafts the fuel cell is operated at such a high temperature that the water evaporates at the same rate as it is formed. The vapour is condensed and pure water formed is used for drinking by astronauts.

iv. In future, fuel cells can possibly be explored as power generators in hospitals, hotels and homes.

Can you tell ?

In what ways are fuel cells and galvanic cells similar and in what ways are they different ?

5.12 Electrochemical series (Electromotive series) : The standard potentials of a number of electrodes have been determined using standard hydrogen electrode. These electrodes with their half reactions are arranged according to their decreasing standard potentials as shown in Table 5.1. This arrangement is called electrochemical series.

Key points of electrochemical series

i. The half reactions are written as reductions. The oxidizing agents and electrons appear on the left side of half reactions while the reducing agents are shown on the right side in the half reaction.

ii. Below hydrogen electrode the negative standard potential increases and above hydrogen electrode the positive standard potential increases.

iii. E^0 values apply to the reduction half reactions that occur in the forward direction as written.

iv. Higher (more positive) E^0 value for a half reaction indicates its greater tendency to occur in the forward direction and in turn greater tendency for the substance to reduce. Conversely, the low (more negative) E^0 value of a half reaction corresponds to its greater tendency to occur in the reverse direction or for the substance to oxidise.

The half reactions are listed in order of their decreasing tendency in the forward direction.

Remember...

The left side of half reaction has cations of metals or non-metallic molecules (oxidants). There are free metals or anions of non metals on the right side (reductants).

Applications of electrochemical series

i. Relative strength of oxidising agents: The species on the left side of half reactions are oxidizing agents. E^0 value is a measure of the tendency of the species to accept electrons and get reduced. In other words, E^0 value measures the strength of the substances as oxidising agents. Larger the E^0 value greater is the oxidising strength. The species in the top left side of half reactions are strong oxidising agents. As we move down the table, E^0 value and strength of oxidising agents decreases from top to bottom.

Use your brain power

Indentify the strongest and the weakest oxidizing agents from the electrochemical series.

ii. Relative strength of reducing agents: The species on the right side of half reactions are reducing agents.

The half reactions at the bottom of the table with large negative E^0 values have a little or no tendency to occur in the forward direction as written. They tend to favour the reverse direction. It follows, that the species appearing at the bottom right side of half reactions associated with large negative E^0 values are the effective electron donors. They serve as strong reducing agents. The strength of reducing agents increases from top to bottom as E^0 values decrease.

Use your brain power

Identify the strongest and the weakest reducing agents from the electrochemical series.

iii. Spontaneity of redox reactions : A redox reaction in galvanic cell is spontaneous only if the species with higher E^0 value is reduced (accepts electrons) and that with lower E^0 value is oxidised (donates electrons).

The standard cell potential must be positive for a cell reaction to be spontaneous under the standard conditions. Noteworthy application of electromotive series is predicting spontaneity of redox reactions from the knowledge of standard potentials.

Suppose, we ask a question : At standard conditions would $Ag^{\oplus}$ ions oxidise metallic magnesium ? To answer this question, first we write oxidation of Mg by $Ag^{\oplus}$.

$$Mg\,(s) \longrightarrow Mg^{2\oplus}\,(aq) + 2\,e^{\ominus}\ \text{(oxidation)}$$

$$2Ag^{2\oplus}\,(aq) + 2\,e^{\ominus} \longrightarrow 2Ag\,(s)\text{(reduction)}$$

$$Mg\,(s) + 2Ag^{2\oplus}\,(aq) \longrightarrow Mg^{2\oplus}\,(aq) + 2Ag\,(s)\ \text{(overall reaction)}$$

From Table 5.1 of electrochemical series we have

E^0_{Mg} = -2.37 V and E^0_{Ag} = 0.8 V. For the cell having Mg as anode and Ag cathode.

$$E^0_{Cell} = E^0_{Ag} - E^0_{Mg} = 0.8V - (-2.37V)$$

$$= 3.17\ V.$$

EMF being positive the cell reaction is spontaneous. Thus $Ag^{\oplus}$ ions oxidise to metallic Mg.

General rules

i. An oxidizing agent can oxidize any reducing agent that appears below it, and cannot oxidize the reducing agent appearing above it in the electrochemical series.

ii. An reducing agent can reduce the oxidising agent located above it in the electrochemical series.

Use your brain power

From E^0 values given in Table 5.1, predict whether Sn can reduce I_2 or $Ni^{2\oplus}$.

Do you know ?

The fuel cells for power electric vehicles incorporate the proton conducting plastic membrane. These are proton exchange membranes (PEM) fuel cells.

Table 5.1 : The standard aqueous electrode potentials at 298 K (Electrochemical series)

Electrode	Half reaction Left side species (oxidizing agents)	Half reaction	Half reaction Right side species (oxidizing agents)	E^0 V
$F^{\ominus}\|F_2\|Pt$	Increasing strength as oxidising agent ↑	$F_2 + 2\,e^{\ominus} \longrightarrow F^{\ominus}$	Increasing strength as reducing agent ↓	+2.870
$Au^{\oplus}\|Au$		$Au^{\oplus} + e^{\ominus} \longrightarrow Au$		+1.680
$Ce^{4\oplus}, Ce^{3\oplus}\|Pt$		$Ce^{4\oplus} + e^{\ominus} \longrightarrow Ce^{3\oplus}$		+1.610
$Au^{3\oplus}\|Au$		$Au^{3\oplus} + 3e^{\ominus} \longrightarrow Au$		+1.500
$Cl^{\ominus}\|Cl_2\|Pt$		$Cl_2 + 2e^{\ominus} \longrightarrow 2Cl^{\ominus}$		+1.360
$Pt^{2\oplus}\|Pt$		$Pt^{2\oplus} + 2e^{\ominus} \longrightarrow Pt$		+1.200
$Br^{\ominus}\|Br_2\|Pt$		$Br_2 + 2e^{\ominus} \longrightarrow 2Br^{\ominus}$		+1.080
$Hg^{2\oplus}\|Hg$		$Hg^{2\oplus} + 2e^{-} \longrightarrow Hg$		+0.854
$Ag^{\oplus}\|Ag$		$Ag^{\oplus} + e^{\ominus} \longrightarrow Ag$		+0.799
$Hg_2^{\ 2\oplus}\|Hg$		$Hg_2^{\ 2\oplus} + 2e^{\ominus} \longrightarrow 2Hg$		+0.79
$Fe^{3\oplus}, Fe^{2\oplus}\|Pt$		$Fe^{3\oplus} + e^{\ominus} \longrightarrow Fe^{2\oplus}$		+0.771
$I^{\ominus}\|I_2(s)\|Pt$		$I_2 + 2e^{\ominus} \longrightarrow 2I^{\ominus}$		+0.535
$Cu^{2\oplus}\|Cu$		$Cu^{2\oplus} + 2e^{\ominus} \longrightarrow Cu$		+0.337
$Ag\|AgCl(s)\|Cl^{\ominus}$		$AgCl\ (s) + e^{\ominus} \longrightarrow Ag + Cl^{-}$		+0.222
$Cu^{2\oplus}, Cu^{\oplus}\|Pt$		$Cu^{2\oplus} + e^{\ominus} \longrightarrow Cu^{\oplus}$		+0.153
$Sn^{4\oplus}, Sn^{2\oplus}\|Pt$		$Sn^{4\oplus} + 2e^{\ominus} \longrightarrow Sn^{2\oplus}$		+0.15
$H^{\oplus}\|H_2\|Pt$		$2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2$		0.00
$Pb^{2\oplus}\|Pb$		$Pb^{2\oplus} + 2e^{\ominus} \longrightarrow Pb$		-0.126
$Sn^{2\oplus}\|Sn$		$Sn^{2\oplus} + 2e^{\ominus} \longrightarrow Sn$		-0.136
$Ni^{2\oplus}\|Ni$		$Ni^{2\oplus} + 2e^{\ominus} \longrightarrow Ni$		-0.257
$Co^{2\oplus}\|Co$		$Co^{2\oplus} + 2e^{-} \longrightarrow Co$		-0.280
$Cd^{2\oplus}\|Cd$		$Cd^{2\oplus} + 2e^{\ominus} \longrightarrow Cd$		-0.403
$Fe^{2\oplus}\|Fe$		$Fe^{2\oplus} + 2e^{\ominus} \longrightarrow Fe$		-0.440
$Cr^{3\oplus}\|Cr$		$Cr^{3\oplus} + 3e^{\ominus} \longrightarrow Cr$		-0.740
$Zn^{2\oplus}\|Zn$		$Zn^{2\oplus} + 2e^{\ominus} \longrightarrow Zn$		-0.763
$Al^{3\oplus}\|Al$		$Al^{3\oplus} + 3e^{\ominus} \longrightarrow Al$		-1.66
$Mg^{2\oplus}\|Mg$		$Mg^{2\oplus} + 2e^{\ominus} \longrightarrow Mg$		-2.37
$Na^{\oplus}\|Na$		$Na^{\oplus} + e^{\ominus} \longrightarrow Na$		-2.714
$Ca^{2\oplus}\|Ca$		$Ca^{2\oplus} + 2e^{\ominus} \longrightarrow Ca$		-2.866
$K^{\oplus}\|K$		$K^{\oplus} + e^{\ominus} \longrightarrow K$		-2.925
$Li^{\oplus}\|Li$		$Li^{\oplus} + e^{\ominus} \longrightarrow Li$		-3.045

Note : (i) all ions are at 1 M concentration in water.
(ii) all gases are at 1 atm pressure.

Exercises

1. Choose the most correct option.

i. Two solutions have the ratio of their concentrations 0.4 and ratio of their conductivities 0.216. The ratio of their molar conductivities will be

a. 0.54 b. 11.574

c. 0.0864 d. 1.852

ii. On diluting the solution of an electrolyte

a. both $\wedge$ and k increase

b. both $\wedge$ and k decrease

c. $\wedge$ increases and k decreases

d. $\wedge$ decreases and k increases

iii. 1 S m^2 mol^{-1} is eual to

a. 10^{-4} S m^2 mol^{-1}

b. 10^4 Ω^{-1} cm^2 mol^{-1}

c. 10^{-2} S cm^2 mol^{-1}

d. 10^2 Ω^{-1} cm^2 mol^{-1}

iv. The standard potential of the cell in which the following reaction occurs

H_2 (g,1atm) + $Cu^{2\oplus}$(1M) $\longrightarrow$ $2H^{\oplus}$(1M) + Cu (s), ($E^0_{Cu} = 0.34V$) is

a. -0.34 V b. 0.34 V

c. 0.17 V d. -0.17 V

v. For the cell, Pb (s)|$Pb^{2\oplus}$(1M)||$Ag^{\oplus}$(1M) |Ag (s), if concentraton of an ion in the anode compartment is increased by a factor of 10, the emf of the cell will

a. increase by 10 V

b. increase by 0.0296 V

c. decrease by 10 V

d. decrease by 0.0296 V

vi. Consider the half reactions with standard potentials

i. $Ag^{\oplus}$ (aq) + $e^{\ominus}$ $\longrightarrow$ Ag (s)

$E^0 = 0.8V$

ii. I_2 (s) + $2e^{\ominus}$ $\longrightarrow$ $2I^{\ominus}$ (aq)

$E^0 = 0.53V$

iii. $Pb^{2\oplus}$ (aq) + $2e^{\ominus}$ $\longrightarrow$ Pb (s)

$E^0 = -0.13V$

iv. $Fe^{2\oplus}$ (aq) + $2e^{\ominus}$ $\longrightarrow$ Fe (s)

$E^0 = -0.44V$

The strongest oxidising and reducing agents respectively are

a. Ag and $Fe^{2\oplus}$ b. $Ag^{\oplus}$ and Fe

c. $Pb^{2\oplus}$ and $I^{\ominus}$d. I_2 and $Fe^{2\oplus}$

vii. For the reaction Ni(s) + $Cu^{2\oplus}$ (1M) $\longrightarrow$ $Ni^{2\oplus}$ (1M) + Cu (s), E^0_{cell} = 0.57V ΔG^0 of the reaction is

a. 110 kJ b. -110 kJ

c. 55 kJ d. -55 kJ

viii. Which of the following is not correct?

a. Gibbs energy is an extensive property

b. Electrode potential or cell potential is an intensive property.

c. Electrical work = - ΔG

d. If half reaction is multiplied by a numerical factor, the corresponding E^0 value is also multiplied by the same factor.

ix. The oxidation reaction that takes place in lead storage battery during discharge is

a. $Pb^{2\oplus}$ (aq) + $SO_4^{2\ominus}$(aq) $\longrightarrow$ $PbSO_4$(s)

b. $PbSO_4$(s) + $2H_2O$ (l) $\longrightarrow$ PbO_2(s) + $4H^{\oplus}$(aq) + $SO_4^{2\ominus}$(aq) + $2e^{\ominus}$

c. Pb(s) + $SO_4^{2\ominus}$(aq) $\longrightarrow$ $PbSO_4$(s) + $2e^{\ominus}$

d. $PbSO_4$(s) + $2e^{\ominus}$ $\longrightarrow$ Pb(s) + $SO_4^{2\ominus}$(aq)

x. Which of the following expressions represent molar conductivity of $Al_2(SO_4)_3$?

a. $3\ \lambda^0_{Al^{3\oplus}} + 2\ \lambda^0_{SO_4^{2\ominus}}$

b. $2\ \lambda^0_{Al^{3\oplus}} + 3\ \lambda^0_{SO_4^{2\ominus}}$

c. $1/3\ \lambda^0_{Al^{3\oplus}} + 1/2\ \lambda^0_{SO_4^{2\ominus}}$

d. $\lambda^0_{Al^{3\oplus}} + \lambda^0_{SO_4^{2\ominus}}$

2. Answer the following in one or two sentences.

i. What is a cell constant ?

ii. Write the relationship between conductivity and molar conductivity and hence unit of molar conductivity.

iii. Write the electrode reactions during electrolysis of molten KCl.

iv. Write any two functions of salt bridge.

v. What is standard cell potential for the reaction

$3Ni\ (s) + 2Al^{3\oplus}(1M) \longrightarrow 3Ni^{2\oplus}(1M)$

$+ 2Al(s)$ if $E^0_{Ni} = -\ 0.25$ V and $E^0_{Al} =$ -1.66V?

vi. Write Nerst equation. What part of it represents the correction factor for nonstandard state conditions ?

vii. Under what conditions the cell potential is called standard cell potential ?

viii. Formulate a cell from the following electrode reactions :

$Au^{3\oplus}(aq) + 3e^{\ominus} \longrightarrow Au(s)$

$Mg(s) \longrightarrow Mg^{2\oplus}(aq) + 2e^{\ominus}$

ix. How many electrons would have a total charge of 1 coulomb ?

x. What is the significance of the single vertical line and double vertical line in the formulation galvanic cell.

3. Answer the following in brief

i. Explain the effect of dilution of solution on conductivity ?

ii. What is a salt bridge ?

iii. Write electrode reactions for the electrolysis of aqueous NaCl.

iv. How many moles of electrons are passed when 0.8 ampere current is passed for 1 hour through molten $CaCl_2$?

v. Construct a galvanic cell from the electrodes $Co^{3\oplus}|Co$ and $Mn^{2\oplus}|Mn$. $E^0_{Co} = 1.82$ V, $E^0_{Mn} = -\ 1.18$V. Calculate E^0_{cell}.

vi. Using the relationsip between ΔG^0 of cell reaction and the standard potential associated with it, how will you show that the electrical potential is an intensive property ?

viii. Derive the relationship between standard cell potential and equilibrium constant of cell reaction.

ix. It is impossible to measure the potential of a single electrode. Comment.

x. Why do the cell potential of lead accumulators decrease when it generates electricity ? How the cell potential can be increased ?

xi. Write the electrode reactions and net cell reaction in NICAD battery.

4. Answer the following :

i. What is Kohrausch law of independent migration of ions? How is it useful in obtaining molar conductivity at zero concentration of a weak electrolyte ? Explain with an example.

ii. Explain electrolysis of molten NaCl.

iii. What current strength in amperes will be required to produce 2.4 g of Cu from $CuSO_4$ solution in 1 hour ? Molar mass of Cu = 63.5 g mol^{-1}. (2.03 A)

iv. Equilibrium constant of the reaction,

$2Cu^{\oplus}(aq) \longrightarrow Cu^{2\oplus}(aq) + Cu(s)$ is 1.2×10^6. What is the standard potential of the cell in which the reaction takes place ? (0.36 V)

v. Calculate emf of the cell

$Zn(s)|Zn^{2\oplus}(0.2M)||H^{\oplus}(1.6M)|H_2(g, 1.8 atm)|Pt$ at 25^0C.
(0.785V)

vi. Calculate emf of the following cell at 25^0C.

$Zn(s)|Zn^{2\oplus}(0.08M)||Cr^{3\oplus}(0.1M)|Cr$

$E^0_{Zn} = -0.76$ V, $E^0_{Cr} = -0.74$ V

(0.0327 V)

vii. What is a cell constant ? What are its units? How is it determined experimentally?

viii. How will you calculate the moles of electrons passed and mass of the substance produced during electrolysis of a salt solution using reaction stoichiometry.

ix. Write the electrode reactions when lead storage cell generates electricity. What are the anode and cathode and the electrode reactions during its recharging?

x. What are anode and cathode of H_2-O_2 fuel cell ? Name the electrolyte used in it. Write electrode reactions and net cell reaction taking place in the fuel cell.

xi. What are anode and cathode for Leclanche' dry cell ? Write electrode reactions and overall cell reaction when it generates electricity.

xii. Identify oxidising agents and arrange them in order of increasing strength under standard state conditions. The standard potentials are given in parenthesis.

Al (-1.66V), $Al^{3\oplus}$(-1.66V), Cl_2 (1.36V), $Cd^{2\oplus}$(-0.4V), Fe(-0.44V), I_2(0.54V), $Br^{\ominus}$(1.09V).

xiii. Which of the following species are reducing agents? Arrange them in order of increasing strength under standard state conditions. The standard potentials are given in parenthesis.

K (-2.93V), Br_2(1.09V), Mg(-2.36V), $Ce^{3\oplus}$(1.61V), $Ti^{2\oplus}$(-0.37V), $Ag^{\oplus}$(0.8 V), Ni (-0.23V).

xiv. Predict whether the following reactions would occur spontaneously under standard state conditions.

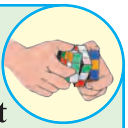
a. $Ca(s) + Cd^{2\oplus}(aq) \longrightarrow Ca^{2\oplus}(aq) + Cd(s)$

b. $2Br^{\ominus}(s) + Sn^{2\oplus}(aq) \longrightarrow Br_2(l) + Sn(s)$

c. $2Ag(s) + Ni^{2\oplus}(aq) \longrightarrow 2Ag^{\oplus}(aq) + Ni(s)$

(use information of Table 5.1)

Activity :



1. **Write electrode reactions net cell reaction in the electrolysis of molten barium chloride.**
2. **Prepare the salt bridge and set up the Daniel cell in your laboratory. Measure its emf using voltmeter and compare it with the value calculated from the information in Table 5.1**
3. **k_1 and k_2 are conductivities of two solutions and c_1 and c_2 are their concentrations. Establish the relationship between k_1, k_2, c_1, c_2 and molar conductivities $\wedge_1$ and $\wedge_2$ of the two solutions.**
4. **Find and search working of power inverters in day-to-day life.**
5. **Collect information of pollution free battery.**

6. CHEMICAL KINETICS

Can you recall ?

- What is the influence of particle size of reacting solid on rate of a chemical reaction ?
- Why is finely divided nickel used in hydrogenation of oil ?
- What is effect of change of temperature on the rate of a chemical reaction ?

6.1 Introduction : Three important characteristics of chemical reactions include : extent of reaction, feasibility and its rate. In standard XI, we learnt how equibrium constants predict the extent of reaction. In unit 3 of this text, we learnt how thermodynamic properties such as change in entropy or enthalpy tell us whether under the given set of conditions chemical reaction represented by chemical equation occurs or not. Chemical kinetics is a branch of chemistry which deals with the rate of chemical reactions and the factors those affect them.

A chemist wants to know the rates of reactions for different reasons. One the study of reaction rates help us to predict how rapidly the reaction approaches equilibrium. Secondly it gives information on the mechanism of chemical reactions.

A number of reactions occur as a sequence of elementary steps constituting the mechanism of reaction.

6.2 Rate of reactions : The rate of reaction describes how rapidly the reactants are consumed or the products are formed.

6.2.1 Average rate of chemical reaction : The average rate of a reaction can be described by knowing change in concentration of reactant or product divided by time interval over which the change occurs. Thus,

$$\text{Average rate} = \frac{\text{change in concentration of a species}}{\text{change in time}}$$

$$= \frac{\Delta c}{\Delta t}$$

Consider the reaction A $\longrightarrow$ B in which A is consumed and B is produced.

$$\text{average rate of consumption of A} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{Average rate of formation of B} = +\frac{\Delta[B]}{\Delta t}$$

$$\text{Therefore, average rate of reaction} = -\frac{\Delta[A]}{\Delta t}$$

$$= +\frac{\Delta[B]}{\Delta t}$$

The rate of reaction represents a decrease in concentration of the reactant per unit time or increase in concentration of product per unit time. The dimensions of rate are concentration divided by time, that is, mol dm^{-3} sec^{-1}.

6.2.2 Instantaneous rate of : To determine the instantaneous rate of a reaction the progress of a reaction is followed by measuring the concentrations of reactant or product for different time intervals. The changes in concentration are relatively fast in the

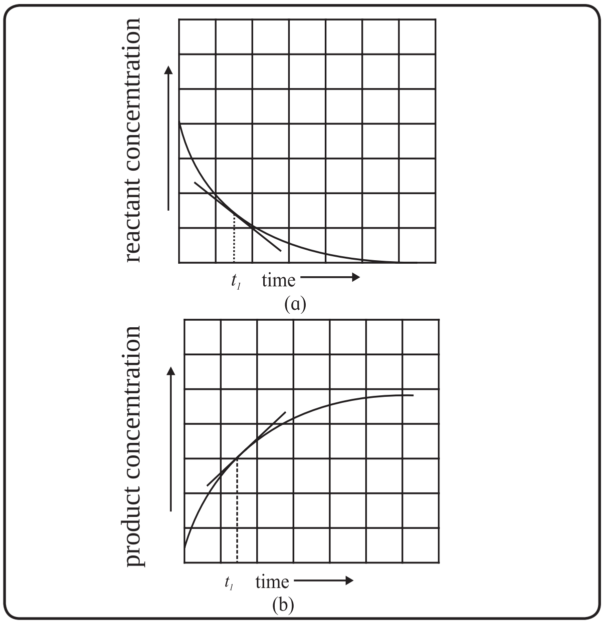


Fig. 6.1 : Determination of instantaneous rate

beginning which later become slow. The concentration of a reactant or a product plotted against time are shown in Fig. 6.1 (a) and 6.1 (b). A tangent drawn to the curve at time t_1 gives the rate of the reaction. The slope thus obtained gives the instantaneous rate of the reaction at time t_1. The instantaneous rate *dc/dt*, is represented by replacing Δ by derivative *dc/dt* in the expression of average rate. In chemical kinetics we are concerned with instantaneous rates.

For the reaction, $A \longrightarrow B$,

Rate of consumption of A at any time $t = -\frac{d[A]}{dt}$

Rate of formation of B at any time $t = \frac{d[B]}{\Delta t}$

Rate of reaction at time $t = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$

For the reaction involving one mole of A and B each, the rate of consumption of A equals the rate of formation of B. This is not true for the reactions involving different stoichiometries. Consider, for example, a reaction :

$$A + 3B \longrightarrow 2\,C$$

When one mole of A is consumed three moles of B are consumed and two moles of C are formed. The stoichiometric coefficients of the three species are different. Thus the rate of consumption of B is three times the rate of consumption of A. Likewise the rate of formation of C is twice the rate of consumption of A. We write,

$$-\frac{d[B]}{dt} = -3\frac{d[A]}{dt} \text{ and } \frac{d[C]}{dt} = -2\frac{d[A]}{dt}$$

With this

$$-\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{2}\frac{d[C]}{dt}$$

or rate of reaction $= -\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt}$

$$= \frac{1}{2}\frac{d[C]}{dt}$$

Write the expression for:

$2\,N_2O(g) \longrightarrow 4\,NO_2(g) + O_2(g)$?

In general, For

$aA + bB \longrightarrow cC + dD$,

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$

$$= \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Problem 6.1 : For the reaction $2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$ in liquid bromine, N_2O_5 disappears at a rate of 0.02 moles dm^{-3} sec^{-1}. At what rate NO_2 and O_2 are formed? What would be the rate of reaction?

Solution :

Given : $\frac{d[N_2O_5]}{dt} = 0.02$ $\frac{1}{4}\frac{d[NO_2]}{dt}$

$$= \frac{d[O_2]}{dt}$$

Rate of reaction $= -\frac{1}{2}\frac{d[N_2O_5]}{dt}$

$$= \frac{1}{2} - \frac{d[N_2O_5]}{dt}$$

Rate of formation of $O_2 = \frac{d[O_2]}{dt}$

$$= \frac{1}{2} \times 0.02$$

$= \frac{1}{2} - \frac{d[N_2O_5]}{dt} = \frac{1}{2} \times 0.02$ moles dm^{-3} sec^{-1}

$= 0.01$ moles dm^{-3} sec^{-1}

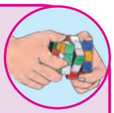
Rate of formation of $NO_2 = \frac{d[NO_5]}{dt}$

$$= \frac{4}{2} - \frac{d[N_2O_5]}{dt}$$

$= 2 \times$ moles dm^3 sec^{-1}

$= 0.04$ moles dm^3 sec^{-1}

Try this...



For the reaction,

$3I^{\ominus}(aq) + S_2O_8^{2\ominus}(aq) \longrightarrow I_3^{\ominus}(aq) + 2\,SO_4^{2\ominus}(aq)$

Calculate the rate of formation of $I_3^{\ominus}$, the rates of consumption of I^- and $S_2O_8^{2\ominus}$ and the overall rate of reaction if the rate of formation of $SO_4^{2\ominus}$ is 0.022 moles dm^{-3} sec^{-1}

6.3 Rate of reaction and reactant concentration : The rate of a reaction at a given temperature for a given time instant depends on the concentration of reactant. Such rate-concentration relation is the rate law.

6.3.1 Rate law : Consider the general reaction,

$$aA + bB \longrightarrow cC + dD \qquad .... (6.1)$$

The rate of reaction at a given time is proportional to its molar concentration at that time raised to simple powers or

Rate of reaction $\propto [A]^x [B]^y$ or

$$\text{rate} = k\,[A]^x[B]^y \qquad .... (6.2)$$

where k the proportionality constant is called the rate constant, which is independent of concentration and varies with temperature. For unit concentrations of A and B, k is equal to the rate of reaction. Equation (6.2) is called *differential rate law*.

The powers x and y of the concentration terms A and B in the rate law not necessarily equal to stoichiometric coefficients (a and b) appearing in Eq. (6.1). Thus x and y may be simple whole numbers, zero or fraction. Realize that x and y are experimentally determined. The rate law in Eq. (6.2) is determined experimentally and expresses the rate of a chemical reaction in terms of molar concentrations of the reactants and not predicted from the stoichiometries of the reactants.

The exponents x and y appearing in the rate law tell us how the concentration change affects the rate of the reaction.

(i) For $x = y = 1$, Eq. (6.2) gives

$$\text{rate} = k[A][B]$$

The equation implies that the rate of a reaction depends linearly on concentrations of A and B. If either of concentration of A or B is doubled, the rate would be doubled.

(ii) For $x = 2$ and $y = 1$. The Eq. (6.2) then leads to rate $= k[A]^2[B]$. If concentration of A is doubled keeping that of B constant, the rate of reaction will increase by a factor of 4.

(iii) If $x = 0$, the rate is independent of concentration of A.

(iv) If $x < 0$ the rate decreases as [A] increases.

6.3.2 Writing the rate law

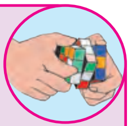
Consider the reaction,

$$2H_2O_2(g) \longrightarrow 2\,H_2O(l) + O_2(g).$$

If the rate of the reaction is proportional to concentration of H_2O_2. The rate law is given by

$$\text{rate} = k[H_2O_2]$$

Try this...



For the reaction,

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$,

the rate of reaction is experimetally found to be proportional to the squre of the concentration of NO_2 and independent that of CO. Write the rate law.

Problem 6.2 : Write the rate law for the reaction, $A + B \longrightarrow P$ from the following data :

[A] moles dm^{-3} *sec*$^{-1}$ (Initial)	[B] moles dm^{-3} *sec*$^{-1}$ (Initial)	Initial rate/ moles dm^{-3} sc^{-1}
(i) 0.4	0.2	4.0×10^{-5}
(ii) 0.6	0.2	6.0×10^{-5}
(iii) 0.8	0.4	3.2×10^{-4}

Solution :

a. From above data (i) and (ii), when [A] increases by a factor 1.5 keeping [B] as constant, the rate increases by a factor 1.5. It means rate $\propto$ [A] and $x = 1$

b. From observations (i) and (iii), it can be seen that when concentrations of A and B are doubled, the rate increases by a factor 8. Due to doubling of [A] the rate is doubled (because $x = 1$) that is rate increases by a factor 2.

This implies that doubling [B], the rate increases by a factor 4. or rate $\propto [B]^2$ and $y = 2$. Therefore, rate $= k[A]\,[B]^2$

contd....

Problem 6.2 contd....

Alternatively

The rate law gives rate = k $[A]^x[B]^y$.

a. From above observations (i) and (ii)

(i) $4 \times 10^{-5} = (0.4)^x(0.2)^y$

(ii) $6 \times 10^{-5} = (0.6)^x(0.2)^y$

Dividing (ii) by (i), we have

$$\frac{6 \times 10^{-5}}{4 \times 10^{-5}} = 1.5 = \frac{(0.6)^x(\cancel{0.2})^y}{(0.4)^x(\cancel{0.2})^y} = \left(\frac{0.6}{0.4}\right)^x$$

$= (1.5)^x$

Hence x = 1

b. From observations (i) and (iii) separately in the rate law gives

iii) $4 \times 10^{-5} = (0.4) \times (0.2)^y$ since x = 1

iv) $3.2 \times 10^{-4} = 0.8 \times (0.4)^y$

Dividing (iv) by (iii) we write

$$\frac{3.2 \times 10^{-4}}{4 \times 10^{-5}} = \frac{0.8\ (0.4)^y}{0.4\ (0.2)^y}$$

or $8 = 2 \times \left(\frac{0.6}{0.2}\right)^y$

or $4 = 2^2 = 2^y$

Therefore y = 2.

The rate law is then rate = $k[A][B]^2$.

Problem 6.3 : For the reaction,

$2\ NOBr(g) \longrightarrow 2\ NO_2(g) + Br_2(g)$,

the rate law is rate = $k[NOBr]^2$. If the rate of the reaction is 6.5×10^{-6} mol L^{-1} s^{-1} when the concentration of NOBr is 2×10^{-3} mol L^{-1}. What would be the rate constant for the reaction?

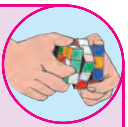
Solution :

rate = $k[NOBr]^2$ or $k = \frac{\text{rate}}{[NOBr]^2}$

$$= \frac{6.5 \times 10^{-6}\ \text{mol L}^{-1}\text{s}^{-1}}{(2 \times 10\text{-}3\text{mol L}^{-1})^2}$$

$= 1.625$ mol^{-1} L^{1} s^{-1}

Try this...



- For the reaction

$2A + 2B \longrightarrow 2C + D$, if concentration of A is doubled at constant [B] the rate increases by a factor of 4. If the concentration of B is doubled with [A] being constant the rate is doubled. Write the rate law of the reaction.

- The rate law for the reaction

$A + B \longrightarrow C$ is found to be

rate = $k[A]^2[B]$.

The rate constant of the reaction at 25 ^{0}C is 6.25 $M^{-2}s^{-1}$. What is the rate of reaction when [A] = 1.0 moles dm^{-3} sec $^{-1}$ and [B] = 0.2 moles dm^{-3} sec $^{-1}$?

6.3.3 Order of the reaction :

For the reaction,

$$aA + bB \longrightarrow cC + dD \text{ is}$$

If the rate of the reaction is given as

$$\text{rate} = k[A]^x[B]^y.$$

Then the sum x + y gives overall order of the reaction. Thus overall order of the chemical reaction is given as the sum of powers of the concentration terms in the rate law expression. For example :

i. For the reaction,

$2H_2O_2(g) \longrightarrow 2H_2O(l) + O_2(g)$ experimentally determined rate law is

rate = $k[H_2O_2]$.

The reaction is of first order.

ii. If the experimentally determined rate law for the reaction

$H_2(g) + I_2(g) \longrightarrow 2\ HI(g)$ is

rate = $k[H_2][I_2]$.

The reaction is of first order in H_2 and I_2 each and hence overall of second order.

Key points about the order of reaction

a. The order of chemical reaction is experimentally determined.

b. The order can be integer or fractional.
Look at the reaction,

$CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$.

The rate law for the reaction was found to be rate = $k[CH_3CHO]^{3/2}$.

Here the order of the reaction is 3/2.

c. The order of the reaction, can be zero for :

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

The rate expression for this is : rate = $k[NO_2]^2$. This shows that order of reaction with respect to NO_2 is 2 and with CO is zero or the rate is independent of concentration of CO. The overall order of reaction is 2.

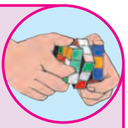
d. Only a few reactions of third order are known. Reactions with the orders higher than three are scanty.

Problem 6.4 : For the reaction

$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$, the rate law is rate = $k[NO]^2\,[H_2]$. What is the order with respect to NO and H_2? What is the overall order of the reaction ?

Solution : In the rate law expression, the exponent of [NO] is 2 and that of $[H_2]$ is 1. Hence, reaction is second order in NO, first order in H_2 and the reaction is third order.

Try this...



The reaction, $CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g)$ is first order in $CHCl_3$ and 1/2 order in Cl_2. Write the rate law and overall order of reaction.

Problem 6.5 : The rate of the reaction,

$A + B \longrightarrow P$ is 3.6×10^{-2} mol dm^{-3} s^{-1} when [A] = 0.2 moles dm^{-3} and [B] = 0.1 moles dm^{-3}. Calculate the rate constant if the reaction is first order in A and second order in B.

Solution : The reaction is first order in A and second order in B. Hence, the rate law gives

$$\text{rate} = k[A][B]^2$$

$$\text{or } k = \frac{\text{rate}}{[A][B]^2}$$

rate = 3.6×10^{-2} mol/s,

[A] = 0.2 mol dm^{-3} and [B] = 0.1 mol dm^{-3}

Substitution gives

$$k = \frac{3.6 \times 10^{-2}\ \text{mol dm}^{-3}\text{s}^{-1}}{0.2\ \text{mol dm}^{-3} \times (0.1\ \text{mol dm}^{-3})^2}$$

$$= \frac{3.6 \times 10^{-2}\ \text{s}^{-1}}{0.2 \times 0.01\ \text{mol}^2\ \text{dm}^{-6}\ \text{sec}^{-1}}$$

$$= 18\ \text{mol}^{-2}\ \text{dm}^{-6}\ \text{sec}^{-1}$$

Use your brain power

The rate of the reaction $2A + B \longrightarrow 2C + D$ is 6×10^{-4} mol dm^{-3} s^{-1} when [A] = [B] = 0.3 mol dm^{-3}. If the reaction is of first order in A and zeroth order in B, what is the rate constant?

Problem 6.6 : Consider,

$A + B \longrightarrow P$. If the concentration of A is doubled with [B] being constant, the rate of the reaction doubles. If the concentration of A is tripled and that of B is doubled, the rate increases by a factor 6. What is order of the reaction with respect to each reactant ? Determine the overall order of the reaction.

Solution :

The rate law of the reaction :

rate = $k[A]^x[B]^y$ .... (i)

If [A] is doubled, the rate doubles.

Hence 2 × rate = $k\,[2A]^x[B]^y$

$= k\,2^x\,[A]^x[B]^y$ ....(ii)

6 × rate = $k\,[3A]^x[2B]^y$ ....(iii)

$$\frac{(iii)}{(i)} \text{ gives } \frac{6 \times \cancel{\text{rate}}}{\cancel{\text{rate}}} = \frac{3\,\cancel{k}[\cancel{A}]2^y\,[\cancel{B}]^y}{\cancel{k}\,[\cancel{A}][\cancel{B}]^y}$$

or 6 = 3 × 2^y or 2 = 2^y and y =1

The reaction is first order in A and first order in B. The overall reaction is of the second order.

6.4 Molecularity of elementary reactions :

Complex reactions are those which constitute a series of elementary reactions.

6.4.1 Elementary reaction

Consider,

$$O_3(g) \longrightarrow O_2(g) + O(g)$$

$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$

These reactions occur in a single step and cannot be broken down further into simpler reactions. These are elementary reactions.

6.4.2 Molecularity of reaction : The molecularity refers to how many reactant molecules are involved in reactions. In the above reactions there is only one reactant molecule. These are unimolecular reactions or their molecularity is one.

$$O_3(g) + O(g) \longrightarrow 2\ O_2(g)$$

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

The elementary reactions involving two reactant molecules are bimolecular reactions or they have molecularity as two.

The molecularity of an elementary reaction is the number of reactant molecules taking part in it.

6.4.3 Order and molecularity of elementary reactions:

The rate law for the elementary reaction $2NO_2(g) \longrightarrow 2NO_2(g) + O_2(g)$ is found to be rate = $k[NO_2]^2$. The reaction is second order and bimolecular. The order of reaction is 2 and its molecularity is also 2.

For the elementary reaction,

$$C_2H_5\ I(g) \longrightarrow C_2H_4(g) + HI(g)$$

$$\text{rate} = k[C_2H_5I]$$

It is unimolecular and first order. However the order and molecularity of the reaction may or may not be the same.

6.4.4 Rate determining step : A number of chemical reactions are complex. They take place as a series of elementary steps. One of these steps is slower than others. The slowest step is the rate determining step.

The slowest step determines the rate of overall reaction.

Consider, $2NO_2Cl(g) \longrightarrow 2NO_2(g) + Cl_2(g)$.

The reaction takes place in two steps:

i. $NO_2Cl(g) \xrightarrow{k_1} NO_2(g) + Cl(g)$ (slow)

ii. $NO_2Cl(g) + Cl\ (g) \xrightarrow{k_2} NO_2(g) + Cl_2(g)$(fast)

Overall $2NO_2Cl(g) \longrightarrow 2NO_2(g) + Cl_2(g)$

The first step being slower than the second it is the rate determining step.

The rate law is

$$\text{rate} = k[NO_2Cl]$$

This also represents the rate law of the overall reaction. The reaction thus is of the first order.

Reaction intermediate:

In the above reaction Cl is formed in the first step and consumed in the second. Such species represents the reaction intermediate. The concentration of reaction intermediate does not appear in the rate law.

Distinction between order and molecularity of a reaction :

Order	Molecularity
1. It is experimentally determined property.	i. It is theoretical entity.
2. It is the sum of powers of the concerntration terms of reactants those appear in the rate equation.	ii. It is the number of reactant molecules taking part in an elementary reaction.
3. It may be an integer, fraction or zero.	iii. It is integer.

Problem 6.7 : A reaction occurs in the following steps

i. $NO_2(g) + F_2(g) \longrightarrow NO_2F(g) + F(g)$ (slow)

ii. $F(g) + NO_2(g) \longrightarrow NO_2F(g)$ (fast)

a. Write the equation of overall reaction.

b. Write down rate law.

c. Identify the reaction intermediate.

Solution :

a. The addition of two steps gives the overall reaction as

$$2NO_2(g) + F_2(g) \longrightarrow 2\,NO_2F(g)$$

b. Step (i) is slow. The rate law of the reaction is predicted from its stoichiometry. Thus,

$$\text{rate} = k[NO_2]\,[F_2]$$

c. F is produced in step (i) and consumed in step (ii) or F is the reaction intermediate.

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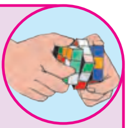


A complex reaction takes place in two steps:

i) $NO(g) + O_3(g) \longrightarrow NO_3(g) + O(g)$

ii) $NO_3(g) + O(g) \longrightarrow NO_2(g) + O_2(g)$

The predicted rate law is rate = $k[NO][O_3]$.

Identify the rate determining step. Write the overall reaction. Which is the reaction intermediate? Why?

6.5 Integrated rate law :

We introduced the differential rate law earlier. It describes how rate of a reaction depends on the concentration of reactants in terms of derivatives.

The differential rate laws are converted into integrated rate laws. These tell us the concentrations of reactants for different times.

6.5.1 Integrated rate law for the first order reactions in solution :

Consider first order reaction,

$$A \longrightarrow \text{product} \qquad \text{...........} (6.3)$$

The differential rate law is given by

$$\text{rate} = -\frac{d[A]}{dt} = k\,[A] \qquad \text{...........} (6.4)$$

where [A] is the concentration of reactant at time t.

Rearranging Eq. (6.4),

$$\frac{d[A]}{[A]} = -k\,dt \qquad \text{...........} (6.5)$$

Let $[A]_0$ be the initial concentration of the reactant A at time t = 0. Suppose $[A]_t$ is the concentration of A at time = t.

The equation (6.5) is integrated between limits $[A] = [A]_0$ at $t = 0$ and $[A] = [A]_t$ at $t = \mathrm{t}$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$$

On integration,

$$\Big[\ln[A]\Big]_{[A]_0}^{[A]_t} = -k\,(t)_0^t$$

Substitution of limits gives

$$\ln[A]_t - \ln[A]_0 = -k\,t$$

or $$\ln\frac{[A]_t}{[A]_0} = -kt \qquad \text{...........} (6.6)$$

or $$k = \frac{1}{t}\ln\frac{[A]_0}{[A]_t}$$

Converting ln to $\log_{10}$, we write

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t} \qquad \text{...........} (6.7)$$

Eq. (6.7) gives the integrated rate law for the first order reactions.

The rate law can be written in the following forms

i. Eq. (6.6) is $\ln\dfrac{[A]_t}{[A]_0} = -\mathrm{kt}$

By taking antilog of both sides we get

$$\frac{[A]_t}{[A]_0} = e^{-kt} \text{ or } [A]_t = [A]_0 e^{-kt} \qquad \text{...........} (6.8)$$

ii. Let 'a' mol dm^{-3} be the initial concentration of A at $t = 0$

Let x mol dm^{-3} be the concentration of A that decreases (reacts) during time t. The concentration of A that remains unreacted at time t would be (a - x) mol/dm^3

Substitution of $[A]_0$ and $[A]_t = (a - x)$

$$k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)} \qquad \text{...........}(6.9)$$

Equations (6.7), (6.8) and (6.9) represent the integrated rate law of first order reactions.

6.5.2 Units of rate constant for the first order reaction:

The integrated rate law is

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

Because $\log_{10}\frac{[A]_0}{[A]_t}$ is unitless quantity, the dimensions of *k* will be (time)$^{-1}$. The units of *k* will be s^{-1}, min^{-1}or (hour)$^{-1}$

6.5.3 Half life of the first order reactions ($t_{1/2}$)

Radioactive processes follow the first order kinetics. The half life of reaction is time required for the reactant concentration to fall to one half of its initial value.

6.5.4 Half life and rate constant of the first order reaction :

The integrated rate law for the first order reaction is

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t}$$

where $[A]_0$ is the initial concentration of reactant at $t = 0$. It falls to $[A]_t$ at time *t* after the start of the raction. The time required for $[A]_0$ to become $[A]_0/2$ is denoted as $t_{1/2}$

or

$[A]_t = [A]_0/2$ at $t = t_{1/2}$

Putting this condition in the integrated rate law we write

$$k = \frac{2.303}{t_{1/2}}\log_{10}\frac{[A]_t}{[A]_0/2}$$

$$= \frac{2.303}{t_{1/2}}\log_{10} 2$$

$$= \frac{2.303}{t_{1/2}} \times 0.3010$$

$$k = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = \frac{0.693}{k_{1/2}} \qquad \text{............}(6.10)$$

Eq. (6.10) shows that half life of the first order reaction is independent of initial reactant concentration. This is shown in Fig (6.2) as a plot of $[A]_t$ versus t.

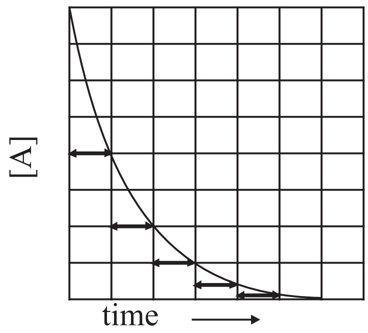


Fig. 6.2 : Half life period of first order reaction

6.5.5 Graphical representation of the first order reactions

i. The differential rate law for the first order reaction A ⟶ P is

$$\text{rate} = -\underset{\substack{\updownarrow\\ y}}{\frac{d[A]}{dt}} = \underset{\substack{\updownarrow\\ m}}{k}\,\underset{\substack{\updownarrow\\ x}}{[A]_t} + \underset{\substack{\updownarrow\\ c}}{0}$$

The equation is of the form y = mx + c. A plot of rate versus $[A]_t$ is a straight line passing through origin. This is shown in Fig. 6.3. The slope of straight line = *k*.

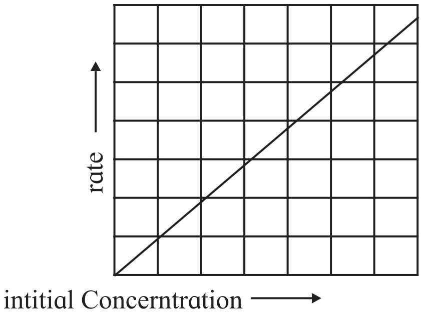


Fig. 6.3 : Variation of rate with [A]

ii. From Eq. (6.7) the integrated rate law is

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

On rearrangement, the equation becomes

$$\frac{kt}{2.303} = \log_{10} [A]_0 - \log_{10} [A]_t$$

Hence, $\underset{\substack{\updownarrow \\ y}}{\log_{10} [A]_t} = - \underset{\substack{\updownarrow \\ m}}{\frac{k}{2.303}} \underset{\substack{\updownarrow \\ x}}{t} + \underset{\substack{\updownarrow \\ c}}{\log_{10} [A]_0}$

The equation is of the straight line. A graph of $\log_{10}\frac{[A]_0}{[A]_t}$ versus t yields a stright line with slope $-k/2.303$ and y-axis intercept as $\log_{10}[A]_0$

This is shown in Fig. 6.4

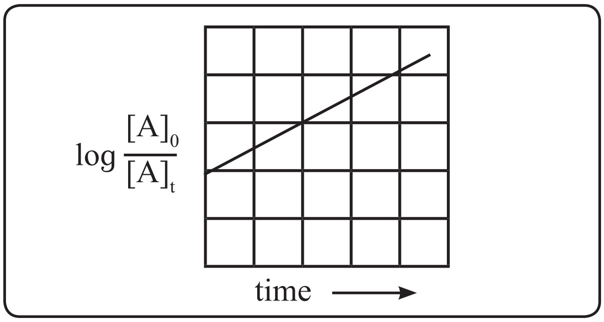


Fig. 6.4 : A plot showing log [At]t/[A]0 vs time

iii. Eq. (6.7) gives

$$\underset{\substack{\updownarrow \\ v}}{\log_{10} \frac{[A]_0}{[A]_t}} = \underset{\substack{\updownarrow \\ m}}{\frac{k}{2.303}} \underset{\substack{\updownarrow \\ x}}{t}$$

The equation has a straight line form y = mx .

Hence, the graph of $\log_{10}\frac{[A]_0}{[A]_t}$ versus t is straight line passing through origin as shown in Fig. 6.5.

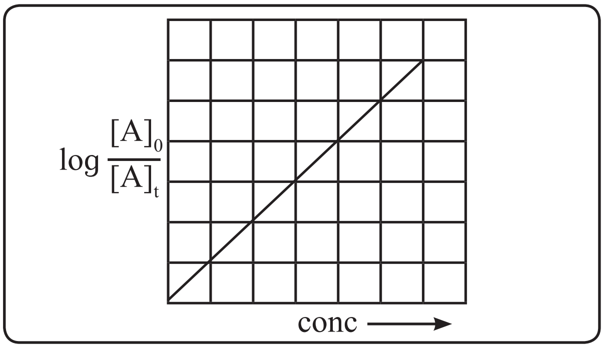


Fig. 6.5 :

6.5.6 Examples of first order reactions

Some examples of reactions of first order are :

i. $2\ H_2O_2(l) \longrightarrow 2\ H_2O(l) + O_2(g)$,

rate = $k[H_2O_2]$

ii. $2\ N_2O_5(g) \longrightarrow 4\ NO_2(g) + O_2(g)$,

rate = k $[N_2O_5]$

6.5.7 Integrated rate law for gas phase *f* reactions

For the gas phase reaction,

$$A(g) \longrightarrow B(g) + C(g)$$

Let initial pressure of A be P_i that decreases by x within time *t*.

Pressure of reactant A at time t

$$P_A = P_i - x \qquad .... (6.11)$$

The pressures of the products B and C at time t are

$$P_B = P_C = x$$

The total pressure at time t is then

$$P = P_i - x + x + x = P_i + x$$

Hence, x = P - P_i ....(6.12)

Pressure of A at time t is obtained by substitution of Eq. (6.12) into Eq. (6.11). Thus

$$P_A = P_i - (P - P_i) = P_i - P + P_i = 2P_i - P$$

The integrated rate law turns out to be

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

The concentration now expressed in terms of pressures.

Thus, $[A]_0 = P_i$ and $[A]_t = P_A = 2\ P_i - P$

Substitution gives in above

$$k = \frac{2.303}{t} \log_{10} \frac{P_i}{2\ P_i - P} \qquad ....(6.13)$$

P is the total pressure of the reaction mixture at time t.

Problem 6.8 : The half life of first order reaction is 990 s. If the initial concentration of the reactant is 0.08 mol dm^{-3}, what concentration would remain after 35 minutes?

Solution :

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{990\ \text{s}} = 7 \times 10^{-4}\ \text{s}^{-1}$$

$$k = \frac{2.303}{t}\ \log_{10}\frac{[A]_0}{[A]_t}$$

$[A]_0 = 0.08$ mol dm^{-3}, t = 35 min or 2100 s, $[A]_t = ?$

$$\log_{10}\frac{[A]_0}{[A]_t} = \frac{k\,t}{2.303} = \frac{7 \times 10^{-4}\ \text{s}^{-1} \times 2100\ \text{s}}{2.303}$$

$$= 0.6383$$

$$\frac{[A]_0}{[A]_t} = \text{antilog } 0.6383 = 4.35$$

Hence, $[A]_t = \frac{[A]_0}{4.35} = \frac{0.08}{4.35}$

$$= 0.0184\ \text{mol dm}^{-3}$$

Problem 6.9 : In a first order reaction 60% of the reactant decomposes in 45 minutes. Calculate the half life for the reaction

Solution :

$$k = \frac{2.303}{t}\ \log_{10}\frac{[A]_0}{[A]_t}$$

$[A]_0 = 100$, $[A]_t = 100 - 60 = 40$, t = 45 min

Substitution of these in above

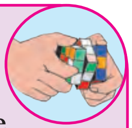
$$k = \frac{2.303}{t}\ \log_{10}\frac{100}{40}$$

$$= \frac{2.303}{45}\ \log_{10} 2.5$$

$$= \frac{2.303}{45} \times 0.3979 = 0.0204\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0204\ \text{min}^{-1}} = 34\ \text{min}$$

Try this...



The half life of a first order reaction is 0.5 min. Calculate time needed for the reactant to reduce to 20% and the amount decomposed in 55 s.

Problem 6.10 : Following data were obtained during the first order decomposition of SO_2Cl_2 at the constant volume.

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Times/s	Toatl pressure/bar
0	0.5
100	0.6

Calculate the rate constant of the reaction.

Solution :

$$k = \frac{2.303}{t}\ \log_{10}\frac{P_i}{2\,P_i - P}$$

$P_i = 0.5$ bar, $P = 0.6$ bar, $t = 100$ s

$$k = \frac{2.303}{100}\ \log_{10}\left(\frac{0.5\ \text{bar}}{2 \times 0.5\ \text{bar} - 0.6\ \text{bar}}\right)$$

$$= \frac{2.303}{100}\log_{10}\left(\frac{0.5}{0.4}\right) = 2.23 \times 10^{-3}\ \text{s}^{-1}$$

6.5.8 Zero order reactions:

The rate of zero order reaction is independent of the reactant concentration.

Integrated rate law for zero order reactions : For zero order reaction,

$$A \longrightarrow P$$

the differntial rate law is given by

$$\text{rate} = -\frac{d[A]}{[A]} = k\,[A]^0 = k \qquad .....(6.14)$$

Rearrangement of Eq. (6.14) gives

$$d[A] = -k\ dt$$

Integration between the limits

$[A] = [A]_0$ at $t = 0$ and $[A] = [A]_t$ at $t = t$ gives

$$\int_{[A]_0}^{[A]^t} d[A] = -k\int_0^t dt$$

or $[A]_t - [A]_0 = -\,kt$

Hence, $k\,t = [A]_0 - [A]_t$ .... (6.15)

Units of rate constant of zero order reactions

$$k = \frac{[A]_0 - [A]_t}{t} = \frac{\text{mol L}^{-1}}{t} = \text{mol dm}^{-3}\ t^{-1}$$

The units of rate constant of zero order reaction are the same as the rate.

Half life of zero order reactions : The rate constant of zero order reaction is given by eqn (6.15)

$$k = \frac{[A]_0 - [A]_t}{t}$$

Using the conditions $t = t_{1/2}$, $[A]_t = [A]_{1/2}$,

Eq. (6.15) becomes

$$k = \frac{[A]_0 - [A]_{0/2}}{t_{1/2}} = \frac{[A]_0}{2\, t_{1/2}}$$

Hence, $t_{1/2} = \frac{[A]_0}{2\,k}$ 6.16

The half life of zero order reactions is proportional to the initial concentration of reactant.

Graphical representation of zero oder reactions : The rate law in Eq. (6.15) gives

$$\underset{y}{\underset{\updownarrow}{[A]_t}} = -\underset{m}{\underset{\updownarrow}{k}}\,\underset{x}{\underset{\updownarrow}{t}} + \underset{c}{\underset{\updownarrow}{[A]_0}} \qquad \text{............ 6.17}$$

Which is straight line given by y = mx + c.

A plot of $[A]_t$ versus t is a straight line as shown in Fig 6.6.

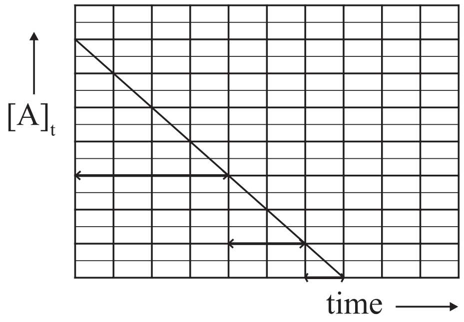


Fig. 6.6 : [A]t vs t for zero order reaction

The slope of straight line is -k and its intercept on y-axis is $[A]_0$.

The $t_{1/2}$ of zero order reaction is directly proportional to the initial concentration.

Examples of zero order reactions :

Here follow some examples

Decomposition of NH_3 on platinum metal

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

The metals surface gets completely covered by a layer of NH_3 molecules. A number of NH_3 molecules attached on platinum surface is small compared to ammonia. A large number of the NH_3 molecules tend to remain as gas which do not react. The molecules present on the metal surface only react. The rate of a reaction was thus independent of the total concentration of NH_3 and remains constant.

ii. Decomposition of nitrous oxide in the presence of Pt catalyst.

$$2\,N_2O(g) \xrightarrow{Pt} 2\,N_2(g) + O_2(g)$$

iii. The catalytic decomposition of PH_3 on hot tungsten at high pressure.

6.5.9 Pseudo-first order reactions :

Certain reactions which are expected to be of higher order follow the first order kinetics. Consider hydrolysis of methyl acetate.

$$CH_3COOCH_3(aq) + H_2O(l) \longrightarrow CH_3COOH(aq) + CH_3OH(aq)$$

The rate law is

$$\text{rate} = k'\,[CH_3COOCH_3]\,[H_2O]$$

The reaction was expected to follow the second order kinetics, however, obeys the first order.

The reason is that solvent water is present in such large excess that the change in its concentration is negligible compared to initial one or its concentration remains constant.

Thus $[H_2O]$ = constant = k''. The rate law becomes

$$\text{rate} = k'\,[CH_3COOCH_3]\,k''$$
$$= k\,[CH_3COO\,CH_3]$$

where $k = k'k''$

The reaction is thus of first order.

The reaction $C_{12}H_{22}O_{11}(aq) + H_2O\,(l)$ (excess) $\longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)}$
Can it be of pseudo-first order type ?

6.6 Collision theory of bimolecular reactions

6.6.1 Collision between reactant molecules

Chemical reactions occur as a result of collisions between the reactant species. It may be expected that the rate of the reaction is equal to the rate of collision. For the gas-phase reactions the number of collisions is far more and typically many powers of tens compared to the observed rate.

6.6.2 Activation : For the reaction to occur the colliding reactant molecules must possess the minimum kinetic energy. This minimum kinetic energy is the activation energy. The reaction would occur only if colliding molecules possess kinetic energies equal to or greater than the activation energy.

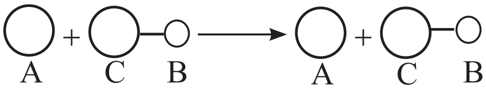
6.6.3 Orientation of reactant molecules

The requirement for successful collision described above is sufficient for reactions involving simple molecules (or ions) however not for those involving complex molecules.

Besides the above considerations the colliding molecules must have proper orientation. The molecules need to be so oriented relative to each other that the reacting groups approach closely.

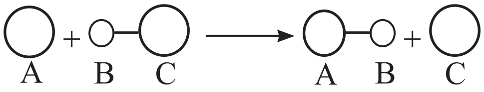
Consider, $A + C - B \longrightarrow A - B + C$

i. The collision of A with C approaching toward A would not lead to reaction.



No reaction will takes place. The reactant molecules would collide and separate owing to the improper orientation of C - B.

ii.



The reaction is successful as a result of proper orientation of C - B. A fraction of such collisions bring forth conversion of reactants to products.

6.6.4 Potential energy barrier

Consider again the reaction

$A + C - B \longrightarrow A - B + C$

During a course of collision, new bond A - B developes. At the same time bond C - B breaks. A configuration in which all the three atoms are weakly connected together is called activated complex.

$A + B - C \longrightarrow A \cdots\cdots B \cdots\cdots C \longrightarrow A - B + C$

To attain the configuration A ····· B ····· C atoms need to gain energy, which comes from the kinetic energy of colliding molecules.

The energy barrier between reactants and products is shown in Fig. 6.7. The reactant molecules need to climb up and overcome this before they get converted to products. The height of the barrier is called as activation energy (E_a). Thus the reactant molecules transform to products only if they possess energy equal to or greater than such activation energy. A fraction of molecules those possess energy greater than E_a is given by $f = e^{-Ea/RT}$.

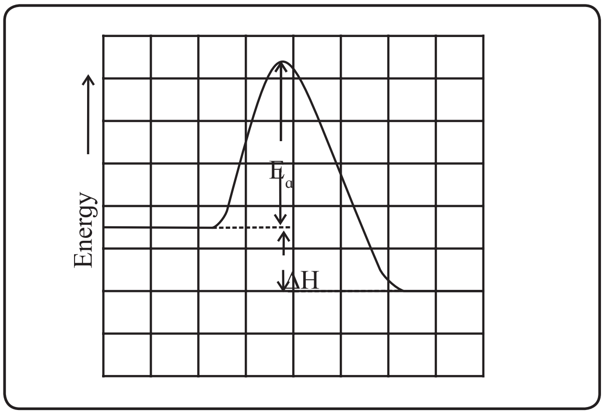


Fig. 6.7 : Potential energy barrier

As a result only a few collisions lead to products. The number of successful collisions are further reduced by the orientation requirement already discussed.

Do you know ?

For a gaseous reaction at 298 K, $E_a = 75$ kJ/mol. The fraction of successful collisions is given by $f = e^{-Ea/RT}$ $= e^{-75000/8.314 \times 298} = 7 \times 10^{-14}$ or only 7 collisions in 10^{14} collisions are sufficiently energetic to lead to the reaction.

Remember...

All collisions of reactant molecules do not lead to a chemical reaction. The colliding molecules need to possess certain energy which is greater than the activation energy E_a and proper orientation.

6.7 Temperature dependence of reaction rates

Do you know ?

It has been observed that the rates of most of the chemical reactions usually increase with temperature. In everyday life we see that the fuels such as oil, coal are inert at room temperature but burn rapidly at higher temperatures. Many foods spoil rapidly at room temperature and lasts longer in freezer.

The concentrations change only a little with temperature. The rate constant shows a strong dependence on the temperature.

6.7.1 Arrhenius equation:

Arrhenius suggested that the rate of reactions varies with temperature as

$$k = A\, e^{-E_a/RT} \qquad ....\ 6.18$$

where k is the rate constant, E_a is the activation energy, R molar gas constant, T temperature in kelvin, and A is the pre-exponential factor. Eq. (6.18) is called as the Arrhenius equation.

The pre exponential factor A and the rate constant have same unit in case of the first order reactions. Besides A is found to be related to frequency of collisions.

6.7.2 Graphical determination of activation energy :

Taking logarithm of both sides of eqn (6.18) we obtain

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad ....(6.19)$$

Converting natural base to base 10 we write

$$\underset{\overset{\updownarrow}{y}}{\log_{10}k} = -\underset{\overset{\updownarrow}{m}}{\frac{E_a}{2.303\,R}}\ \underset{\overset{\updownarrow}{x}}{\frac{1}{T}} + \underset{\overset{\updownarrow}{c}}{\log_{10}A} \qquad ....(6.20)$$

This equation is of the form of straight line y = mx + c.

The Arrhenius plot of $\log_{10} k$ versus 1/T giving a straight line is shown in fig. (6.8). A slope of the line is $-E_a/2.303R$ with its intercept being $\log_{10}$ A.

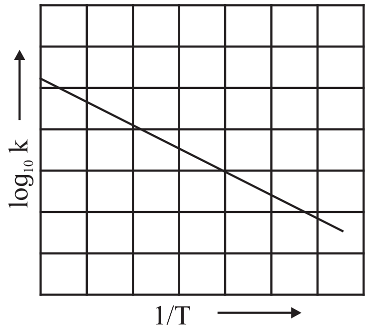


Fig. 6.8 : Variation of $\log_{10}$k with 1/T

From a slope of the line the activation energy can be determined. Eq. (6.18) shows that with an increase of temperature, $-E_a/RT$ and in turn, the rate of reaction would increase.

6.7.3 Determination of activation energy :

For two different temperatures T_1 amd T_2

$$\log_{10} k_1 = \log_{10}A - \frac{E_a}{2.303\ RT_1} \qquad ....(6.21)$$

$$\log_{10} k_2 = \log_{10}A - \frac{E_a}{2.303\ RT_2} \qquad ....(6.22)$$

where k_1 and k_2 are the rate constants at temperatures T_1 and T_2 respectively. Subtracting Eq. (6.21) from Eq. (6.22),

$$\log_{10}k_2 - \log_{10} k_1 = -\frac{E_a}{2.303\ R}\frac{1}{T_2} + \frac{E_a}{2.303\ R}\frac{1}{T_1}$$

$$\text{Hence, } \log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{E_a}{2.303\ R}\left(\frac{T_2 - T_1}{T_1T_2}\right) \qquad \text{..........(6.23)}$$

6.7.4 Graphical description of effect of temperature : It has been realized that average kinetic energy of molecules is proportional to temperature. The collision theory suggested a bimolecular reaction occurs only if the reacting molecules have sufficient kinetic energies (at least E_a) and proper orientation when they collide.

At a given temperature, the fraction of molecules with their kinetic energy equal to or greater than E_a may lead to the product. With an increase of temperature the fraction of molecules having their energies (E_a) would increases. The rate of the reaction thus would increase. This is depicted by plotting a fraction of molecules with given kinetic energy versus kinetic energy for two different temperatures T_1 and T_2 (T_2 being > T_1) in Fig. 6.9.

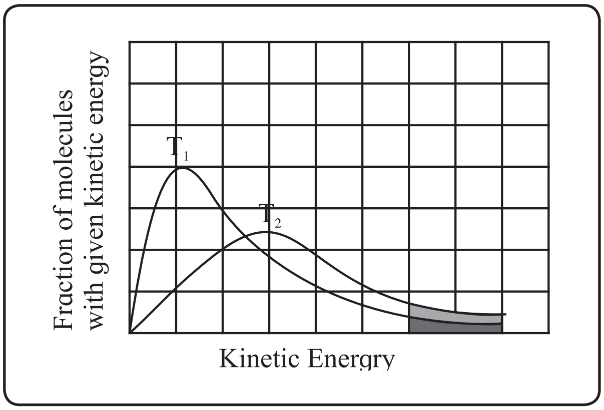


Fig. 6.9 : Comparison of fraction of molecules activated at T_1 and T_2

The shaded areas is proportional to total number of molecules. The total area is the same at T_1 and T_2. The area (a + b) represents a fraction of molecules with kinetic energy exceeding Ea is larger at T_2 than at T_1 (since $T_2 > T_1$). This indicates that a fraction of molecules possessing energies larger than E_a increase with temperature. The rate of reaction increases accordingly.

Problem 6.12 : The rate constants for a first order reaction are 0.6 s^{-1} at 313 K and 0.045 s^{-1} at 293 K. What is the activation energy?

Solution -

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

k_1 = 0.045 s^{-1}, k_2 = 0.6 s^{-1}, T_1 = 293 K, T_2 = 313 K, R = 8.314 J $K^{-1}mol^{-1}$

Substituting

$$\log_{10}\frac{0.6}{0.045} = \frac{E_a}{2.303 \times 8.314} \times \left[\frac{313 - 293}{293 \times 313}\right]$$

$$\log_{10} 13.33 = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{293 \times 313}$$

$$1.1248 = \frac{E_a}{19.15} \times 2.18 \times 10^{-4}$$

$$E_a = 1.1248 \times 19.15 \text{ J mol}^{-1} / 2.18 \times 10^{-4}$$

$$= 98810 \text{ J/mol}^{-1} = 98.8 \text{ kJ/mol}^{-1}$$

Problem 6.13 : A first order gas phase reaction has activation energy of 240 kJ mol^{-1}. If the pre-exponential factor is 1.6 × 10^{13} s^{-1}. what is the rate constant of the reaction at 600 K?

Solution : Arrhenius equation

$k = A\, e^{-Ea/RT}$ is written as

$$\log_{10}\frac{A}{k} = \frac{E_a}{2.303\ RT}$$

E_a = 240 kJ mol^{-1} = 240 × 10^3 J mol^{-1},

T = 600 K, A = 1.6 × 10^{13} s^{-1}

$$\text{Hence } \log_{10}\frac{A}{k} =$$

$$\frac{240 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1}\text{ K}^{-1} \times 600 \text{ K}} = 20.89$$

contd....

$$\frac{A}{k} = \text{antilog } 20.89$$

$$= 7.78 \times 10^{20}$$

$$\text{and } k = \frac{A}{7.78 \times 10^{20}}$$

$$= \frac{1.6 \times 10^{13} \text{ s}^{-1}}{7.78 \times 10^{20}}$$

$$= 2.055 \times 10^{-8} \text{ s}^{-1}$$

Problem 6.14 : The half life of a first order reaction is 900 min at 820 K. Estimate its half life at 720 K if the activation energy is 250 kJ mol^{-1}.

Solution :

$$t_{1/2} = \frac{0.693}{k}$$

Rate constants at two different temperatures, T_1 and T_2 are k_1 and k_2 respectively, and the corresponding half lives $(t_{1/2})_1$ and $(t_{1/2})_2$.

$$(t_{1/2})_1 = \frac{0.693}{k} \text{ and } (t_{1/2})_2 = \frac{0.693}{k}$$

$$\text{Hence, } \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{k_2}{k_1}$$

$$\text{The equation, } \log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303\,RT} \times \left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log_{10}\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{\mathrm{E_a}}{2.303\ \mathrm{RT}} \left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$E_a = 250$ kJ mol^{-1}, $T_1 = 720$ K,

$T_2 = 820$ K, $(t_{1/2})_2 = 900$ min

$$\text{Thus, } \log_{10}\frac{(t_{1/2})_1}{(t_{1/2})_2} =$$

$$\frac{250 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1}\text{mol}^{-1}} \left[\frac{820\text{ K} - 720\text{ K}}{820\text{ K} \times 720\text{ K}}\right]$$

$$= 2.212$$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \text{antilog } 2.212 = 162.7$$

$$(t_{1/2})_1 = (t_{1/2})_2 \times 162.7 \quad = 900 \times 162.7$$

$$= 1.464 \times 10^5 \text{ min}$$

6.8 Effect of a catalyst on the rate of reaction

A catalyst is a substance added to the reactants that increases the rate of the reaction without itself being consumed in the reaction.

Consider

$$2\ \mathrm{KClO_3(s)} + 3\mathrm{O_2(g)} \xrightarrow{\mathrm{MnO_2}} 2\ \mathrm{KCl(s)}$$

Here MnO_2 is the catalyst. It has been observed that the decomposition rate increases with the addition of catalyst. A catalyst provides alternative pathway associated with lower activation energy.

Fig. 6.10 compares the potential energy barriers for the catalysed and uncatalysed reactions. The barrier for uncatalysed reaction (E_a) is larger than that for the same reaction in the presence of a catalyst E_a.

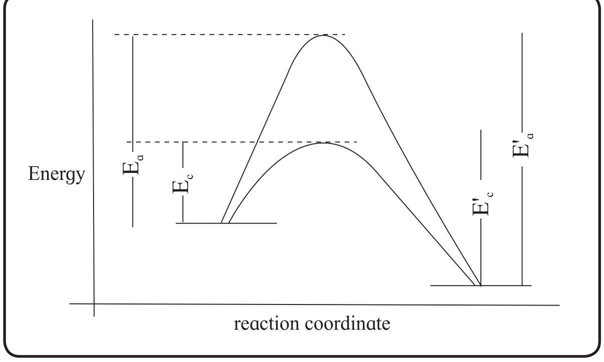


Fig. 6.10 : Potential energy barriers for catalyzed and uncatalyzed reactions

Consider the decomposition of H_2O_2 in aqueous solution catalysed by I$^-$ ions.

$$2\mathrm{H_2O_2}(l) \xrightarrow{\mathrm{I^-}} 2\ \mathrm{H_2O}(l) + \mathrm{O_2(g)}$$

At room temperature the rate of reaction is slower in the absence of catalyst with its activation energy being 76 kJ mol^{-1}. In the presence of iodide ion/ the catalyst I$^-$ the reaction is faster since the activation energy decreases to 57 kJ mol^{-1}.

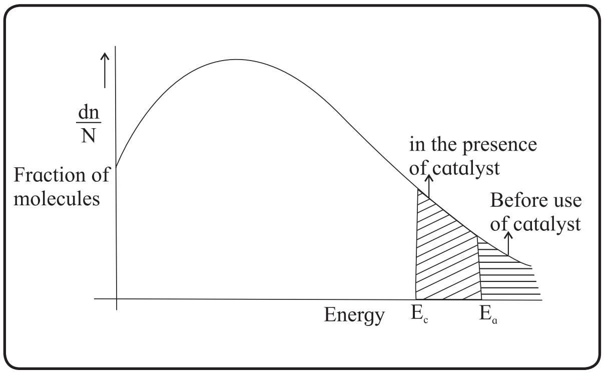


Fig. 6.11 : Comparison of fraction of molecules for catalyzed and uncatalyzed reactions

Fig 6.11 shows a plot of fraction of molecules as a function of energy. A catalyst lowers the the threshold energy. Consequently more molecules acquire the minimum amount of energy and tend to cross the energy barrier. A fraction of activated molecules is greater for the catalyzed reaction. The rate of catalyzed reaction thus is larger than the reaction with no catalyst.

Exercises

1. Choose the most correct option.

i. The rate law for the reaction $aA + bB \longrightarrow P$ is rate = $k[A]\,[B]$. The rate of reaction doubles if

a. concentrations of A and B are both doubled.

b. [A] is doubled and [B] is kept constant

c. [B] is doubled and [A] is halved

d. [A] is kept constant and [B] is halved.

ii. The order of the reaction for which the units of rate constant are mol dm^{-3} s^{-1} is

a. 1 b. 3

c. 0 d. 2

iii. The rate constant for the reaction

$2\,N_2O_5(g) \longrightarrow 2\,N_2O_4(g) + O_2(g)$ is $4.98 \times 10^{-4}\ s^{-1}$. The order of reaction is

a. 2 b. 1

c. 0 d. 3

iv. Time required for 90 % completion of a certain first order reaction is t. The time required for 99.9 % completion will be

a. t b. 2t

c. t/2 d. 3t

v. Slope of the graph $\ln[A]_t$ versus t for first order reaction is

a. $-k$ b. k

c. $k/2.303$ d. $-k/2.303$

vi. What is the half life of a first order reaction if time required to decrease concentration of reactant from 0.8 M to 0.2 M is 12 h?

a. 12 h b. 3 h

c. 1.5 h d. 6 h

vii. The reaction, $3\ ClO^{\ominus} \rightarrow ClO_3^{\ominus} + 2\ Cl^{\ominus}$ occurs in two steps,
(i) $2\ ClO^{-} \longrightarrow ClO_2^{\ominus}$
(ii) $ClO_2^{\ominus} + ClO^{\ominus} \longrightarrow ClO_3^{\ominus} + Cl^{\ominus}$
The reaction intermediate is

a. $Cl^{\ominus}$ b. $ClO_2^{\ominus}$

c. $ClO_3^{\ominus}$ d. $ClO^{\ominus}$

viii. The elementary reaction

$O_3(g) + O(g) \longrightarrow 2\ O_2(g)$ is
a. unimolecular and second order

b. bimolecular and first order
c. bimolecular and second order
d. unimolecular and first order

ix. Rate law for the reaction,

$2\ NO + Cl_2 \longrightarrow 2\ NOCl$ is
rate = $k[NO_2]^2[Cl_2]$. Thus of k would increase with

a. increase of temperature
b. increase of concentration of NO
c. increase of concentration of Cl_2
d. increase of concentrations of both Cl_2 and NO

x. For an endothermic reaction, $X \rightleftharpoons Y$. If E_f is activation energy of the forward reaction and E_r that for reverse reaction, which of the following is correct?

a. $E_f = E_r$ b. $E_f < E_r$
c. $E_f > E_r$
d. $\Delta H = E_f - E_r$ is negative

2. Answer the following in one or two sentences.

i. For the reaction,

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

what is the relationship among $\frac{d[N_2]}{dt}$, $\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$?

ii. For the reaction,

$$CH_3Br(aq) + OH^-(aq) \longrightarrow CH_3OH^{\ominus}(aq) + Br^{\ominus}(aq),$$ rate law is

rate = $k[CH_3Br][OH^{\ominus}]$

a. How does reaction rate changes if $[OH^{\ominus}]$ is decreased by a factor of 5 ?

b. What is change in rate if concentrations of both reactants are doubled?

iii. What is the relationship between coefficients of reactants in a balanced equation for an overall reaction and exponents in rate law. In what case the coefficients are the exponents?

iv. Why all collisions between reactant molecules do not lead to a chemical reaction?

v. What is the activation energy of a reaction?

vi. What are the units for rate constants for zero order and second order reactions if time is expressed in seconds and concentration of reactants in mol/L?

vii. Write Arrhenius equation and explain the terms involved in it.

viii. What is the rate determining step?

ix. Write the relationships between rate constant and half life of first order and zeroth order reactions.

x. How do half lives of the first order and zero order reactions change with initial concentration of reactants?

3. Answer the following in brief.

i. How instantaneous rate of reaction is determined?

ii. Distinguish between order and molecularity of a reaction.

iii. A reaction takes place in two steps,

1. $NO(g) + Cl_2(g) \longrightarrow NOCl_2(g)$
2. $NOCl_2(g) + NO(g) \longrightarrow 2\ NOCl(g)$

a. Write the overall reaction. b. Identify reaction intermediate. c. What is the molecularity of each step?

iv. Obtain the relationship between the rate constant and half life of a first order reaction.

v. How will you represent zeroth order reaction graphically?

vi. What are pseudo-first order reactions? Give one example and explain why it is pseudo-first order.

vii. What are requirements for the colliding reactant molecules to lead to products?

viii. How catalyst increases the rate of reaction? Explain with the help of potential energy diagram for catalyzed and uncatalyzed reactions.

ix. Explain with the help of Arrhenius equation, how does the rate of reaction changes with (a) temperature and (b) activation energy.

x. Derive the integrated rate law for first order reaction.

xi. How will you represent first order reactions graphically.

xii. Derive the integrated rate law for the first order reaction, $A(g) \longrightarrow B(g) + C(g)$ in terms of pressure.

xiii. What is zeroth order reaction? Derive its integrated rate law. What are the units of rate constant?

xiv. How will you determine activation energy: (a) graphically using Arrhenius equation (b) from rate constants at two different temperatures?

xv. Explain graphically the effect of temperature on the rate of reaction.

xvi. Explain graphically the effect of catalyst on the rate of reaction.

xvii. For the reaction $2A + B \longrightarrow$ products, find the rate law from the following data.

[A]/M	[B]/M	rate/M s^{-1}
0.3	0.05	0.15
0.6	0.05	0.30
0.6	0.2	1.20

4. Solve

i. In a first order reaction, the concentration of reactant decreases from 20 mmol dm^{-3} to 8 mmol dm^{-3} in 38 minutes. What is the half life of reaction? (28.7 min)

ii. The half life of a first order reaction is 1.7 hours. How long will it take for 20% of the reactant to react? (32.9 min)

iii. The energy of activation for a first order reaction is 104 kJ/mol. The rate constant at 25 ^{0}C is 3.7×10^{-5} s^{-1}. What is the rate constant at 30^{0}C? (R = 8.314 J/K mol) (7.4×10^{-5})

iv. What is the energy of activation of a reaction whose rate constant doubles when the temperature changes from 303 K to 313 K? (54.66 kJ/mol)

v. The rate constant of a reaction at 500^{0}C is 1.6×10^3 $M^{-1}s^{-1}$. What is the frequency factor of the reaction if its activation energy is 56 kJ/mol. (9.72×10^6 $M^{-1}s^{-1}$)

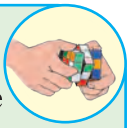
vi. Show that time required for 99.9% completion of a first order reaction is three times the time required for 90% completion.

vii. A first order reaction takes 40 minutes for 30% decomposition. Calculate its half life. (77.66 min)

viii. The rate constant for the first order reaction is given by $\log_{10} k = 14.34 - 1.25 \times 10^4$ T. Calculate activation energy of the reaction. (239.3 kJ/mol)

ix. What fraction of molecules in a gas at 300 K collide with an energy equal to activation energy of 50 kJ/mol ? (2×10^{-9})

Activity :



1. You wish to determine the reaction order and rate constant for the reaction, $2AB_2 \longrightarrow A_2 + 2B_2$. a) What data would you collect? b) How would you use these data to determine whether the reaction is zeroth or first order?

2. The activation energy for two reactions are E_a and E'_a with $E_a > E'_a$. If the temperature of reacting system increase from T_1 to T_2, predict which of the following is correct?

a. $\frac{k'_1}{k_1} = \frac{k'_2}{k_2}$ b. $\frac{k'_1}{k_1} > \frac{k'_2}{k_2}$

c. $\frac{k'_1}{k_1} < \frac{k'_2}{k_2}$ d. $\frac{k'_1}{k_1} < 2\frac{k'_2}{k_2}$

k_s are rate constants at lower temperature and k'_s at higher temperature.

7. ELEMENTS OF GROUPS 16, 17 AND 18

Can you recall ?

- How does the valence shell electronic configuration of the elements vary in the p-block of periodic table ?
- Name the first element of groups 16, 17 and 18.

7.1 Introduction : You have learnt in Std. XI that in the p-block elements the differentiating electron (the last filling electron) enters the p-orbital of the outermost shell. Since maximum of six electrons can be accommodated in a p-subshell it gives rise to groups 13 to 18, in the p-block. In this chapter we shall study the properties of elements of groups 16, 17 and 18.

7.2 Occurence : The elements oxygen (${}_{8}O$), sulfur (${}_{16}S$), selenium (${}_{34}Se$), tellurium (${}_{52}Te$) and polonium (${}_{84}Po$) constitute Group 16, called the oxygen family. Large number of metal ores are oxides or sulfides. Group 16 elements are also called **chalcogens** or ore forming elements.

Oxygen is the most abundant of all the elements on earth. Oxygen forms 20.95 % by volume of air and about 46.6 % by mass of earth's crust. Sulfur forms 0.034% by mass of the earths crust. It occurs mainly in combined forms as sulfates such as **gypsum** ($CaSO_4.2H_2O$), **epsom salt** ($MgSO_4.7H_2O$), **baryte** ($BaSO_4$) and sulfides such as **galena** (PbS), **zinc blende** (ZnS), **copper pyrites** ($CuFeS_2$).

Selenium and tellurium are also found as metal selenides and tellurides in sulfide ores. Polonium which is radioactive is a decay product of thorium and uranium.

Fluorine (${}_{9}F$), chlorine (${}_{17}Cl$), bromine (${}_{35}Br$), iodine (${}_{53}I$) and astatine (${}_{85}At$) constitute Group 17. These are collectively known as **halogens** (Greek halo means salt, gene means born), that is, salt producing element.

Halogens are very reactive due to high electronegativities and hence they are not found in free sate. They occur in the form of compounds.

Fluorine occurs mainly as insoluble fluorides (**fluorspar** CaF_2, **cryolite** Na_3AlF_6, **fluorapatite** $3Ca_3(PO_4)_2.CaF_2$) and small quantities are present in soil, fresh water plants, and bones and teeth of animals. Sea water contains chlorides, bromides and iodides of Na, K, Mg and Ca. However it mainly contains NaCl (2.5 % by mass). The deposits of dried up sea beds contain sodium chloride and **carnallite**, $KCl.MgCl_2.6H_2O$. Marine life also contains iodine in their systems. For example, sea weed contains upto 0.5 % iodine and **chile saltpetre** contains upto 0.2 % of sodium iodate. Astatine, the last member of halogen family is radioactive and has a half life of 8.1 hours.

The elements helium (${}_{2}He$), neon (${}_{10}Ne$), argon (${}_{18}Ar$), krypton (${}_{36}Kr$), xenon (${}_{54}Xe$) and radon (${}_{86}Rn$) constitute the Group 18.

All the noble gases except radon occur in the atmosphere. Their abundance in dry air is ~ 1% (by volume) with argon as the major constituent. The main commercial source of helium is natural gas. Helium and neon are found in minerals of radioactive origin e.g. **pitchblende**, **monazite**, **cleveite**. Xenon and radon are the rarest elements of the group. Radon is a decay product of ${}^{226}Ra$.

Table 7.1 : Condensed electronic configuration of elements of group 16, 17 and 18

Group 16 (Oxygen family)		Group 17 (Halogen family)		Group 18 (Noble gases)	
Element	Condensed Electronic Configuration	Element	Condensed Electronic Configuration	Element	Condensed Electronic Configuration
				$_{2}He$	$1s^2$
$_{8}O$	$[He]2s^22p^4$	$_{9}F$	$[He]2s^22p^5$	$_{10}Ne$	$[He]2s^22p^6$
$_{16}S$	$[Ne]3s^23p^4$	$_{17}Cl$	$[Ne]3s^23p^5$	$_{18}Ar$	$[Ne]3s^23p^6$
$_{34}Se$	$[Ar]3d^{10}4s^24p^4$	$_{35}Br$	$[Ar]3d^{10}4s^24p^5$	$_{36}Kr$	$[Ar]3d^{10}4s^24p^6$
$_{52}Te$	$[Kr]4d^{10}5s^25p^4$	$_{53}I$	$[Kr]4d^{10}5s^25p^5$	$_{54}Xe$	$[Kr]4d^{10}5s^25p^6$
$_{84}Po$	$[Xe]4f^{14}5d^{10}6s^26p^4$	$_{85}At$	$[Xe]4f^{14}5d^{10}6s^26p^5$	$_{86}Rn$	$[Xe]4f^{14}5d^{10}6s^26p^6$

7.3 Electronic configuration of elements of group 16, 17 and 18: : The general electronic configuration of the group 16 elements is ns^2np^4 while that of group 17 elements is ns^2np^5. The group 18 elements are shown by ns^2np^6 configuration.

The elements of groups 16 and 17 repectively have two and one electrons less than the stable electronic configuration of the nearest noble gas.

Table 7.1 shows the condensed electronic configuration of the elements of group 16, 17 and 18.

7.4 Atomic and physical properties of elements of group 16, 17 and 18.

7.4.1 Atomic properties of Group 16, 17 and 18 elements : These properties are given in Tables 7.2, 7.3 and 7.4.

i. Atomic and Ionic radii : In group 16, 17 and 18 atomic and ionic radii increase down the group, as a result of increase in the number of quantum shells.

Across a period atomic or ionic radii decrease with increasing atomic number, consequent to increase in (Z_{eff}) effective nuclear charge. Group 17 elements (Halogens) have the smallest atomic radii in their respective periods.

ii. Ionisation enthalpy : The group 16, 17 and 18 elements have high ionisation enthalpy. The ionisation enthalpy decreases down the group due to increase in the atomic size.

Across a period ionisation enthalpy increases with increase of atomic number. This is due to addition of electrons in the same shell. However the elements of group 16 have lower ionisation enthalpy values compared to those of group 15 in the corresponding periods, owing to extra stable half filled electronic configuration of p-orbitals in elements of group 15.

Table 7.2 : Atomic and physical properties of group 16 elements.

Element	Atomic number	Atomic mass g/mol	Atomic radius (pm)	Ionic radius $E^{2\ominus}$ (pm)	Ionization enthalpy (Δ_iH_1) kJ/mol	Electro-negativity	Electron gain enthalpy kJ/mol	Density g /cm³	M.P. (K)	B.P. (K)
O	8	16.00	66	140	1314	3.50	-141	1.32	55	90
S	16	32.06	104	184	1000	2.44	-200	2.06	393	718
Se	34	78.96	117	198	941	2.48	-195	4.19	490	958
Te	52	127.60	137	221	869	2.01	-190	6.25	725	1260
Po	84	210.00	146	230	813	1.76	-174	-	520	1235

Table 7.3 : Atomic and physical properties of group 17 elements

Element	Atomic number	Atomic mass g/mol	Atomic radius (pm)	Ionic radius $E^{\ominus}$(pm)	Ionization enthalpy (Δ_iH_1) kJ/mol	Electro negativity	Electron gain enthalpy kJ/mol	Density g/cm^3	M.P. (K)	B.P. (K)
F	9	19.00	64	133	1680	4.0	-333	1.5	54.4	84.9
Cl	17	35.45	99	184	1256	3.2	-349	1.66	172.0	239.0
Br	35	79.90	114	196	1142	3.0	-325	3.19	265.8	332.5
I	53	126.90	133	220	1008	2.7	-296	4.94	386.6	458.2
At	85	210	-	-	-	2.2	-	-	-	-

Table 7.4 : Atomic and physical properties of group 18 elements.

Element	Atomic number	Atomic mass g/mol	Atomic radius (pm)	Ionization enthalpy (Δ_iH_1) kJ/mol	Electron gain enthalpy kJ/mol	Density g/cm^3	M.P. (K)	B.P. (K)	Atmospheric content (% by volume)
He	2	4.00	120	2372	48	1.8×10^{-4}	-	4.2	5.24×10^{-4}
Ne	10	20.18	160	2080	116	9.0×10^{-4}	24.6	27.1	-
Ar	18	39.95	190	1520	96	1.8×10^{-3}	83.8	87.2	1.82×10^{-3}
Kr	36	83.80	200	1351	96	3.7×10^{-3}	115.8	119.7	0.934
Xe	54	131.30	220	1170	77	5.9×10^{-3}	161.3	165.0	1.14×10^{-4}
Rn	86	222.00	-	1037	68	9.7×10^{-3}	202	211	8.7×10^{-6}

iii. Electronegativity : In a group (16, 17 and 18) the electronegativity decreases down the group.

* Oxygen has the highest electronegativity next to fluorine amongst all the elements.

* Halogens have very high electronegativity. Fluorine is the most electronegative element in the periodic table.

iv. Electron gain enthalpy : In the groups 16 and 17 electron gain enthalpy becomes less negative down the group.

However in group 16, oxygen has less negative electron gain enthalpy than sulfur due to its small atomic size.

* In group 17, fluorine has less negative electron gain enthalpy than that of chlorine. This is due to small size of fluorine atom.

* Group 18 elements (noble gases) have no tendency to accept electrons because of their stable electronic configuration (ns^2np^6) and thus have large positive electron gain enthalpy.

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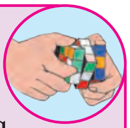


- Observe Table no 7.3 and explain the trend in following atomic properties of group 17 elements.

i. Atomic size, ii. Ionisation enthalpy, iii. electronegativity, iv. electron gain enthalpy

- Oxygen has less negative electron gain enthalpy than sulfur. Why ?

Problem 7.1 : Elements of group 16 generally show lower values of first ionisation enthalpy compared to the elements of corresponding period of group 15. Why ?

Solution : Group 15 elements have extra stable, half filled p-orbitals with electronic configuration (ns^2np^3). Therefore more amount of energy is required to remove an electron compared to that of the partially filled orbitals (ns^2np^4) of group 16 elements of the corresponding period.

Problem 7.2 : The values of first ionisation enthalpy of S and Cl are 1000 and 1256 kJ mol^{-1}, respectively. Explain the observed trend.

Solution : The elements S and Cl belong to second period of the periodic table.

Across a period effective nuclear charge increases and atomic size decreases with increase in atomic number.

Therefore the energy required for the removal of electron from the valence shell (I.E.) increases in the order S < Cl.

7.4.2 Physical properties of group 16, 17 and 18 elements :

a. Group 16 elements (Oxygen family or chalcogens) : Oxygen is a gas while other elements are solids at room temperature.

Oxygen and sulfur are nonmetals, selenium and tellurium are metalloids, while polonium is a metal. Polonium is radioactive with its half life of 13.8 days.

Melting and boiling points increase with increasing atomic number.

All the elements of group 16 exhibit allotropy.

Problem 7.3 : Why is there a large difference between the melting and boiling points of oxygen and sulfur ?

Solution : Oxygen exists as diatomic molecule (O_2) where as sulfur exists as polyatomic molecule (S_8).

The van der Waals forces of attraction between O_2 molecules are relatively weak owing to its much smaller size.

The large van der Waals attractive forces in the S_8 molecules can be noticed because of large molecular size. Therefore oxygen has low m.p. and b.p. as compared to sulfur.

b. Group 17 elements (Halogen family) :

Fluorine, chlorine are gases, bromine is a liquid and iodine is a solid at room temperature. F_2 is yellow, Cl_2 greenish yellow, Br_2 red and I_2 is violet, in colour.

Fluorine and chlorine react with water. Bromine and iodine are only sparingly soluble in water and are soluble in various organic solvents such as chloroform, carbon disulfide, carbon tetrachloride, hydrocarbons which give coloured solutions. Bond dissociation enthalpies of halogen molecules follow the order : Cl - Cl > Br - Br > F - F > I - I.

Problem 7.4 : Fluorine has less negative electron gain affinity than chlorine. Why ?

Solution : The size of fluorine atom is smaller than chlorine atom. As a result, there are strong inter electronic repulsions in the relatively small 2p orbitals of fluorine and therefore, the incoming electron does not experience much attraction. Thus fluorine has less negative electron gain affinity than chlorine.

Problem 7.5 : Bond dissociation enthalpy of F_2 (158.8 KJ mol^{-1}) is lower than that of Cl_2 (242.6 KJ mol^{-1}) Why ?

Solution : Fluorine has small atomic size than chlorine. The lone pairs on each F atoms in F_2 molecule are so close together that they strongly repel each other, and make the F - F bond weak (fig. 7.1) Thus it requires less amount of energy to break the F - F bond. In Cl_2 molecule the lone pairs on each Cl atom are at a larger distance and the repulsion is negligible. Thus Cl - Cl bond is comparitively stronger. Therefore bond dissociation enthalpy of F_2 is lower than that of Cl_2.

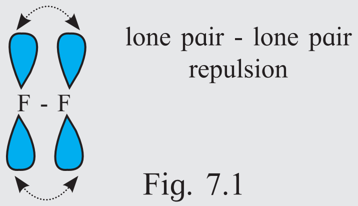


Fig. 7.1

c. Group 18 elements (Noble gases) :

Noble gases are monoatomic.

They are sparingly soluble in water.

Noble gases have very low melting and boiling points. Helium has the lowest boiling point (4.2 K) of any known substances.

Problem 7.6 : Noble gases have very low melting and boiling points. Why ?

Solution : Noble gases are monoatomic, the only type of inter atomic interactions which exist between them are van der Waals forces. Therefore, they can be liquified at very low temperatures and have very low melting or boiling points.

Can you tell ?

The first member of a group usually differs in properties from the rest of the members of the group. Why ?

7.5 Anamalous Behaviour

7.5.1 Anomalous behaviour of oxygen :

Oxygen shows the following anomalous properties compared to other members of group 16 :

i. Atomicity : Oxygen is a diatomic molecule (O_2) while others are polyatomic molecules. For example P_4, S_8.

ii. Magnetic property : Oxygen is paramagnetic while others are diamagnetic.

iii. Oxidation state : Oxygen shows -2, -1, and +2 oxidation states while other elements show, -2, +2, +4, +6 oxidation states. Oxygen can not exhibit higher oxidation state due to absence of vacant d orbitals.

Use your brain power

- Oxygen forms only OF_2 with fluorine while sulfur forms SF_6. Explain. Why ?

iv. Nature of hydrides : Hydride of oxygen (H_2O) is liquid at room temperature while hydrides of other members of the group are gases.

Use your brain power

- Which of the following possess hydrogen bonding ? H_2S, H_2O, H_2Se, H_2Te
- Show hydrogen bonding in the above molecule with the help of a diagram.

v. Common covalency of oxygen is 2. In rare cases it is four. But for the other members of the group 16 the covalency can exceed four.

The anomalous behaviour of oxygen is due to the following reasons.

i. small atomic size

ii. high electronegativity.

iii. absence of inner d-orbitals.

7.5.2 Anomalous behaviour of fluorine :

Fluorine, the first member of group 17, differs in properties from the other members of the group. The anomalous behaviour of fluorine is due to the following reasons.

i. small atomic size

ii. high electronegativity

iii. absence of d-orbitals in valence shell

iv. low F-F bond dissociation enthalpy

Some anomalous properties of fluorine :

i. Ionisation enthalpy, electronegativity, electrode potential are all higher for fluorine than expected trends shown by other halogens.

ii. Ionic and covalent radii, m.p., b.p. and electron gain enthalpy are quite lower than expected.

iii. Most of the reactions of fluorine are exothermic (due to the short and strong bond formed by it with other elements).

iv. It forms only one oxoacid (HOF) while other halogens form a number of oxoacids.

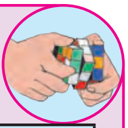
v. Hydrogen fluoride is a liquid (b.p. 293K) due to strong hydrogen bonding while other hydrogen halides are gases.

7.6 Chemical Properties of elements of groups 16, 17 and 18

7.6.1 Oxidation state : i. The group 16 elements have the valence shell electronic configuration ns^2np^4. They attain a noble gas configuration either by gaining two electrons, forming $E^{2\ominus}$ ions or by sharing two electrons, forming two covalent bonds. These elements, thus, show -2 and +2 oxidation states in their compounds.

Oxygen being highly electronegative, shows common oxidation state of -2 except two cases. In the case of OF_2, its oxidation state is +2 and in peroxides, it shows oxidation state -1 (H_2O_2, Na_2O_2). Other elements of the group exhibit +2, +4, +6 oxidation states with +4 and +6 being more common. The stability of higher (+6) oxidation state decreases down the group while the stability of the lower oxidation state (+4) increases down the group due to inert pair effect. Bonding in +4 and +6 oxidation states are primarily covalent.

Try this...



Complete the following tables

Element	O	O	S	F
compound	H_2O	OF_2	H_2S	HF
Oxidation state	-2	......	......	......
Element	Se	Se	Te	Cl
compound	SeO_2	SeO_3	TeF_6	HOCl
Oxidation state	......	+6	......	......

ii. The group 17 elements are represented by their valence shell electronic configuration as ns^2np^5. They attain noble gas configuration either by gaining one electron forming $E^{\ominus}$ ions or by sharing one electron forming one covalent bond.

All halogens exhibit -1 oxidation state. However Cl, Br and I exhibit +1, +3, +5 and +7 oxidation states as well. This is because they are less electronegative than F and possess empty d-orbitals in the valence shell and therefore, can expand the octet. The oxidation states +4 and +6 occur in the oxides and oxoacids of Cl and Br.

The fluorine atom has no d - orbitals in its valence shell and therefore cannot expand its octet. Thus fluorine being most electronegative exhibits mostly -1 oxidation state.

iii. Group 18 elements (noble gases) have stable valence shell electronic configuration ns^2np^6 with completely filled orbitals. Thus they have no tendency to gain or lose electrons, that is, they are zero valent and mostly exist as monoatomic gases. However, xenon has large atomic size and lower ionisation enthalpy compared to He, Ne, Ar and Kr. Hence xenon exhibits higher oxidation states. Its outermost shell has d-orbitals. The paired electrons of the valence shell can be unpaired and promoted to empty d-orbitals. The unpaired electrons are shared with fluorine or oxygen atoms and covalent compounds showing higher oxidation state such as XeF_2(+2), XeF_4 (+4), XeF_6 (+6), XeO_3 (+6) and $XeOF_4$ (+6) are formed.

7.6.2 Chemical Reactivity towards hydrogen:

i. Group 16 elements : The elements of group 16 react with hydrogen to form hydrides of the type H_2E. (Where E = O, S, Se, Te, Po).

For example, H_2O, H_2S, H_2Se, H_2Te and H_2Po. Some properties of hydrides of group 16 are given in Table 7.5.

H_2O is a colourless, odourless liquid, while H_2S, H_2Se, H_2Te and H_2Po are colourless bad smelling, poisonous gases at ambient conditions.

All hydrides have angular structures which involve sp^3 hybridisation of central atom (E).

The hydrides of group 16 elements are weakly acidic. The acidic character of the hydrides increases, while thermal stability decreases from H_2O to H_2Te. This is due to decrease in the bond dissociation enthalpy of the H-E bond down the group (Table 7.5).

All hydrides except H_2O possess reducing property which increases in the order H_2S < H_2Se < H_2Te.

ii. Group 17 elements : The elements of group 17 react with hydrogen to give hydrogen halides.

$$H_2 + X_2 \longrightarrow 2HX$$

(Where X = F, Cl, Br, I)

Some of the properties of hydrogen halides are given in Table 7.6.

Acidic strength of halogen acids increases in the order :

HF < HCl < HBr < HI

It is due to decreasing bond dissociation enthalpy of H-X bond in the order
HF > HCl > HBr > HI.

Thermal stability of hydrogen halides decreases in the order HF>HCl>HBr>HI. It is due to decrease in bond dissociation enthalpy of H-X bond down the group.

Table 7.5 Properties of hydrides of group 16 elements

Property	H_2O	H_2S	H_2Se	H_2Te
m.p (K)	273	188	208	222
b.p (K)	373	213	232	269
H-E Bond length (pm)	96	134	146	169
$\Delta_{diss}H$ (H-E) kJ/mol	463	347	276	238
$\Delta_f H$ kJ/mol	-286	-20	73	100
HEH angle (°)	104	92	91	90
pK_a	14.0	7.0	3.8	2.6

Table 7.6 Properties of hydrides of group 17 elements.

Property	HF	HCl	HBr	HI
m.p (K)	190	159	185	222
b.p (K)	293	189	206	238
Bond length (H-X) pm	91.7	127.4	141.4	160.9
$\Delta_{diss}H^0$ kJ/mol	574	432	363	295
pKa	3.2	-7.0	-9.5	-10.0

iii. Group 18 elements (Noble gases) :

Noble gases are chemically inert towards hydrogen due to their stable electronic configuration.

7.6.3 Reactivity towards oxygen :

i. Group 16 elements : All the elements of group 16 form oxides of the type EO_2 and EO_3 where E = S, Se, Te, Po.

EO_2 type oxides, Ozone (O_3) and sulfur dioxide (SO_2) are gases, while selenium dioxide (SeO_2) is solid. They are acidic in nature and react with water to form acids.

$SO_2 + H_2O \longrightarrow H_2SO_3$ (Sulfurous acid)

$SeO_2 + H_2O \longrightarrow H_2SeO_3$ (Selenious acid)

Reducing property of dioxides decreases from SO_2 to TeO_2. SO_2 is reducing while TeO_2 serves as an oxidising agent.

EO_3 type oxides, SO_3, SeO_3, TeO_3 are also acidic in nature. They dissolve in water to form acids.

$SeO_3 + H_2O \longrightarrow H_2SeO_4$ (Selenic acid)

$TeO_3 + 3H_2O \longrightarrow H_6TeO_6$ (Telluric acid)

ii. Group 17 elements : Elements of group 17 (Halogens) form many oxides with oxygen, but most of them are unstable.

Fluorine forms two oxides OF_2 and O_2F_2. However, only the OF_2 is thermally stable at 298 K. Both are strong fluorinating agents. O_2F_2 oxidises plutonium to PuF_6 and the reaction is used in removing plutonium as PuF_6 from spent nuclear fuel.

Chlorine oxides, Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7 are highly reactive oxidising agents and tend to explode.

ClO_2 is used as bleaching agent for paper pulp and textiles and in water treatment.

Bromine oxides, Br_2O, BrO_2, BrO_3 are the least stable halogen oxides (middle row anomally). They are very powerful oxidising agents.

Iodine oxides, I_2O_4, I_2O_5 and I_2O_7 are insoluble solids and decompose on heating. I_2O_5 is a very good oxidising agent and used for the estimation of carbon monoxide.

The higher oxides of halogens are more stable than the lower ones.

iii. Group 18 elements : Noble gas elements are chemically inert and do not directly react with oxygen.

7.6.4 Reactivity towards halogens :

i. Group 16 elements : Elements of group 16 react with halogens to give a large number of halides of the types EX_6 , EX_4 and EX_2. (Where E = S, Se, Te)

Hexahalides, SF_6, SeF_6 and TeF_6 are formed by direct combination. They are colourless gases. They have sp^3d^2 hybridisation and possess octahedral structure. SF_6 is exceptionally stable halide for steric reasons.

Stability of halides decreases in the order fluorides > chlorides > bromides > iodides

Tetrahalides, SF_4, SeF_4, TeF_4, $TeCl_4$ have sp^3 hybridisation and thus trigonal bipyramidal geometry with one equatorial position occupied by a lone pair.

Dihalides, SCl_2, $SeCl_2$, $TeCl_2$ have sp^3 hybridisation and thus possess tetrahedral structure with two equatorial positions occupied by lone pairs.

Monohalides are dimeric in nature. For example, S_2F_2, S_2Cl_2, Se_2Cl_2 and $SeBr_2$. These dimeric halides undergo disproportionation.

$$2\ Se_2Cl_2 \longrightarrow SeCl_4 + 3Se$$

Internet my friend

Find and draw the structures of SeF_4 and SCl_2.

ii. Group 17 elements :

Halogens (Group 17 elements) combine amongst themselves to form a number of compounds known as interhalogen compounds.

These are of following types : XX', XX'_3, XX'_5, XX'_7,

Where X is the halogen atom with larger size and X' is the halogen atom with smaller size. More details of interhalogen compounds are included in section 7.12.

iii. Group 18 elements : Group 18 elements (Noble gases) are chemically inert. Krypton and xenon, however react directly with fluorine to give their fluorides. For example,

$$Xe(g) + F_2(g) \xrightarrow[1\ atm]{673K} XeF_2(s)$$

Xenon fluorides XeF_2, XeF_4 and XeF_6 are crystalline and colourless which sublime readily at 298 K. They are powerful fluorinating agents.

7.6.5 Reactivity towards metals :

i. Group 16 elements : Elements of group 16 react with metals to form corresponding compounds.

e.g. $4Al + 3O_2 \longrightarrow 2Al_2O_3$

$Cu + S \longrightarrow CuS$

$Mg + Se \longrightarrow MgSe$

magnesium selenide

Do you know ?

Tellurium has the unusal property of combining with gold metal to form telluride.

$$2Au + 3Te \longrightarrow Au_2Te_3$$

(gold telluride)

Internet my friend

www.chemistry.explained.com

ii. Group 17 elements :

Elements of group 17 (Halogens) react with metals instantly to give metal halides.

$2Na\ (s) + Cl_2\ (l) \longrightarrow 2NaCl\ (s)$

$Mg\ (s) + Br_2\ (l) \longrightarrow MgBr_2\ (s)$

magnesium bromide

Ionic character of halides decreases in the order MF > MCl > MBr > MI, where M is a monovalent metal.

The metal halides having metals in their higher oxidation states are more covalent than the ones having metals in lower oxidation state. For example, $SnCl_4$, $PbCl_4$, $SbCl_5$ and UF_6 are more covalent than $SnCl_2$, $PbCl_2$, $SbCl_3$ and UF_4 respectively.

iii. Group 18 elements : Noble gases do not directly react with metals.

7.7 Allotropy :

Can you tell ?

- What is allotropy ?
- What is the difference between allotropy and polymorphism ?

Elements of the group 16 exhibit allotropy. Oxygen has two allotropes O_2 and O_3 (ozone). Sulfur exists in a number of allotropic forms. Rhombic and monoclinic sulfur are the important allotropes of sulfur. Both are non metallic.

- Selenium exists in two allotropic forms red (non metallic) and grey (metallic).

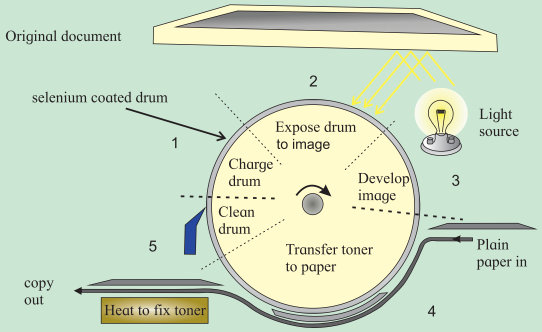
Do you know ?

Grey selenium allotrope of is a photoconductor used in photocells.

Do you know ?

The photocopying process.

A selenium-coated rotating drum is given a uniform positive charge (step 1) and is then exposed to an image (step 2). Negatively charged toner particles are attracted to the charged area of the drum (step 3) and the image is transferred from the drum to a sheet of paper (step 4). Heating then fixes the image and the drum is flooded with light and cleaned to ready the machine for another cycle (step 5). Figure of photocopying process using Se is as shown below :



- Tellurium exists in two allotropic forms (i) crystalline and (ii) amorphous.
- Polonium reveals two allotropic forms α and β (both metallic).

7.7.1 Allotropes of sulfur :

Sulfur exhibits numerous allotropic forms. However rhombic sulfur (α- sulfur) and monoclinic sulfur (β - sulfur) are the most important allotropes of sulfur (Table 7.7).

Problem 7.7 : Which form of sulfur shows paramagnetic behaviour ?

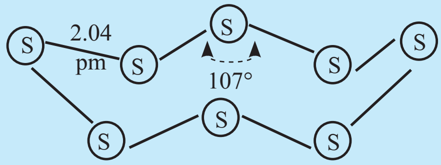
Solution : In vapour state, sulfur partly exists as S_2 molecule, which has two unpaired electrons in the antibonding π^* orbitals like O_2. Hence it exhibits paramagnetism.

Table 7.7 Allotropes of sulfur

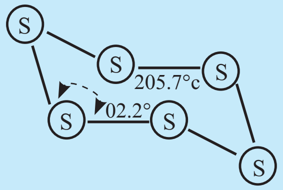
	Rhombic Sulfur (α - Sulfur)	**Monoclinic Sulfur (β - Sulfur)**
Color	Pale Yellow	Bright yellow solid
Shape	Orthorhombic crystals	Needle shaped monoclinic crystals
M. P.	385.8 K	393 K
Density	2.069/ cm^3	1.989 / cm^3
Solubility	Insoluble in water and soluble in CS_2	Soluble in CS_2
Stability	Stable below 369 K and transforms to β - Sulphur above this temperature.	Stable above 369 K and transforms into α - Sulphur below this temperature.
Structure	S_8 molecules having puckered ring structure	S_8 molecules with puckered ring structure
Method of preparation	It is prepared by evaporation of roll sulphur in CS_2.	Rhomic sulphur melted in a dish and cooled till crust is formed. Two holes are made in the crust and remaining liquid is poured out to give needle shaped crystals of β - Sulphur

Remember...

Several modifications of sulfur containing 6-20 sulfur atoms per ring, have been synsthesised. In the S_8 molecule the ring is puckered and has a crown shape. In cyclo - S_6, the ring adopts the chair form. At elevated temperature (~ 1000 K), S_2 is the dominant species which like O_2 is paramagnetic.



Structure of S_8 ring in rhombic sulfur



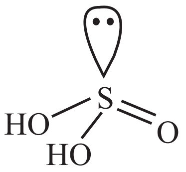
Chair form of S_6

7.8 Oxoacids

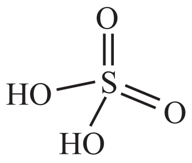
7.8.1 Oxoacids of sulfur : Sulfur forms a number of oxoacids. Some of them are unstable and cannot be isolated. They are known to exist in aqueous solutions or in the form of their salts.

Some important oxoacids of sulfur and their structures are given below.

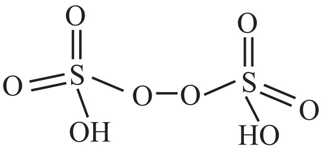
i. Sulfurous acid, H_2SO_3



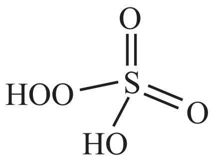
ii. Sulfuric Acid, H_2SO_4



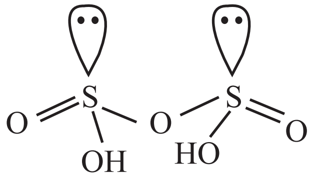
iii. Di or pyrosulfuric acid, $H_2S_2O_7$



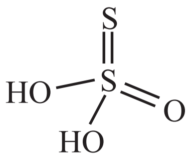
iv. Peroxy monosulfuric acid, H_2SO_5



v. Peroxy disulfuric acid, $H_2S_2O_8$



vi. Thiosulfuric acid, $H_2S_2O_3$

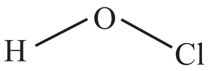


7.8.2 Oxoacids of halogens : : Halogens form several oxoacids (See Table 7.8). Only four oxoacids have been isolated in pure form: hypofluorous acid (HOF), perchloric acid ($HClO_4$), iodic acid (HIO_3), metaperiodic acid (H_2IO_6). The others are stable only in aqueous solutions or in the form of their salts.

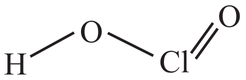
The acid strength of the halogen oxoacids increases with the increasing oxidation state of halogen. For example, acid strength increases from HClO, a weak acid ($K_a = 3.5 \times 10^{-8}$), to $HClO_4$, a very strong acid ($K_a >> 1$).

Strucutres of oxoacids of chlorine :

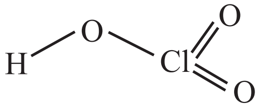
i. Hypochlorous acid, HOCl



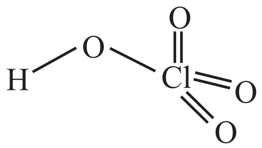
ii. Chlorous acid, HOClO or $HClO_2$



iii. Chloric acid, $HClO_3$



iv. Perchloric acid, $HClO_4$



7.9 Oxygen and Compounds of oxygen

7.9.1 Dioxygen

a. Preparation

i. Laboratory methods :

- By heating oxygen containing salts such as chlorates, nitrates and permanganates.

$$2KClO_{3(s)} \xrightarrow[MnO_2]{Heat} 2KCl_{(s)} + 3O_{2(g)}$$

- By thermal decomposition of oxides of metals.

$$2Ag_2O_{(s)} \xrightarrow{\Delta} 4Ag_{(s)} + O_{2(g)}$$

$$2HgO_{(s)} \xrightarrow{\Delta} 2Hg_{(l)} + O_{2(g)}$$

Table 7.8 Oxoacids of halogens

oxidation state of X	Generic name	Oxoacids of fluorine	Oxoacids of chlorine	Oxoacids of bromine	Oxoacids of iodine
+1	Hypohalous acid (HXO)	HOF	HOCl	HOBr	HOI
+3	Halous acid (HXO_2)	-	HOClO	-	-
+5	Halic acid (HXO_4)	-	$HOClO_2$	$HOBrO_2$	$HOIO_2$
+7	Perhalic acid (HXO_4)	-	$HOClO_3$	$HOBrO_3$	$HOIO_3$

$$2PbO_{2(s)} \xrightarrow{\Delta} 2PbO_{(s)} + O_{2(g)}$$

- By decomposition of hydrogen peroxide in presence of catalyst such as finely divided metals and manganese dioxide.

$$2H_2O_{2(aq)} \xrightarrow[MnO_2]{\Delta} 2H_2O_{(l)} + O_{2(g)}$$

ii. Electrolysis : Dioxygen can be prepared on large scale by electrolysis of water, when hydrogen is liberated at cathode and oxygen at anode.

$$2H_2O \xrightarrow{\text{Electrolysis}} 2H_2 + O_2$$

iii. Industrial method : Dioxygen is obtained from air, by first removing carbon dioxide and water vapour. The remaining gases are liquified subsequently. This is followed by fractional distillation which gives dinitrogen and dioxygen.

b. Physical properties :

- Dioxygen is colourless and odourless gas.
- Dioxygen is sparingly soluble in water, 30.8 cm^3 of O_2 dissolves in 1000 cm^3 of water at 293 K. A small amount of dissolved dioxygen is sufficient to sustain marine and aquatic life.
- It liquifies at 90 K and freezes at 55 K.
- Oxygen has three stable isotopes ^{16}O, ^{17}O and ^{18}O.
- Molecular oxygen, O_2 exhibits paramagnetism.

c. Chemcial Properties :

i. Reaction with metals : Dioxygen directly reacts with almost all metals except Au, Pt to form their oxides.

$$2Ca + O_2 \longrightarrow 2CaO$$

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

ii. Reaction with nonmetals : Dioxygen reacts with nonmetals (except noble gases) to form their oxides.

$$C + O_2 \longrightarrow CO_2$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

iii. Reaction with some compounds :

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

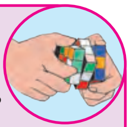
$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

$$4HCl + O_2 \xrightarrow[\Delta]{CuCl_2} 2Cl_2 + 2H_2O$$

d. Uses

- Dioxygen is important for respiration to sustain animal and aquatic life.
- It is used in the manufacture of steel.
- It is used in oxyacetylene flame for welding and cutting of metals.
- Oxygen cylinders are widely used in hospitals, high altitude flying and mountaineering.
- It is used in combustion of fuels; for example, hydrazine in liquid oxygen provides tremendous thrust (energy) in rockets.

Try this...



Why water in the fish pot needs to be changed time to time ?

Problem : 7.8

Dioxygen is paramagnetic inspite of having even number of electrons. Explain.

Solution : Dioxygen is a covalently bonded molecule.

:Ö::Ö: or :Ö=Ö:

Paramagnetic behaviour of O_2 can be explained with the help of molecular orbital theory .

Electronic configuration of O_2

KK $\sigma(2s)^2$ $\sigma^*(2s)^2$ $\sigma(2p_z)^2$ $\pi(2p_x)^2$ $\pi(2p_y)^2$ $\pi^*(2p_x)^1$ $\pi^*(2p_y)^1$. Presence of two unpaired electrons explains paramagnetic nature of dioxygen.

7.9.2 Simple Oxides : A binary compound of oxygen with another element is called an oxide.

Oxides can be classified into

a. Acidic oxides b. Basic oxides

c. Amphoteric oxides d. Neutral oxides

a. Acidic oxides : An oxide which dissolves in water to give an acid or reacts with a base to give a salt is called acidic oxide. For example, SO_2, SO_3, CO_2, N_2O_5, Cl_2O_7 etc.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$$

Generally, oxides of nonmetals are acidic oxides.

b. Basic oxides : An oxide which dissolves in water to give a base or reacts with an acid to give salt is called basic oxide. For example,

Na_2O, CaO, BaO etc.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$BaO + 2HCl \longrightarrow BaCl_2 + H_2O$$

c. Amphoteric oxides : The oxide which reacts with a base as well as with an acid to give salt is called an amphoteric oxide. For example, Al_2O_3

$$Al_2O_3 + 6NaOH_{(aq)} + 3H_2O_{(l)} \longrightarrow 2Na_3[Al(OH)_6]$$

(Acidic)

$$Al_2O_{3(s)} + 6HCl_{(aq)} + 9H_2O_{(l)} \longrightarrow 2[Al(H_2O)_6]^{3\oplus} + 6Cl^{\ominus}_{(aq)}$$

(Basic)

d. Neutral oxides : The oxides which are neither acidic nor basic, are called as neutral oxides. For example, CO, NO, N_2O etc.

7.9.3 Ozone : Ozone (O_3) is an allotrope of oxygen. Oxygen in the upper atmosphere absorbs energy in the form of ultra-violet light and changes to atomic oxygen, which combines with molecular oxygen to form O_3.

$$O_2 \xrightarrow{\text{U.V. light}} O + O$$

$$O_2 + O \longrightarrow O_3$$

The layer of ozone protects the earth's surface from harmful ultraviolet (U.V) radiations. Hence, it is called as 'ozone umbrella'.

a. Preparation of Ozone : Ozone is prepared in the laboratory by passing silent electric discharge through pure and dry oxygen in an apparatus called ozoniser. As the conversion of oxygen to ozone is only 10%, the product is known as ozonised oxygen. It is an endothermic process.

$$3O_{2(g)} \rightleftharpoons 2O_3 \qquad \Delta H = +142 \text{ kJ/mol}$$

b. Physical properties of ozone :

i. Pure Ozone is a pale - blue gas, dark blue liquid and violet - black solid.

ii. Ozone has a characteristic smell. When inhaled in concerntration above 100 ppm, it causes nausea and headache.

iii. It is diamagnetic in nature.

Problem 7.9 : High concerntration of ozone can be dangerously explosive. Explain.

Solution : i. Thermal stability : Ozone is thermodynamically unstable than oxygen and decomposes into O_2. The decomposition is exothermic and results in the liberation of heat (ΔH is -ve) and an increase in entropy (ΔS is positive). This results in large negative Gibbs energy change (ΔG). Therefore high concerntration of ozone can be dangerously explosive.

Eq. $O_3 \longrightarrow O_2 + O$

c. Chemical Properties :

i. Oxidising property :

Ozone is a powerful oxidising agents as it easily decomposes to liberate nascent oxygen. ($O_3 \longrightarrow O_2 + O$).

Ozone oxidises lead sulfide to lead sulfate and iodide ions to iodine.

$$PbS(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$$

$$2KI(aq) + H_2O(l) + O_3(g) \longrightarrow 2KOH(aq) + I_2(g) + O_2(g)$$

Ozone oxidises nitrogen oxide and gives nitrogen dioxide.

$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$

Hence the nitrogen oxide emmited from the exhaust systems of supersonic jet aeroplanes can bringforth depletion of ozone layer in the upper atmosphere.

ii. Bleaching property : Ozone acts as a good bleaching agent due to its oxidising nature.

$O_3 \longrightarrow O + O_2$

Coloured matter + O $\longrightarrow$ colourless matter

Ozone bleaches in absence of moisture so it is also known as dry bleach.

iii. Reducing property : Ozone reduces peroxides to oxides.

e.g. $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

$BaO_2 + O_3 \longrightarrow BaO + 2O_2$

Try this...

a. Ozone is used as bleaching agent. Explain.

b. Why does ozone act as a powerful oxidising agent ?

iv. Ozone depletion : Thinning of ozone layer in upper atmosphere is called ozone depletion.

- The ozone (O_3) layer in the upper atmosphere, absorbs harmful UV radiations from the sun, thus protecting people on the earth.
- Depletion of ozone layer in the upper atmosphere is caused by nitrogen oxide released from exhausts system of car or supersonic jet aeroplanes.

$NO\ (g) + O_3\ (g) \longrightarrow NO_2\ (g) + O_2\ (g)$

- Depletion (thining) of ozone layer can also be caused by chlorofluoro carbons (freons) used in aerosol and refrigerators and their subsequent escape into the atmosphere.
- The depletion of ozone layer has been most pronounced in polar regions, especially over Antarctica.
- Ozone depletion is a major environmental problem because it increases the amount of ultraviolet (UV) radiation that reaches earth's surface, thus causing an increase in rate of skin cancer, eye cataracts and genetic as well as immune system damage among people.

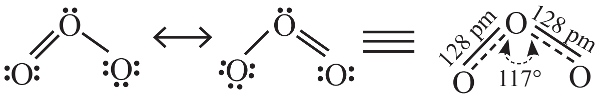
Do you know ?

Ozone reacts with unsaturated compounds containing double bonds to form addition products called ozonides. Ozonides are decomposed by water or dilute acids to give aldehydes or ketones. This reaction is termed as ozonolysis.

Internet my friend

www.britannica.com
ozone depletion.

d. Structure of Ozone : Ozone (O_3) is an angular molecule. The two O — O bond lengths in the ozone molecule are identical, 128 pm and the O — O — O bond angle of about 117°. It is a resonance hybrid of two canonical forms.



e. Uses of ozone :

- Ozone is used for air purification at crowded places like cinema halls, tunnels, railways, etc.
- In sterilizing drinking water by oxidising all germs and bacteria.
- For bleaching ivory, oils, starch, wax and delicate fabrics such as silk.
- In the manufacture of synthetic camphor, potassium permanganate, etc.

7.10 Compounds of sulfur :

7.10.1 Sulfur dioxide

a. Preparation :

i. From sulfur : Sulfur dioxide gas can be prepared by burning of sulfur in air.

$$S(s) + O_2\,(g) \longrightarrow SO_2\,(g)$$

ii. From sulfite : In the laboratory sulfur dioxide is prepared by treating sodium sulfite with dilute sulfuric acid.

$$Na_2SO_3 + H_2SO_4(aq) \longrightarrow Na_2SO_4 + H_2O(l) + SO_2(g)$$

iii. From sulfides : (Industrial method)

Sulfur dioxide can be prepared by roasting zinc sulfide and iron pyrites.

$$2ZnS(s) + 3O_2(g) \xrightarrow{\Delta} 2ZnO(s) + 2SO_2(s)$$

$$4FeS_2(s) + 11O_2\,(g) \xrightarrow{\Delta} 2Fe_2O_3(s) + 8SO_2(g)$$

b. Physical properties of SO_2

i. Sulfur dioxide is a colourless gas with a pungent smell.

ii. It is poisonous in nature.

iii. SO_2 is highly soluble in water and its solution in water is called sulfurous acid.

iv. It liquifies at room temperature under a pressure of 2 atm and boils at 263 K.

c. Chemical Properties :

i. Reaction with Cl_2 : Sulfur dioxide reacts with chlorine in the presence of charcoal (catalyst) to form sulfuryl chloride.

$$SO_2(g) + Cl_2(g) \xrightarrow{\text{charcoal}} SO_2Cl_2(l)$$

ii. Reaction with O_2 : Sulfur dioxide is oxidised by dioxygen in presence of vanadium (V) oxide to sulfur trioxide.

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

iii. Reaction with NaOH : Sulfur dioxide readily reacts with sodium hydroxide solution to form sodium sulfite.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

iv. Reaction with Na_2SO_3 : Sulfur dioxide reacts with sodium sulfite solution to form sodium hydrogen sulfite.

$$Na_2SO_3 + H_2O(l) + SO_2 \longrightarrow 2NaHSO_3$$

v. Reducing property : Sulfur dioxide acts as a reducing agent in the presence of moisture.

- Moist sulfur dioxide reduces ferric salts into ferrous salts.

$$2Fe^{3\oplus} + SO_2 + 2H_2O \longrightarrow 2Fe^{2\oplus} + SO_4^{2\ominus} + 4H^{\oplus}$$

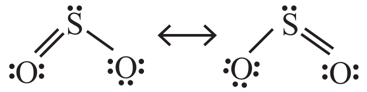
- Moist sulfur dioxide decolourises acidified potassium permangnate (VII) solution.

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

- Moist sulfur dioxide reduces halogens to halogen acids.

$$I_2 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2HI$$

d. Structure of SO_2 : Sulfur dioxide is angular with O — S — O bond angle of 119.5°.



The S — O double bond arises from dπ - pπ bonding. It is a resonance hybrid of two canonical forms.

e. Uses : Sulfur dioxide is used

- In refining of petroleum and sugar.
- In bleaching wool and silk.
- As an anti-chlor, disinfectant.
- As a preservative.
- In the manufacture of H_2SO_4, $NaHSO_3$.
- Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

7.10.2 Sulfuric acid, H_2SO_4

a. Preparation : Sulfuric acid is manaufactured by **Contact process**, which involves the following three steps.

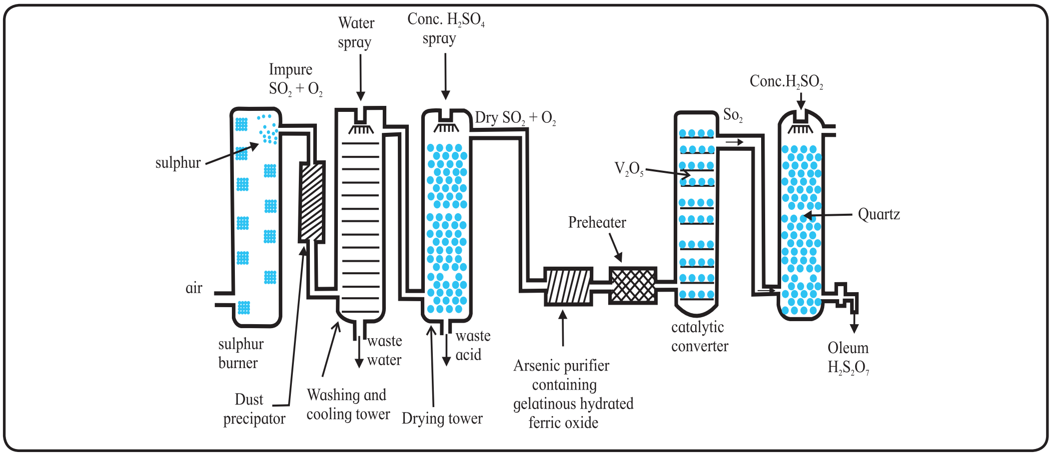


Fig. 7.1 : Flow diagram for manufacture of Sulfuric acid

i. Sulfur or sulfide ore (iron pyrites) on burning or **roasting in air** produces sulfur dioxide.

$$S(s) + O_2(g) \xrightarrow{\Delta} SO_2\,(g)$$

$$4FeS_2(s) + 11O_2(g) \xrightarrow{\Delta} 2Fe_2O_3(s) + 8SO_2(g)$$

ii. **Sulfur dioxide is oxidised catalytically** with oxygen to sulfur trioxide, in the presence of V_2O_5 catalyst.

$$2SO_2(g) + O_2 \xrightarrow{V_2O_5} 2SO_3(g)$$

The reaction is exothermic and reversible and the forward reaction leads to decrease in volume. Therefore low temperature (720K) and high pressure (2 bar) are favourable conditions for maximum yield of SO_3.

iii. **Sulfur trioxide gas** (from the catalytic converter) **is absorbed in concentrated H_2SO_4** to produce oleum.

Dilution of oleum with water gives sulfuric acid of desired concentration.

$$SO_3(g) + H_2SO_4 \longrightarrow \underset{\text{oleum}}{H_2S_2O_7}$$

$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

The sulfuric acid obtained by contact process is 96 - 98 % pure.

b. Physical properties of H_2SO_4 :

i. Sulfuric acid is a colourless, dense, oily liquid.

ii. It has a density (specific gravity) of 1.84 g/cm^3 at 298 K.

iii. It freezes at 283 K and boils at 611 K.

iv. It is highly corrosive and produces severe burns on the skin.

Do you know ?

Sulfuric acid dissolves in water with the evolution of a large quantity of heat. Hence care must be taken while preparing solution of sulfuric acid from concentrated sulfuric acid. Concentrated H_2SO_4 must be added slowly to water with constant stirring by keeping the beaker in water bath.

c. Chemcial Properties :

i. Acidic Property : Sulfuric acid ionises in aqueous solution in two steps.

$$H_2SO_4(aq)+H_2O(l) \longrightarrow H_3O^{\oplus}(aq)+HSO_4^{\ominus}(aq) \qquad K_a > 10$$

$$HSO^{\ominus}_4(aq)+ H_2O(l) \longrightarrow H_3O^{\oplus}(aq) + SO_4^{2\ominus}(aq) \qquad K_a = 1.2 \times 10^{-2}$$

The greater value of K_a (K_a>10) means that H_2SO_4 is largely dissociated into $H^{\oplus}$ and $HSO_4^{\ominus}$ ions. Thus H_2SO_4 is a strong acid.

ii. Reaction with metals and nonmetals (oxidising property) : Metals and nonmetals both are oxidised by hot, concentrated sulfuric acid which itself gets reduced to SO_2.

$$Cu + \underset{\text{(Conc.)}}{2H_2SO_4} \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$\underset{\text{(Conc.)}}{S + 2H_2SO_4} \longrightarrow 3SO_2 + 2H_2O$$

$$\underset{\text{(Conc.)}}{C + 2H_2SO_4} \longrightarrow CO_2 + 2SO_2 + 2H_2O$$

Remember...
Oxidizing properties of sulfuric acid depend on its concentration and temperature. In dilute solutions, at room temperature, H_2SO_4 behaves like HCl, oxidizing metals that stand above hydrogen in the e.m.f. series.

$$Fe\ (s) + 2\ H^{\oplus}\ (aq) \longrightarrow Fe^{2\oplus}\ (aq) + H_2\ (g)$$

Hot, concentrated H_2SO_4 is a better oxidizing agent than the dilute, cold acid. It oxidises metals like copper.

iii. Dehydrating property : Concentrated sulfuric acid is a strong dehydrating agent.

Sulfuric acid removes water from sugar and carbohydrates. Carbon left behind is called sugar charcoal and the process is called charring.

$$C_{12}H_{22}O_{11} \xrightarrow{\text{conc. } H_2SO_4} 12C + 11H_2O$$

iv. Reaction with salts : Concentrated sulfuric acid decomposes the salts of more volatile acids to the corresponding acid

e.g. $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

Problem 7.10 : What is the action of concentrated H_2SO_4 on (a) HBr (b) HI

Solution : Concerntrated sulfuric acid oxidises hydrobromic acid to bromine.

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

It oxidises hydroiodic acid to iodine.

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

d. Uses : Sulfuric acid is a very important industrial chemical. It is used

- In the manufacture of fertilizers. For example, ammonium sulfate, superphosphate, etc.
- In the manufacture of pigments, paints and dyestuff intermediates.
- In petroleum refining.
- In detergent industry.
- In metallurgy, for cleaning of metals electroplating and galvanising.
- In storage batteries.
- As a laboratory reagent.
- In the manufacture of nitrocellulose products.

7.11 Chlorine and compounds of chlorine

7.11.1 Chlorine : Chlorine was discovered by Scheele, a German Swedish chemist in 1774 by the action of HCl on MnO_2. In 1810, Davy established its elementary nature and suggested the name chlorine on account of its colour.
(Greek, Chloros = greenish yellow).

a. Preparation :

1. Chlorine can be prepared by the oxidation of hydrochloric acid with any of the following oxidising agents.

i. Manganese dioxide :

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

ii. Potassium permanganate :

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

2. Chlorine can also be prepared by the action of concentrated sulfuric acid on a mixture of sodium chloride (common salt) and manganese dioxide. The reaction takes place in two steps.

$$4NaCl + 4H_2SO_4 \longrightarrow 4NaHSO_4 + 4HCl$$

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow 4NaHSO_4 + MnCl_2 + 2H_2O + Cl_2$$

b. Manufacture of chlorine :

i. Deacon's process :

Chlorine is manufactured by the oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ as catalyst at 723 K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

ii. Electrolytic process :

By the electrolysis of brine (concentrated NaCl solution), chlorine is liberated at the anode.

$$NaCl \rightleftharpoons Na^{\oplus} + Cl^{\ominus}$$

Cathode: $2H_2O + 2e^{\ominus} \longrightarrow H_2 + 2OH^{\ominus}$

$Na^{\oplus} + OH^{\ominus} \longrightarrow NaOH$

Anode : $Cl^{\ominus} \longrightarrow Cl + e^{\ominus}$

$Cl + Cl \longrightarrow Cl_2$

c. Physical Properties of Chlorine :

i. Chlorine is a greenish-yellow gas having pungent and suffocating odour.

ii. It is poisonous in nature.

iii. It can be easily liquified into a greenish yellow liquid, which boils at 293 K.

iv. It dissolves in water to give chlorine water.

v. It is 2-5 times heavier than air.

d. Chemical properties of chlorine :

i. Reaction with metals : Chlorine reacts with metals to form chlorides.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

$$2Na + Cl_2 \longrightarrow 2NaCl$$

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

ii. Reaction with nonmetals : Chlorine reacts with nonmetals to form their chlorides.

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

$$S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$$

iii. Affinity for hydrogen : Chlorine has great affinity for hydrogen. It reacts with hydrogen and compounds containing hydrogen to form HCl.

$$H_2 + Cl_2 \longrightarrow 2HCl$$

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

iv. Reaction with NH_3 : Chlorine when reacted with excess of ammonia gives ammonium chloride and nitrogen.

$$\underset{\text{(Excess)}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

Excess of chlorine reacts with ammonia to give nitrogen trichloride (explosive).

$$NH_3 + \underset{\text{(Excess)}}{3Cl_2} \longrightarrow NCl_3 + 3HCl$$

v. Reaction with alkali : Chlorine reacts with cold and dilute alkali to produce a mixture of chloride and hypochlorite. When reacted with hot concentrated alkali, chloride and chlorate are produced.

$$\underset{\text{(Cold and dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

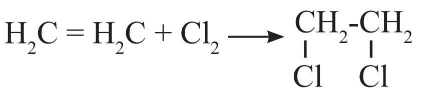
$$\underset{\text{(Hot and conc.)}}{6NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

Chlorine when reacted with dry slaked lime gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

vi. Reaction with hydrocarbons : Chlorine reacts with saturated hydrocarbons to give substitution products and with unsaturated hydrocarbons gives addition products.

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{U.V} \underset{\text{Methylchloride}}{CH_3Cl + HCl}$$



$$H_2C = H_2C + Cl_2 \longrightarrow \underset{Cl}{CH_2}-\underset{Cl}{CH_2}$$

Ethene 1,2 - Dichloroethane

vii. Oxidising property : Chlorine oxidises ferrous salts to ferrric salts and sulfites to sulfates.

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

It oxidises sulfur dioxide to sulfur trioxide and iodine to iodate. In presence of water they form sulfuric acid and iodic acid respectively.

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$$

viii. Bleaching Property : Chlorine requires the presence of moisture (water) for bleaching. It liberates nascent oxygen from water which is responsible for its oxidising and bleaching property

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$HOCl \longrightarrow HCl + [O]$$

Chlorine bleaches vegetable matter or coloured organic matter in the presence of moisture to colourless matter.

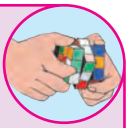
Coloured organic matter + [O] ⟶ Colourless organic matter

e. Uses :

Chlorine is used

- For purification (sterilizing) of drinking water.
- For bleaching wood pulp required for manufacture of paper and rayon, bleaching cotton and textiles.
- For extraction of metals like gold and platinum.
- In the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc.
- In the preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

Try this...



i. Give the reasons for bleaching action of chlorine.

ii. Name the two gases used in war.

Do you know ?

Bleaching by chlorine is permanent. It bleaches cotton fabrics, wood pulp, litmus, etc. However chlorine is not used to bleach delicate materials such as silk, wool etc. as it is a strong bleaching and oxidising agent. This dual action will damage the base material.

7.11.2 Hydrogen Chloride : Hydrogen chloride was prepared by Glauber in 1648 by heating common salt with concentrated sulfuric acid. Davy in 1810 showed that it is a compound of hydrogen and chlorine.

a. Preparation : In the laboratory, hydrogen chloride is prepared by heating sodium chloride (common salt) with concentrated sulfuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{420\ K} Na_2SO_4 + HCl$$

HCl gas can be dried by passing it through concentrated sulfuric acid.

a. Physical properties of HCl

i. Hydrogen chloride is a colourless and pungent smelling gas.

ii. It can be easily liquified to a colourless liquid (b.p. 189 K) which freezes to a white crystalline solid (m.p. 159 K)

iii. It is highly soluble in water.

Chemical properties :

i. Acidic property : Hydrogen chloride is highly soluble in water and ionises as follows :

$$HCl\ (g) + H_2O\ (l) \longrightarrow H_3O^{\oplus}\ (aq) + Cl^{\ominus}\ (aq)$$

$$K_a = 10^7$$

The aqueous solution of HCl gas is called hydrochloric acid. High value of dissociation constant (K_a) indicates that it is a strong acid in water.

ii. Reaction with NH_3 : Hydrochloric acid reacts with ammonia and gives white fumes of ammonium chloride.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

iii. Reaction with noble metals : When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed.

Noble metals like gold, platinum get dissolved in aqua regia.

$$Au + 4\,H^{\oplus} + NO_3^{\ominus} + 4Cl^{\ominus} \longrightarrow AuCl_4^{\ominus} + NO + 2H_2O$$

$$3Pt + 16\,H^{\oplus} + 4NO_3^{\ominus} + 18Cl^{\ominus} \longrightarrow 3PtCl_6^{2\ominus} + 4NO + 8H_2O$$

Can you recall ?

- Which type of bonds do halogens form with other elements?
- Does BrF_5 obey the octet rule?
- What is the oxidation state of Br in BrF_5?
- How many electrons do halogens require to complete their octet ?
- What is the shape of CIF_3?

7.12 Interhalogen compounds

We have seen that all halogen molecules are diatomic. They form binary compounds with hydrogen, with oxygen they form oxyacids, and with halogens they form interhalogen compounds.

Although all halogens belong to the same group they have different electronegativites. Due to this difference in electronegativity two or more halogen atoms combine to form species which may be ionic or neutral. The neutral molecules are called **Interhalogen compounds**. For example, CIF, BrF_3.

An interhalogen compound is a compound formed by combination of atoms of different halogens. The interhalogen compound is regarded as the halide of the more electropositive halogen. A given halogen forms an interhalogen compound only with the halogen having lesser electronegativity.

Do you know ?

The ions formed by combination of different halogens are called **polyhalide ions** or interhalogen ions, For example, $K^{\oplus}[Cl_3^{\ominus}]$, $[NH_4]^{\oplus}$ $[I_5]^{\ominus}$, which contain $Cl_3^{\ominus}$ and $I_5^{\ominus}$ ions.

Use your brain power

- Chlorine and fluorine combine to form interhalogen compounds. The halide ion will be of chlorine or fluorine ?
- Why does fluorine combine with other halogens to form maximum number of fluorides ?

Table 7.9 Various types of interhalogen compounds

Element	Fluoride	Chloride	Bromide	Iodide
Chlorine	CIF, CIF_3, CIF_5	-	-	-
Bromine	BrF, BrF_3, BrF_5	BrCl	-	-
Iodine	IF, IF_3, IF_5, IF_7	ICl, ICl_3	IBr	-

Do you know ?

ICl Iodine monochloride in glacial acetic acid called Wijs solution is used in determination of iodine value of an oil.

7.12.1 Classification :

Depending on their composition, interhalogen compounds are classified into four types.

Type	Example
XX'	CIF, BrF, BrCl, ICl, IBr
XX'_3	CIF_3, BrF_3, IF_3
XX'_5	CIF_5, BrF_5,IF_5
XX'_7	IF_7

In the general formula XX'_n. X is the halogen having larger size and is more electropositive. X' is the halogen having smaller size and more electronegativity.

7.12.1 General characteristics of interhalogen compounds

1. The compound is considered as the halide of X. For example, ClF. Here the halogen having larger size is chlorine, it is more electropositive than F and hence the interhalogen compound is named as chlorine monofluoride. (n) is the number of atoms of X' attached to X.

As the ratio [radius of X : radius of X'] increases the value of n also increases.

2. Interhalogen compounds have even number of atoms 2, 4, 6, 8. For example, ClF_3 has 4 atoms.

3. The properties of interhalogen compounds are generally intermediate between those of the halogens from which they are made.

4. The central halogen exhibits different oxidation states in different interhalogen compounds.

5. Number of X' atoms in the compounds is always odd.

6. They are all diamagnetic .

Use your brain power

- What will be the names of the following compounds : ICl, BrF.
- Which halogen (X) will have maximum number of other halogen (X') attached?

Do you know ?

XX' compounds are more reactive than X_2 or X'_2. In the X-X' bond X' is more electronegative than X, while in X_2 and X'_2 both atoms have same electronegativity, hence the X-X' bond energy is less than the X-X or X'-X' bond energy.

Use your brain power

- Which halogen has tendency to form more interhalogen compounds?

Use your brain power

- Which will be more reactive ?

a. ClF_3 or ClF, b. BrF_5 or BrF

- Complete the table

Formula	Name
ClF	Chlorine monofluoride
ClF_3	……….
……….	Chlorine penta fluoride
BrF	……….
……….	Bromine penta fluoride
ICl	……….
ICl_3	……….

Table 7.10 : States of Interhalogen compounds at 25°C

XX'	
ClF	Colorless gas
BrF	Pale brown gas
BrCl	Gas
ICl	Ruby red solid (α- form) Brown red soid (β - form)
IBr	Black solid
XX'_3	
ClF_3	Colorless gas
BrF_3	Yellow green liquid
IF_3	Yellow powder
ICl_3	Orange solid dimerises to form (I_2Cl_6 having Cl - bridges)
XX'_5	
IF_5	Colorless gas at R. T. but solid below 77 K
BrF_5	Colorless liquid
ClF_5	Colorless liquid
XX'_7	
IF_7	Colorless gas

Methods of Preparation of Interhalogen compounds

Method	XX’	XX’$_3$
1.Direct combination	Both in equal volumes $Cl_2+F_2 \xrightarrow[\text{Cu-vessel}]{523\text{ K}} 2ClF$ $I_2+Cl_2 \xrightarrow[\text{boil}]{HCl + HNO_3} 2ICl$ $Br_2+Cl_2 \longrightarrow 2BrCl$	Cl_2+3F_2 (excess)$\longrightarrow$2ClF3 Br2+3F2$\longrightarrow$2BrF3 I_2+3Cl_2(excess)$\longrightarrow 2ICl_3$
2.Reaction of halogen with interhalogen compounds.	$Br_2+BrF_3 \longrightarrow 3BrF$	Br_2+ ClF3 $\longrightarrow$2BrF3+ BrCl
Special reaction for ICl	$I_2+KClO_3 \xrightarrow{\Delta} ICl+KIO_3$	-------

Use your brain power

In the above special reaction for ICl, identify the oxidant and reductant ? Denote oxidation states of the species.

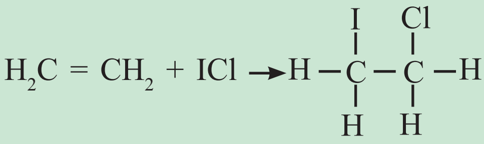
Do you know ?

ICl in liquid state, undergoes autoionization like water, to form a cation and an anion.

$$2\ ICl \rightleftharpoons I^{\oplus} + ICl_2^{\ominus}$$

(solvent cation) (solvent anion)

Some Properties of Interhalogen compounds

	Reaction/Property	XX’	XX’$_3$
1	Thermal stability	ClF > ICl > IBr > BrCl > BrF	
2	Hydrolysis Gives oxoacids	$BrCl+H_2O \longrightarrow HOBr+HCl$ $5ICl+3H_2O \longrightarrow HIO_3+5HCl+2I_2$	$ICl_3+H_2O \longrightarrow$ $HIO_3+5HCl+ICl$
3	Disproportionation/ Autoionisation	$BrF \longrightarrow 2Br_2 + BrF_5$	$2ClF_3 \rightarrow ClF_2^{\oplus}+ClF_4^{\ominus}$ $ICl_3 \xrightarrow{341\text{ K}} ICl + Cl_2$
4	Flourination	---------	$U+ClF_3 \longrightarrow UF_6(l)+ClF(g)$
5	Addition across olefins	 $H_2C = CH_2 + ICl \rightarrow H-\underset{H}{\overset{I}{C}}-\underset{H}{\overset{Cl}{C}}-H$	

Uses of interhalogen compound

XX'	XX'$_3$
ICl is used to determine iodine value of oils	For Preparation of polyhalides
As catalyst for oxidation of As(III)	As fluorinating agent
For Preparation of polyhalides	As nonaqueous solvent

Table 7.11 Structures of some Interhalogen Compounds

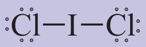
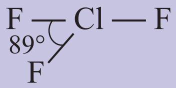
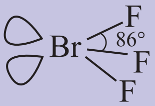
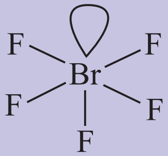
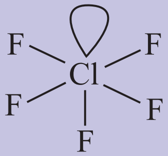
Formula	Name	Structure	Shape
ICl	Iodine monochloride		Linear
ClF_3	Chloride trifluoride		Bent T- shaped
BrF_3	Bromine trifluoride		Bent T- shaped
BrF_5	Bromine pentafluoride		Square Pyramidal
ClF_5	Chlorine pentafluoride		Square pyramidal

Table 7.12 Oxidation states of central halogen atom in interhalogen compounds.

O.S. central Halogen	No. of lone pairs of electrons	Examples
+7	0	IF_7
+5	1	ClF_5, BrF_5, IF_5
+3	2	ClF_3, BrF_3, IF_3, I_2Cl_6
+1	3	ClF, BrF, IF, BrCl, ICl, IBr

7.13 Compounds of Xenon

Can you recall ?

- What is the correlation between ionization energies and reactivity of elements?
- Trends in ionization energy down a group.

We have studied earlier in this chapter that group 18 elements have very high ionisation energies and due to this property they are unreactive. Each noble gas atom has a completely filled valence electron shell which makes it inert.

The first ionization potential decreases down the group, hence heavier noble gases Kr, Xe and Rn can form compounds due to low ionization energy.

Do you know ?

First true compound of noble gas was made in 1962 by Neil Bartelt and Lohman.

$$Xe + 2[PtF_6] \rightleftharpoons [XeF]^{\oplus}\ [Pt_2F_{11}]^{\ominus}$$

Only Xenon reacts directly with fluorine to form Xenon fluorides.

Remember...

XeF_2, XeF_4, XeF_6 are stable fluoride of xenon.

Xenon also forms compounds with oxygen, such as XeO_3, $XeOF_2$, $XeOF_4$, XeO_2F_2.

7.13.1 Xenon fluorides

a. Preparation of Xenon Fluorides : Xenon fluorides are generally prepared by direct reaction of xenon and fluorine in different ratios and conditions, such as temperature, electric discharge and photochemical reaction.

i. $Xe + F_2 \xrightarrow[\text{Ni tube, 400}^{0}\text{C}]{\text{sealed}} XeF_2$

iv. $Xe + F_2 \xrightarrow[\text{5-6 atmos}]{\text{Ni tube, 400}^{0}\text{C}} XeF_4$
$1 : 5$

v. $Xe + 2F_2 \xrightarrow[-80\ ^{0}\text{C}]{\text{electric discharge}} XeF_4$

vi. $Xe + 3F_2 \xrightarrow[\text{low temp.}]{\text{electric discharge}} XeF_6$

b. Important chemical reactions of XeF_2

i. **Hydrolysis :** XeF_2 undergoes hydrolysis to form HF

$$2XeF_2 + 2H_2O \longrightarrow 4HF + 2Xe + O_2$$

ii. **Reaction with PF_5 :** XeF_2 forms adducts on reaction with PF_5.

$$XeF_2 + PF_5 \longrightarrow XeF_2.PF_5$$

7.13.2 Xenon trioxide

a. Preparation of Xenon trioxide (XeO_3) :

Fluorides of Xenon react with water to form XeO_3.

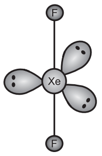
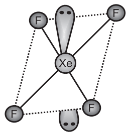
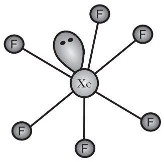
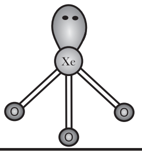
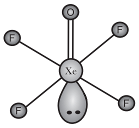
$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12\ HF + 1\frac{1}{2}\ O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

7.13.3 Oxyfluorides of Xenon : Xenon forms the following oxyfluorides :

$XeOF_2$, XeO_2F_2, XeO_3F_2, XeO_2F_4

Table 7.13 : Structure of Xenon Compounds

Sr. No.	Formula	Oxidation state of Xe	Structure
1.	XeF_2	+2	Linear 
2.	XeF_4	+4	Square planar 
3.	XeF_6	+6	Distorted octahedral 
4.	XeO_3	+6	Trigonal pyramidal 
5.	$XeOF_4$	+6	Square pyamidal 

a. Preparation

i. Partial hydrolysis of Xenon fluorides yields different oxyfluorides.

$$XeF_4 + H_2O \xrightarrow{80\ ^{0}C} XeOF_2 + 2HF$$

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

ii. Reaction of Xenon oxyfluoride with SiO_2 or hydrolysis yields xenon dioxydifluoride.

$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$

$$XeOF_4 + H_2O \longrightarrow XeO_2F_2 + 2HF$$

Use your brain power

What are the missing entries ?

Formula	Name
$XeOF_2$....................	Xenon mono oxyfluoride
....	Xenon dioxydifluoride
XeO_3F_2	....
XeO_2F_4	....

Table 7.14 : Uses of helium, neon and argon

Element	Uses
Helium	i. Mixture of He and O_2 is used for artificial breathing of asthma patients. ii. Mixture of He and O_2 is used for respiration by sea divers. iii. For filling balloons, a mixture of helium (85%) and hydrogen (15 %) is used. iv. Helium is used for producing inert atmosphere required for welding purpose and metallury of some metals. v. Liquid helium is used for producing low temperature required for research. vi. In low temperature gas thermometry, for production of lasers. vii. Used to pressurise fuel tanks of liquid fueled rockets. viii. Used as shielding gas for arc welding. ix. In supersonic wind tunnels. x. Helium nucleus is used as a bombarding particle for disintegration of atoms. xi. Used for magnetic resonance imaging.
Neon	i. In Neon discharge lamps and signs. These signs are visible from the long distances and also in mist or fog. ii. Mixture of Ne and He is used in certain protective electrical devices such as voltage stabilizers and current rectifiers. iii. For production of lasers. iv. In fluorescent tubes.
Argon	i. For producing inert atmosphere in welding and steel production. ii. Mixture of 85 % Ar and 15 % N_2 is filled in electric bulb to increase life of filament. iii. In filling fluorescent tubes and radio valves. iv. It is mixed with neon to get lights of various colors.

Exercises

1. Select appropriate answers for the following.

i. Which of the following has highest electron gain enthalpy ?
A. Fluorine   B. Chlorine
C. Bromine   D. Iodine

ii. Hydrides of group 16 are weakly acidic. The correct order of acidity is
A. $H_2O > H_2S > H_2Se > H_2Te$
B. $H_2Te > H_2O > H_2S > H_2Se$
C. $H_2Te > H_2Se > H_2S > H_2O$
D. $H_2Te > H_2Se > H_2O > H_2S$

iii. Which of the following element does not show oxidation state of +4 ?
A. O   B. S   C. Se   D. Te

iv. HI acid when heated with conc. H_2SO_4 forms
A. HIO_3 B. KIO_3
C. I_2 D. KI

v. Ozone layer is depleted by
A. NO   B. NO_2
C. NO_3 D. N_2O_5

vi. Which of the following occurs in liquid state at room temperature ?
A. HIO_3 B. HBr
C. HCl   D. HF

vii. In pyrosulfurous acid oxidation state of sulfur is
A. Only +2   B. Only +4
C. +2 and +6   D. Only +6

viii. Stability of interhalogen compounds follows the order
A. BrF > IBr > ICl > ClF > BrCl
B. IBr > BeF > ICl > ClF > BrCl
C. ClF > ICl > IBr > BrCl > BrF
D. ICl > ClF > BrCl > IBr > BrF

ix. BrCl reacts with water to form
A. HBr   B. $Br_2 + Cl_2$
C. HOBr   D. HOBr + HCl

x. Chlorine reacts with excess of fluorine to form.
A. ClF   B. ClF_3
C. ClF_2 D. Cl_2F_3

xi. In interhalogen compounds, which of the following halogens is never the central atom.
A. I   B. Cl   C. Br   D. F

xii. Which of the following has one lone pair of electrons ?
A. IF_3 B. ICl
C. IF_5 D. ClF_3

xiii. In which of the following pairs, molecules are paired with their correct shapes ?
A. $[I_3]$: bent
B. BrF_5 : trigonal bipyramid
C. ClF_3 : trigonal planar
D. $[BrF_4]$: square planar

xiv. Among the known interhalogen compounds, the maximum number of atoms is
A. 3   B. 6   C. 7   D. 8

2. Answer the following.

i. Write the order of the thermal stability of the hydrides of group 16 elements.

ii. What is the oxidation state of Te in TeO_3 ?

iii. Name two gases which deplete ozone layer.

iv. Give two uses of ClO_2

v. What is the action of bromine on magnesium metal ?

vi. Write the names of allotropic forms of selenium.

vii. What is the oxidation state of S in H_2SO_4.

viii. The pK_a values of HCl is -7.0 and that of HI is -10.0. Which is the stronger acid ?

ix. Give one example showing reducing property of ozone.

x. Write the reaction of conc. H_2SO_4 with sugar.

xi. Give two uses of chlorine.

xii. Complete the following.

1. $ICl_3 + H_2O \longrightarrow$ .... + ... + ICl
2. $I_2 + KClO_3 \longrightarrow$ .... + KIO_2
3. $BrCl + H_2O \longrightarrow$ .... + HCl
4. $Cl_2 + ClF_3 \longrightarrow$ ....
5. $H_2C = CH_2 + ICl \longrightarrow$ ....
6. $XeF_4 + SiO_2 \longrightarrow$ .... + SiF_4
7. $XeF_6 + 6H_2O \longrightarrow$ .... + HF
8. $XeOF_4 + H_2O \longrightarrow$ .... + HF

xiii. Match the following

A	B
$XeOF_2$	Xenon trioxydifluoride
XeO_2F_2	Xenon monooxydifluoride
XeO_3F_2	Xenon dioxytetrafluoride
XeO_2F_4	Xenon dioxydifluoride

xiv. What is the oxidation state of xenon in the following compounds.
$XeOF_4$, XeO_3, XeF_6, XeF_4, XeF_2.

3. Answer the following.

i. The first ionisation enthalpies of S, Cl and Ar are 1000, 1256 and 1520 kJ/mol^{-1}, respectively. Explain the observed trend.

ii. "Acidic character of hydrides of group 16 elements increases from H_2O to H_2Te" Explain.

iii. How is dioxygen prepared in laboratory from $KClO_3$?

iv. What happens when
a. Lead sulfide reacts with ozone (O_3).
b. Nitric oxide reacts with ozone.

v. Give two chemical reactions to explain oxidizing property of concentrated H_2SO_4.

vi. Discuss the structure of sulfure dioxide.

vii. Fluorine shows only -1 oxidation state while other halogens show -1, +1, +3, +5 and +7 oxidation states. Explain.

viii. What is the action of chlorine on the following
a. Fe b. Excess of NH_3

ix. How is hydrogen chloride prepared from sodium chloride ?

x. Draw structures of XeF_6, XeO_3, $XeOF_4$, XeF_2.

xi. What are inter-halogen compounds ? Give two examples.

xii. What is the action of hydrochloric acid on the following ?
a. NH_3 b. Na_2CO_3

xiii. Give two uses of HCl.

xiv. Write the names and structural formulae of oxoacids of chlorine.

xv. What happens when
a. Cl_2 reacts with F_2 in equal volume at 437 K.
b. Br_2 reacts with excess of F_2.

xvi. How are xenon fluorides XeF_2, XeF_4 and XeF_6 obtained ? Give suitable reactions.

xvii. How are XeO_3 and $XeOF_4$ prepared ?

xviii. Give two uses of neon and argon.

xix. Describe the structure of Ozone. Give two uses of ozone.

xx. Explain the trend in following atomic properties of group 16 elements.

i. Atomic radii ii. Ionisation enthalpy

iii. Electronegativity.

4. Answer the following.

i. Distinguish between rhombic sulfur and monoclinic sulfur.

ii. Give two reactions showing oxidising property of concentrated H_2SO_4.

iii. How is SO_2 prepared in laboratory from sodium sulfite? Give two physical properties of SO_2.

iv. Describe the manufacturing of H_2SO_4 by contact process.

8. TRANSITION AND INNER TRANSITION ELEMENTS

Do you know ?

In which block of the modern perodic table are the transition and inner transition elements placed ?

8.1 Introduction

The transition elements belong to d block of the periodic table. As per IUPAC convention the transition metal atom has an incomplete d-subshell or it give cations with incomplete d subshell. They exhibit properties between those of s and p block elements. The transition elements of the modern periodic table appear as groups 3 to 12 or as four long periods. The (n-1) d-orbital is comprised of successively filled in each element, where ‘n’ is the ultimate or valence shell. The 3d series is comprised of elements from scandium (Z=21) to zinc (Z=30), 4d series has elements from yttrium (Z=39) to cadmium (Z=48), 5d series from lanthanum (Z=57) to mercury (Z=80) without those from cerium to lutecium, and 6d series has actinium to curium without those fromthorium to lawrentium. The general electronic configuration of transition elements is $(n\text{-}1)d^{1\text{-}10}\ ns^{1\text{-}2}$.

8.2 Position in the periodic table

The transition elements are placed in the periods 4 to 7 and groups 3 to 12 those constitute 3d, 4d, 5d and 6d series (Fig.8.1).

They are placed at the centre with s block on one side and p on the other. The electropositivity, reactivity and other properties show a gradual change from s block to p block through those of the d block elements.

8.3 Electronic configuration

The 3d series begins with Sc (Z = 21) and ends with Zn (Z=30). Argon, Ar is the noble gas preceding to 3d series and its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. Calcium (Z = 20) belonging to ‘s’ block of 4th period has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. Hence 21st electron in scandium (Z = 21) enters in the available 3d orbital. Electronic configuration of Sc is written as $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$ or also can be represented as $[Ar]\ 3d^1\ 4s^2$.

Table 8.1 Shows the four transition series elements

Group / d series	3	4	5	6	7	8	9	10	11	12
3d	Sc(21)	Ti(22)	V(23)	Cr(24)	Mn(25)	Fe(26)	Co(27)	Ni(28)	Cu(29)	Zn(30)
4d	Y(39)	Zr(40)	Nb(41)	Mo(42)	Tc(43)	Ru(44)	Rh(45)	Pd(46)	Ag(47)	Cd(48)
5d	La(57)	Hf(72)	Ta(73)	W(74)	Re(75)	Os(76)	Ir(77)	Pt(78)	Au(79)	Hg(80)
6d	Ac(89)	Rf(104)	Db(105)	Sg(106)	Bh(107)	Hs(108)	Mt(109)	Ds(110)	Rg(111)	Cn(112)

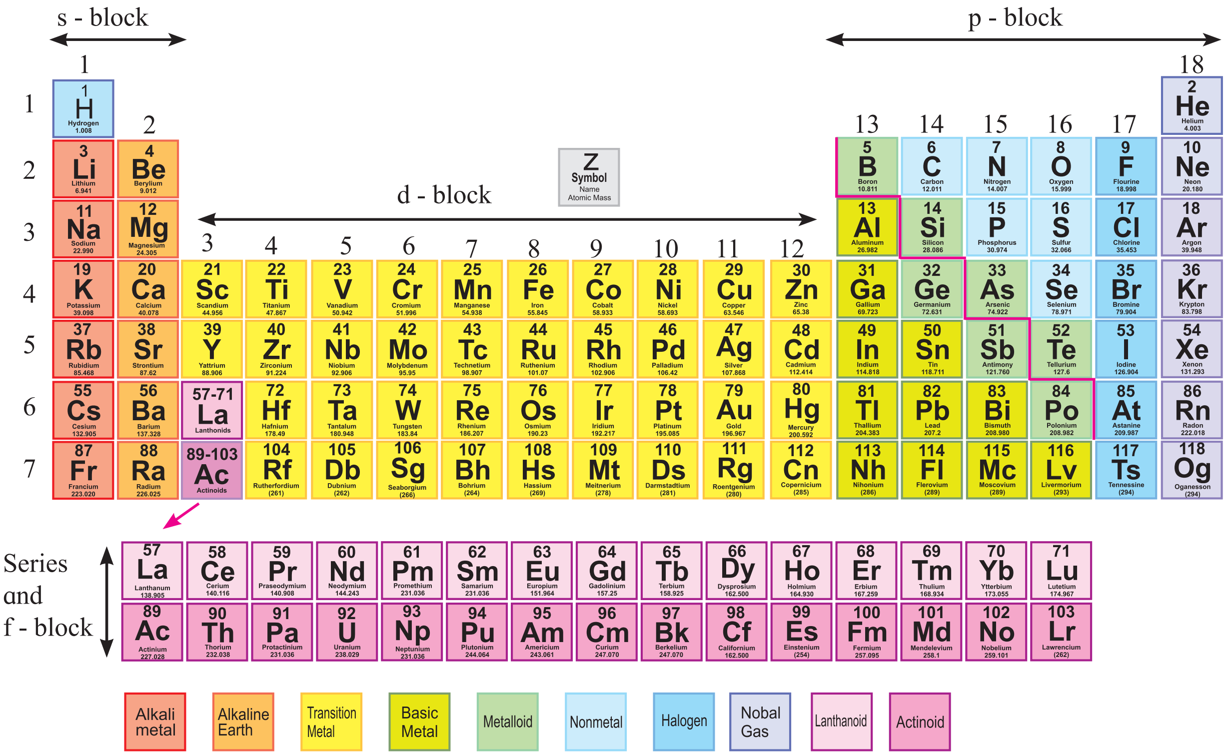


Fig. 8.1 Position of d-block elements in the modern periodic table

The electronic configuration of the elements of 3d series is given in Table 8.2.

Since zinc has completely filled (n - 1)d orbital in the ground state ($3d^{10}$,$4s^2$) and ($3d^{10}$) in its common oxidation state +2, it is not regarded as transition element. On the same ground, cadmium and mercury from 4d and 5d series are not considered as transition elements. Copper in the elementary state ($3d^{10}$ $4s^1$) contains filled 3d orbitals but in the +2 oxidation state it has partly filled 3d orbital ($3d^9$), hence copper is a transition element.

General electronic configuration of four series of d-block elements of periodic table can be represented as given below:

i. 3d series : [Ar] $3d^{1-10}$ $4s^2$

ii. 4d series : [Kr] $4d^{1-10}$ $5s^{0-2}$

iii. 5d series : [Xe] $5d^{1-10}$ $6s^2$

iv. 6d series : [Rn] $6d^{1-10}$ $7s^2$

8.3.1 Electronic configuration of chromium and copper

Table 8.2 indicates that the expected electronic configuration of chromium (Z = 24) differs from the observed configuration.

This can be explained on the basis of the concept of additional stability associated with the completely filled and half filled subshells.

Remember...

Any subshell having a half filled or completely filled electronic configuration has extra stability.

The general electronic configuration of the elements of the 3d series is $3d^{1-10}$ $4s^2$ with the exceptions of Cr and Cu. The 3d and 4s orbitals are close in energy and in order to gain extra stability the last electron instead of occupying 4s orbital occupies the 3d orbital that assigns Cr the $3d^5$, $4s^1$ and Cu $3d^{10}$, $4s^1$ configuration.

Table 8.2 Electronic configuration of 3d series of d-block elements

Elements	Symbol	At. No.	Expected electronic configuration	Observed electronic configuration
Scandium	Sc	21	[Ar] $3d^1 4s^2$	[Ar] $3d^1 4s^2$
Titanium	Ti	22	[Ar] $3d^2 4s^2$	[Ar] $3d^2 4s^2$
Vanadium	V	23	[Ar] $3d^3 4s^2$	[Ar] $3d^3 4s^2$
Chromiun	Cr	24	[Ar] $3d^4 4s^2$	[Ar] $3d^5 4s^1$
Manganese	Mn	25	[Ar] $3d^5 4s^2$	[Ar] $3d^5 4s^2$
Iron	Fe	26	[Ar] $3d^6 4s^2$	[Ar] $3d^6 4s^2$
Cobalt	Co	27	[Ar] $3d^7 4s^2$	[Ar] $3d^7 4s^2$
Nickel	Ni	28	[Ar] $3d^8 4s^2$	[Ar] $3d^8 4s^2$
Copper	Cu	29	[Ar] $3d^9 4s^2$	[Ar] $3d^{10} 4s^1$
Zinc	Zn	30	[Ar] $3d^{10} 4s^2$	[Ar] $3d^{10} 4s^2$

Use your brain power

Fill in the blanks with correct outer electronic configurations.

2nd series										
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
valence shell electronic configuration	$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$		$4d^6 5s^1$		$4d^8 5s^1$	$4d^{10} 5s^0$		$4d^{10} 5s^2$
3rd series										
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
valence shell electronic configuration	$5d^1 6s^2$		$5d^3 6s^2$	$5d^4 6s^2$		$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$		$5d^{10} 6s^2$
4th series										
	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uvb
Z	89	104	105	106	107	108	109	110	111	112
valence shell electronic configuration	$6d^1 7s^2$	$6d^2 7s^2$		$6d^4 7s^2$	$6d^5 7s^2$	$6d^6 7s^2$	$6d^7 7s^2$	$6d^8 7s^2$		$6d^{10} 7s^2$

Table 8.3: Oxidation states of first transition series elements

Elements	Outer elecronic configuration	Oxidation states	Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+2, +3	Fe	$3d^6 4s^2$	+2, +3, +4, +5, +6
Ti	$3d^2 4s^2$	+2, +3, +4	Co	$3d^7 4s^2$	+2, +3, +4, +5
V	$3d^3 4s^2$	+2, +3, +4, +5	Ni	$3d^{10} 4s^2$	+2, +3, +4
Cr	$3d^5 4s^1$	+2, +3, +4, +5, +6	Cu	$3d^{10} 4s^1$	+1, +2
Mn	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7	Zn	$3d^{10} 4s^2$	+2

Remember...

Electronic configuration of Cr is [Ar] $3d^5\ 4s^1$ and

Cu is : [Ar]$3d^{10}$, $4s^1$.

8.4 Oxidation states of first transition series

One of the notable features of transition elements is the great variety of oxidation states they show in their compounds. Table 8.3 lists the common oxidation states of the first row transition elements.

Can you tell ?

Which of the first transition series elements shows the maximum number of oxidation states and why?

Which elements in the 4d and 5d series will show maximum number of oxidation states?

Loss of 4s and 3d electrons progressively leads to formation of ions. The transition elements display a variety of oxidation states in their compounds. Loss of one 4s electron leads to the formation of $M^{\oplus}$ ion, loss of two 4s electrons gives a $M^{2\oplus}$ ion while loss of unpaired 3d and 4s electrons gives $M^{3\oplus}$, $M^{4\oplus}$ ions and so on. Some examples are as shown in Table 8.4

Try this...

Write the electronic configuration of $Mn^{6\oplus}$, $Mn^{4\oplus}$, $Fe^{4\oplus}$, $Co^{5\oplus}$, $Ni^{2\oplus}$

From Table 8.3 it is clear that as the number of unpaired electrons in 3d orbitals increases, the number of oxidation states shown by the element also increases. Scandium has only one unpaired electron. It shows two oxidation states while manganese with 5 unpaired d electrons shows six different oxidation states.

The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, shows oxidation states from +2 to +7.

8.5 Physical properties of first transition series : All transition elements are metals and show properties that are characteristic of metals. They are hard, lustrous, malleable, ductile and form alloys with other metals. They are good conductors of heat and electricity. Except Zn, Cd, Hg and Mn, all the other transition elements have one or more typical metallic structures at ambient temperature. These transition metals (with the exception of Zn, Cd and Hg) are very hard and have low volatility. They possess high melting and boiling points.

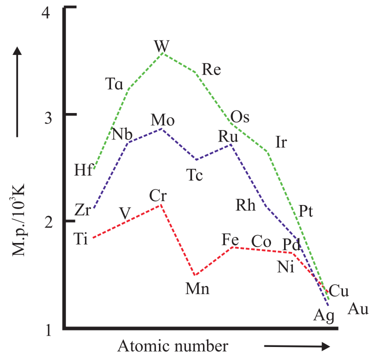


Fig. 8.2 : Trends in melting points of transition elements

Table 8.4: Electronic configuration of various ions of 3d elements

Elements Atomic no :	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	21	22	23	24	25	26	27	28	29	30
Species	Valence shell Electronic Configuration									
M	$3d^1\ 4s^2$	$3d^2\ 4s^2$	$3d^3\ 4s^2$	$3d^5\ 4s^2$	$3d^5\ 4s^2$	$3d^6\ 4s^2$	$3d^1\ 4s^2$	$3d^8\ 4s^2$	$3d^{10}\ 4s^1$	$3d^{10}\ 4s^2$
$M^{\oplus}$	$3d^1\ 4s^1$	$3d^2\ 4s^1$	$3d^3\ 4s^1$	$3d^5$	$3d^5\ 4s^1$	$3d^6\ 4s^1$	$3d^7\ 4s^1$	$3d^8\ 4s^1$	$3d^{10}\ 4s^0$	$3d^{10}\ 4s^1$
$M^{2\oplus}$	$3d^2$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
$M^{3\oplus}$	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	-	-

8.6 Trends in atomic properties of the first transition series

8.6.1 Atomic and ionic radii

Atomic radii of the elements of the transition series decrease gradually from left to right (Fig. 8.3 and Table 8.5). As we move across a transition series from left to right the nuclear charge increases by one unit at a time. The last filled electron enters a penultimate (n-1)d subshell. However, d orbitals in an atom are less penetrating or more diffused and, therefore d electrons offer smaller screening effect. The result is that effective nuclear charge also increases as the atomi number increases along a transition series. Hence the atomic radii decrease gradually across a transition series from left to right.

The explanation for the minor variation in atomic radii within a particular transition series is out of the scope of this textbook.

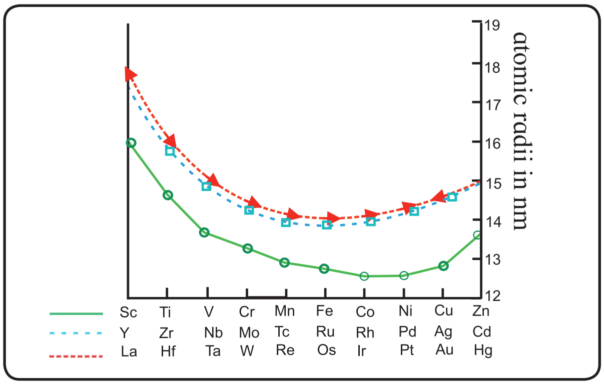


Fig. 8.3 : Trends in atomic radii of d block elements

Ionic radii of transition elements show the same trend as of the atomic radii (Table 8.5)

The elements of first transition series show variable oxidation states. The trends in ionic radii, thus, can be studied with (i) elements having same oxidation state or (ii) considering various oxidation states of the same element.

(i) For the same oxidation state, with an increase of nuclear charge a gradual decrease in ionic radii was observed. The trend is pronounced for the divalent ions of the first transition series ($Cr^{2\oplus}$ - 82 pm, $Cu^{2\oplus}$ - 72 pm).

Table 8.5 Atomic properties of first transition series elements

Element (M)	Atomic number (Z)	Density (g/cm^3)	Atomic/ionic radius (pm)			Ionisation enthalpy (kJ/mol)
			M	$M^{2\oplus}$	$M^{3\oplus}$	
Sc	21	3.43	164	-	73	631
Ti	22	4.1	147	-	67	656
V	23	6.07	135	79	64	650
Cr	24	7.19	129	82	62	653
Mn	25	7.21	127	82	65	717
Fe	26	7.8	126	77	65	762
Co	27	8.7	125	74	61	758
Ni	28	8.9	125	70	60	736
Cu	29	8.9	128	73	-	745
Zn	30	7.1	137	75	-	906

(ii) The oxidation states of the same element shows difference of one unit such as $M^{\oplus}$, $M^{2\oplus}$, $M^{3\oplus}$, $M^{4\oplus}$ and so on. With higher oxidation state the effective nuclear charge also increases and hence, decrease of ionic radii can be observed from $M^{2\oplus}$ to $M^{3\oplus}$ (Table 8.5). Ionic radii of transition elements are smaller than ionic radii of representative elements of the same period.

8.6.2 Ionisation Enthalpy : The ionisation enthalpies of transition elements are intermediate between those of s-block or p-block elements. This suggests that transition elements are less electropositive than elements of group 1 and 2. Depending on the conditions, they form ionic or covalent bonds. Generally in the lower oxidation states these elements form ionic compounds while in the higher oxidation states they form covalent compounds.

Ionisation enthalpies shown in Table 8.6 reveal that for a given element there is substantial increase from the first ionisation enthalpy IE_1 to the third ionisation enthalpy IE_3.

As we move across the transition series, slight variation is observed in the successive enthalpies IE_1, IE_2, IE_3 of these elements (Table 8.6).

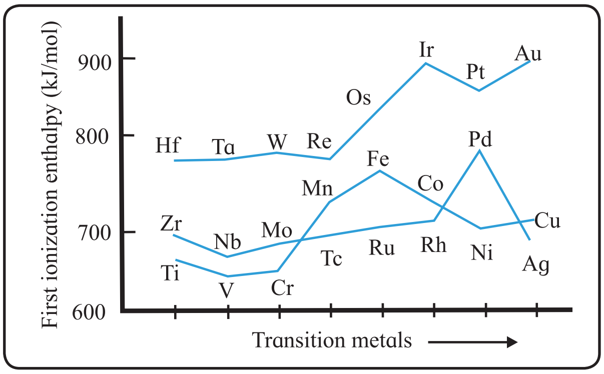


Fig. 8. 4: Trends in first ionisation enthalpies of d block elements

The atoms of elements of third transition series possess filled 4f- orbitals. 4f orbitals show poor shielding effect on account of their peculiar diffused shape. As a result, the valence electrons experience greater nuclear attraction. A greater amount of energy is required to ionize elements of the third transition series. The ionisation enthalpies of the elements of the third transition series are, therefore much higher than the first and second series (Fig.8.4).

8.6.3 Metallic character : Low ionization enthalpies and vacant d orbitals in the outermost shell are responsible for the metallic character of the transition elements. These favour the formation of metallic bonds and thus these elements show typical metallic properties. The hard nature of these elements suggests the formation of covalent bonds in them. This is possible due to the presence of unpaired (n-1)d electrons in these elements.

Nearly all transition metals have simple hexagonal closed packed (hcp), cubic closed packed (ccp) or body centered cubic (bcc) lattices which are characteristic of true metals (You have learnt more about this in Chapter 1).

Remember...

Hardness, high melting points and metallic properties of the transition elements indicate that the metal atoms are held strongly by metallic bonds with covalent character.

Table 8.6 Ionisation enthalpies of first transition series elements

Element IE	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
IE_1	632	659	650	652	717	762	756	736	744	906
IE_2	1245	1320	1376	1635	1513	1563	1647	1756	1961	1736
IE_3	2450	2721	2873	2994	3258	2963	3237	3400	3560	3838

(IE = Ionisation Enthalpy in kJ/mol)

In all the transition series the melting points steadily increase upto d^5 configuration. Cr, Mo and W show highest melting points in their respective series. Mn and Tc display anomalous values of melting points. After this with increasing atomic number the melting point decreases regularly.

8.6.4 Magnetic Properties :

Can you recall ?

1. What happens when magnetic field is applied to substances ?
2. What is meant by the terms paramagnetism and diamagnetism ?

The compounds of transition metals exhibit magnetic properties due to the unpaired electrons present in their atoms or ions. When a magnetic field is applied, substances which are attracted towards the applied magnetic field are called paramagnetic, while the ones which are repelled are called diamagnetic.

Some substances are attracted very strongly and these are called ferromagnetic substances.

Remember...

Paramagnetism and ferromagnetism arises due to presence of unpaired electrons in a species.

When all electron spins are paired, the compound becomes diamagnetic.

Among transition metals Fe, Co, Ni are ferromagnetic. When magnetic field is applied externally all the unpaired electrons in these metals and their compounds align in the direction of the applied magnetic field. Due to this the magnetic susceptibility is enhanced. These metals can be magnetized, that is, they aquire permanent magnetic moment.

Try this...

Pick up the paramagnetic species $Cu^{1\oplus}$, $Fe^{3\oplus}$, $Ni^{2\oplus}$, $Zn^{2\oplus}$, $Cd^{2\oplus}$, $Pd^{2\oplus}$.

Each unpaired electron gives rise to a small magnetic field (magnetic moment) due to its spin angular momentum and orbital angular momentum. In case of the first row transition elements, the contribution from the orbital angular momentum is quenched and hence, can be neglected. The spin-only formula for magnetic moment is :

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

where n is the number of unpaired electrons and μ is the magnetic moment expressed in Bohr Magneton (BM). A single unpaired electron has magnetic moment $\mu = 1.73$ BM.

From the magnetic moment (μ) measurements of the metal complexes of the first row transition elements, the number of unpaired electrons can be calculated, with the use of spin-only formula. As magnetic moment is directly related to number of unpaired electrons, value of μ will vary directly with the number of unpaired electrons.

Try this...

What will be the magnetic moment of transition metal having 3 unpaired electrons ?

a. equal to 1.73 BM,

b. less than 1.73 BM or

c. more than 1.73 BM ?

Magnetic moments are determined experimentally in solution or in solid state where the central metal is hydrated or bound to ligands. A slight difference in the calculated and observed values of magetic moments thus can be noticed.

Use your brain power

A metal ion from the first transition series has two unpaired electrons. Calculate the magnetic moment.

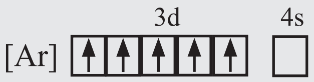
Table 8.7 gives the calculated and observed magnetic moments of cations of 3d series.

Table 8.7 Magnetic moments of ions of first transition series elements (values in BM)

Ion	Outer electronic configuration	Number of unpaired electrons	Calculated value of magnetic moment	Experimental value
$Sc^{3\oplus}$	$3d^0$	0	0	0
$Ti^{3\oplus}$	$3d^1$	1	1.73	1.75
$V^{3\oplus}$	$3d^2$	2	2.84	2.76
$Cr^{3\oplus}$	$3d^3$	3	3.87	3.86
$Cr^{2\oplus}$	$3d^4$	4	4.90	4.80
$Mn^{2\oplus}$	$3d^5$	5	5.92	5.96
$Fe^{2\oplus}$	$3d^6$	4	4.90	5.3-5.5
$Co^{2\oplus}$	$3d^7$	3	3.87	4.4-5.2
$Ni^{2\oplus}$	$3d^8$	2	2.84	2.9-3.0, 4.0
$Cu^{2\oplus}$	$3d^9$	1	1.73	1.8-2.2
$Zn^{2\oplus}$	$3d^{10}$	0	0	0

Problem : Calculate the spin only magnetic moment of divalent cation of a transition metal with atomic number 25.

Solution : For element with atomic number 25, electronic configuration for its divalent cation will be



There are 5 unpaired electrons, so n = 5.

$\therefore\ \mu = \sqrt{5(5+2)} = 5.92$ BM

Try this...

Calculate the spin only magnetic moment of divalent cation of element having atomic number 27.

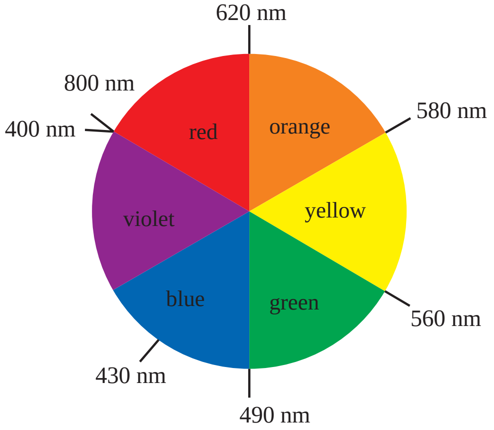
In second and third transition series, orbital angular moment is significant. Therefore, the simple spin only formula is not useful and more complicated equations have to be employed to determine magnetic moments. The magnetic moments further are found to be temperature dependent.

8.6.5 Colour : A substance appears coloured if it absorbs a portion of visible light. The colour depends upon the wavelength of absorption in the visible region of electromagnetic radiation.

Can you tell ?

Compounds of s and p block elements are almost white. What could be the absorbed radiation : uv or visible ?

The ionic and covalent compounds formed by the transition elements are coloured. Transition elements contain unpaired electrons in their d orbitals. When the atoms are free or isolated, the five d orbitals are degenerate; or have the same energy. In complexes, the metal ion is surrounded by solvent molecules or ligands. The surrounding molecules affect the energy of d orbitals and their energies are no longer the same [You will learn more about this in Chapter 9]. As the principal quantum number of 'd' orbitals is the same, the amount of energy required for transition of electron from one d orbital to another is quite small. The small energy required for this transition is available by absorption of radiation having certain wavelength from the visible region. Remaining light is transmitted and the observed colour of the compound corresponds to the complimentary colour of light absorbed. That means, if red light is absorbed then the transmitted light contains excess of other colours in the spectrum, in particular blue, so the compound appears blue. The ions having no unpaired electrons are colorless for example $Cu^{\oplus}(3d^{10})$; $Ti^{4\oplus}(3d^{0})$. Table 8.8 enlists colours of 3d transition metal ions.



Let us see how colour of the transition metal ion depends upon ligand and geometry of the complex formed by metal ion.

When cobalt chloride ($Co^{2\oplus}$) is dissolved in water, it forms a pink solution of the complex $[Co(H_2O)_6]^{2\oplus}$ which has octahedral geometry. But when this solution is treated with concentrated hydrochloric acid, it turns deep blue. This change is due to the formation of another complex $[CoCl_4]^{2\ominus}$ which has a tetrahedral structure.

$$[Co(H_2O)_6]^{2\oplus} + 4Cl^{\ominus} \longrightarrow [CoCl_4]^{2\ominus} + 6H_2O$$

Thus the colour of a transition metal ion relates to

1. presence of unpaired d electrons
2. d - d transitions
3. nature of ligands attached to the metal ion
4. geometry of the complex formed by the metal ion

Do you know ?

Colour of transition metal ions may arise due to a charge transfer. For example, $MnO_4^{\ominus}$ ion has an intense purple colour in solution. In $MnO_4^{\ominus}$, an electron is momentarily transferred from oxygen (O) to metal, thus momentarily changing $O^{2\ominus}$ to $O^{\ominus}$ and reducing the oxidation state of manganese from +7 to +6. For charge transfer transition to take place, the energy levels of the two different atoms involved should be fairly close. Colours of $Cr_2O_7^{2\ominus}$, $CrO_4^{\ominus}$, Cu_2O and Ni-DMG (where DMG = dimethyl glyoxime) complex thus can be explained through charge transfer transitions.

8.6.6 Catalytic Properties : Transition metals and their compounds exhibit good catalytic properties. They have proven to be good homogeneous and heterogeneous catalysts. Partly because of their ability to participate in different oxidation-reduction steps of catalytic reactions.

Table 8.8 Colour of 3d transition metal ions

Ion	Outer electronic configuration	Number of unpairedelectrons	Colour
$Sc^{3\oplus}$	$3d^0$	0	Colourless
$Ti^{3\oplus}$	$3d^1$	1	Purple
$Ti^{4\oplus}$	$3d^0$	0	Colourless
$V^{3\oplus}$	$3d^2$	2	Green
$Cr^{3\oplus}$	$3d^3$	3	violet
$Mn^{2\oplus}$	$3d^5$	5	Light pink
$Mn^{3\oplus}$	$3d^4$	4	Violet
$Fe^{2\oplus}$	$3d^6$	4	Pale green
$Fe^{3\oplus}$	$3d^5$	5	Yellow
$Co^{2\oplus}$	$3d^7$	3	Pink
$Ni^{2\oplus}$	$3d^8$	2	Green
$Cu^{2\oplus}$	$3d^9$	1	Blue
$Cu^{\oplus}$	$3d^{10}$	0	Colourless
$Zn^{2\oplus}$	$3d^{10}$	0	Colourless

These steps involve changes in the oxidation states of these metal ions. Compounds of Fe, Co, Ni, Pd, Pt, Cr, etc. are used as catalysts in a number of reactions. Their compounds enhance the rate of the chemical reactions.

In homogeneous catalysis reactions, the metal ions participate by forming unstable intermediates. In heterogeneous catalysis reactions on the other hand, the metal provides a surface for the reactants to react.

Examples :

1. MnO_2 acts as a catalyst for decomposition of $KClO_3$.
2. In manufacture of ammonia by Haber's process Mo/Fe is used as a catalyst.
3. Co-Th alloy is used in Fischer Tropsch process in the synthesis of gasoline.
4. Finely divided Ni, formed by reduction of the heated oxide in hydrogen is an extremely efficient catalyst in hydrogenation of ethene to ethane at 140 ^{0}C.

$$H_2C = CH_2 + H - H \xrightarrow[\text{Ni, 140 } ^0\text{C}]{\Delta} H_3C - CH_3$$

Commercially, hydrogenation with nickel as catalyst is used to convert inedible oils into solid fat for the production of margarine.

5. In the contact process of industrial production of sulfuric acid; sulphur dioxide and oxygen from the air react reversibly over a solid catalyst of platinised asbestos.

$$2SO_2 + O_2 \underset{\text{asbestos}}{\overset{\text{platinised}}{\rightleftharpoons}} 2SO_3$$

6. Carbon dioxide and hydrogen are formed by reaction of the carbon monoxide and steam at about 500 ^{0}C with an Fe-Cr catalyst.

$$CO + \underset{\text{(steam)}}{H_2O} \underset{\text{catalyst}}{\overset{\text{Fe-Cr}}{\rightleftharpoons}} CO_2 + H_2$$

8.6.7 Formation of interstitial compounds

When small atoms like hydrogen, carbon or nitrogen are trapped in the interstitial spaces within the crystal lattice, the compounds formed are called interstitial compounds. Sometimes sulphides and oxides are also trapped in the crystal lattice of transition elements. Steel and cast iron are examples of interstitial compounds of carbon and iron. Due to presence of carbon, the malleability and ductility of iron is reduced while its tenacity increases.

Some properties of interstitial compounds

i. They are hard and good conductors of heat and electricity.

ii. Their chemical properties are similar to the parent metal.

iii. Their melting points are higher than the pure metals.

iv. Their densities are less than the parent metal.

v. The metallic carbides are chemically inert and extremely hard as diamond.

vi. Hydrides of transition metals are used as powerful reducing agents.

Remember...

- Tungsten carbide is used for cutting tools.
- Iron carbide is used in manufacture of steel.

8.6.8 Formation of Alloys

Can you recall ?

- What is an alloy ?
- Do atomic radii of 3d transition elements differ largely ?

Transition metals form alloys where atoms of one metal are distributed randomly in the lattice of another metal. The metals with similar radii and similar properties readily form alloys.

Alloys are classified into **ferrous and non-ferrous**.

Ferrous alloys have atoms of other elements distributed randomly in atoms of iron in the mixture. As percentage of iron is more, they are termed ferrous alloys eg. nickel steel, chromium steel, stainless steel etc. All steels have 2% carbon.

Non-ferrous alloys are formed by mixing atoms of transition metal other than iron with a non transition element. eg. brass, which is an alloy of copper and zinc. Ferrous and non-ferrous alloys are of industrial importance.

Uses of alloys

- Bronze, an alloy of copper and tin is tough, strong and corrosion resistant. It is used for making statues, medals and trophies.
- Cupra-nickel, an alloy of copper and nickel is used for making machinary parts of marine ships, boats. For example, marine condenser tubes.
- Stainless steels are used in the construction of the outer fuselage of ultra-high speed air craft.
- Nichrome an alloy of nickel and chromium in the ratio 80 : 20 has been developed specifically for gas turbine engines.
- Titanium alloys withstand stress up to high temperatures and are used for ultra-high speed flight, fire proof bulkheads and exhaust shrouds.

8.7 Compounds of Mn and Cr ($KMnO_4$ and $K_2Cr_2O_7$)

Remember...
Both $KMnO_4$ and $K_2Cr_2O_7$ are strong oxidising agents.

8.7.1 Preparation of potassium permaganate

i. Chemical oxidation

When a finely divided manganese dioxide (MnO_2) is heated strongly with fused mass of caustic potash (KOH) and an oxidising agent, potassium chlorate ($KClO_3$), dark green potassium manganate, K_2MnO_4 is formed.

$$3MnO_2 + 6KOH + KClO_3 \xrightarrow{\Delta} 3K_2MnO_4 + KCl + 3H_2O$$

In neutral or acidic medium the green potassium manganate disproportionates to $KMnO_4$ and MnO_2.

$$3K_2MnO_4 + 4CO_2 + 2H_2O \longrightarrow 2KMnO_4 + MnO_2 + 4KHCO_3$$

$$3MnO_4^{2\ominus} + 4H^{\oplus} \longrightarrow 2MnO_4^{\ominus} + MnO_2 + 2H_2O$$

The liquid is filtered through glass wool or sintered glass and evaporated until crystallisation occurs. Potassium permanganate forms small crystals which are almost black in appearance.

ii. Electrolytic oxidation

In electrolytic oxidation, alkaline solution of manganate ion is electrolysed between iron electrodes separated by a diaphragm. Overall reaction is as follows :

$$2K_2MnO_4 + H_2O + [O] \longrightarrow 2KMnO_4 + 2KOH$$

The oxygen evolved at the anode converts manganate to permanganate.

The solution is filtered and evaporated to get **deep purple black coloured** crystals of $KMnO_4$.

8.7.2 Chemical properties of $KMnO_4$:

a. In acidic medium :

The oxidizing reactions of $KMnO_4$ in acidic medium

i. Oxidation of iodide to iodine :

$$2MnO_4^{\ominus} + 10\ I^{\ominus} + 16H^{\oplus} \longrightarrow 2Mn^{2\oplus} + 8H_2O + I_2$$

ii. Oxidation of $Fe^{2\oplus}$ to $Fe^{3\oplus}$

$$MnO_4^{\ominus} + 5Fe^{2\oplus} + 8H^{\oplus} \longrightarrow 5Fe^{3\oplus} + Mn^{2\oplus} + 4H_2O$$

iii. Oxidation of H_2S

$$H_2S \longrightarrow 2H^{\oplus} + S^{2\ominus}$$

$$5S^{2\ominus} + 2MnO_4^{\ominus} + 16H^{\oplus} \longrightarrow 2Mn^{2\oplus} + 5S + 8H_2O$$

iv. Oxidation of oxalic acid :

$$2MnO_4^{\ominus} + 5H_2C_2O_4 + 6H^{\oplus} \longrightarrow 2Mn^{2\oplus} + 10CO_2 + 8H_2O$$

b. In neutral or weakly alkaline medium :

i. Oxidation of iodide $I^{\ominus}$ to iodate $IO_3^{\ominus}$.

$$2MnO_4^{\ominus} + H_2O + I^{\ominus} \longrightarrow 2MnO_2 + 2OH^{\ominus} + IO_3^{\ominus}$$

ii. Thiosulphate ($S_2O_3^{2\ominus}$) is oxidised to sulphate ($SO_4^{2\ominus}$)

$$8MnO_4^{\ominus} + 3S_2O_3^{2\ominus} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2\ominus} + 2OH^{\ominus}$$

iii. Manganous salt is oxidised to MnO_2.

$$2MnO_4^{\ominus} + 3Mn^{2\oplus} + 2H_2O \longrightarrow 5MnO_2 + 4H^{\oplus}$$

8.7.3 Uses of $KMnO_4$:

- An antiseptic.
- For unsaturation test in laboratory.
- In volumetric analysis of reducing agents.
- For detecting halides in qualitative analysis.
- Powerful oxidising agent in laboratory and industry.

8.7.4 $K_2Cr_2O_7$: Preparation of potassium dichromate

In the industrial production, finely powdered chromite ore ($FeOCr_2O_3$) is heated with anhydrous sodium carbonate (Na_2CO_3) and a flux of lime in air in a reverbatory furnace.

$$4(FeO.Cr_2O_3) + 8Na_2CO_3 + 7O_2 \xrightarrow{\Delta} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2.$$

Sodium chromate (Na_2CrO_4) formed in this reaction is then extracted with water and treated with concentrated sulphuric acid to get sodium dichromate and hydrated sodium sulphate :

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + 2NaCl + Na_2Cr_2O_7.H_2O$$

Addition of potassium chloride to concentrated solution of sodium dichromate precipitates less soluble orange-red coloured potassium dichromate, $K_2Cr_2O_7$.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

8.7.5 Chemical properties of $K_2Cr_2O_7$:

i. Oxidation of I^- from aq. solution of KI by acidified $K_2Cr_2O_7$ gives I_2. Potassium dichromate is reduced to chromic sulphate. Liberated I_2 turns the solution brown.

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

ii. When H_2S gas is passed through acidified $K_2Cr_2O_7$ solution, H_2S is oxidised to pale yellow precipitate of sulphur. Simultaneously potassium dichromate is reduced to chromic sulphate, which is reflected as colour change of solution from orange to green.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

8.8 Common properties of d block elements

Physical properties

i. All d block elements are lustrous and shining.

ii. They are hard and have high density.

iii. Have high melting and boiling points.

iv. Are good electrical and thermal conductors.

v. Have high tensile strength and malleability.

vi. Can form alloys with transition and non transition elements.

vii. Many metals and their compounds are paramagnetic.

viii. Most of the metals are efficient catalysts.

Chemical properties

i. All d block elements are electropositive metals.

ii. They exhibit variable valencies and form colored salts and complexes.

iii. They are good reducing agents.

iv. They form insoluble oxides and hydroxides.

v. Iron, cobalt, copper, molybdenum and zinc are biologically important metals

vi. catalyse biological reactions.

Differences : Although most properties exhibited by d block elements are similar, the elements of first row differ from second and third rows in stabilization of higher oxidation states in their compounds.

For example, Mo(V) and W (VI) compounds are more stable than Cr(VI) and Mn (VIII).

Highest oxidation state for elements of first row is +7, and in the case of 3rd row +8 oxidation state as in (RuO_4) and (OsO_4).

Can you recall ?

- How are metals found in nature?
- Name two the salts of metals that are found in nature.

Internet my friend

1. Collect the information on different steps involved in the extraction of metals from their ores.
2. Collect information about place where deposits of iron ores are found.

8.9 Extraction of metals

Most metals are found in the earth's crust in the form of their salts, such as carbonates, sulphates, sulphides and oxides.

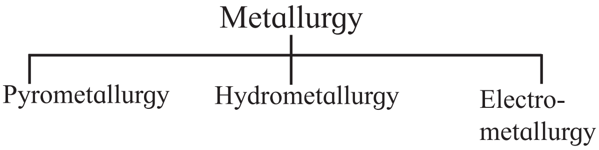
A few metals are nonreactive and occur in the free state in the earth's crust, for example, silver, gold, and platinum.

Mineral : A naturally occuring substance found in the earth's crust containing inorganic salts, solids, siliceous matter etc, is called a mineral.

The mineral which contains high percentage of the metal and from which the metal can be extracted economically is called an **ore**.

Table 8.9 : List of minerals and ores of some transition metals.

Metals	Mineral	Ore
Iron	Haematite Fe_2O_3 Magnetite Fe_3O_4 Limonite $2Fe_2O_3, 3H_2O$ Iron pyrites FeS_2 Siderite $FeCO_3$	Haematite
Copper	Chalcopyrite $CuFeS_2$ Chalcocite Cuprite Cu_2O	Chalcopyrite Chalcocite
Zinc	Zinc blende ZnS Zinccite ZnO Calamine $ZnCO_3$	Zinc blende



8.9.1 Metallurgy :

Commercial extraction of metals from their ores is called metallurgy. Different methods are used for their extraction depending on the nature of a metal and its ore.

a. Pyrometallurgy: A process in which the ore is reduced to metal at high temperature using reducing agents like carbon, hydrogen, aluminium, etc. is called pyrometallurgy.

b. Hydrometallurgy : The process of extracting metals from the aqueous solution of their salts using suitable reducing agent is called hydrometallurgy.

c. Electrometallurgy : A process in which metal is extracted by electrolytic reduction of molten (fused) metallic compound is called electrometallurgy.

Steps Involved in Process of Extraction

Do you know ?

1. Extraction of iron has been known to Indians since 700 BC. Indian blacksmiths also knew the thermo-mechnical process for forging. During Archaeological studies in Harappa, Madhya Pradesh different iron objects belonging to middle iron age were found.
2. Famous iron pillar in Delhi is 1300 years old and is free of rust till to date.

Concentration : After mining the ore from the earth's crust it is subjected to concentration. In this step, impurities termed as gangue are removed from the ore and the ore gets concentrated.

The sand, mud and other unwanted impurities which remain mixed with the ore deposit are called **gangue**.

During the process of concentration, the ore is separated from the gangue material using different methods such as washing, hydraulic classification, magnetic separation, froth floatation, etc.

The method chosen for concentration depends upon the nature of the ore.

8.9.2 Extraction of Iron from Haematite ore using Blast furnace

Do you know ?

Iron is the fourth most abundant element in the earth's crust

Composition of Haematite ore :

$$Fe_2O_3 + \underbrace{SiO_2 + Al_2O_3 + \text{phosphates}}_{\text{Gangue}}$$

Internet my friend

Find percentage of oxygen, silicon, aluminium and iron in earth's crust.

Iron is extracted from haematite by its reduction using coke and limestone. Carbon in the limestone is reduced to carbon monoxide. Carbon and carbon monoxide together reduce Fe_2O_3 to metallic iron.

Limestone acts as flux, it combines with the gangue material to form molten slag. Extraction of iron from haematite ore involves the following steps.

i. Concentration : The powdered ore is washed in a powerful current of water introduced into the hydraulic classifier.

The lighter gangue particles are separated and the concentrated ore is collected at the bottom.

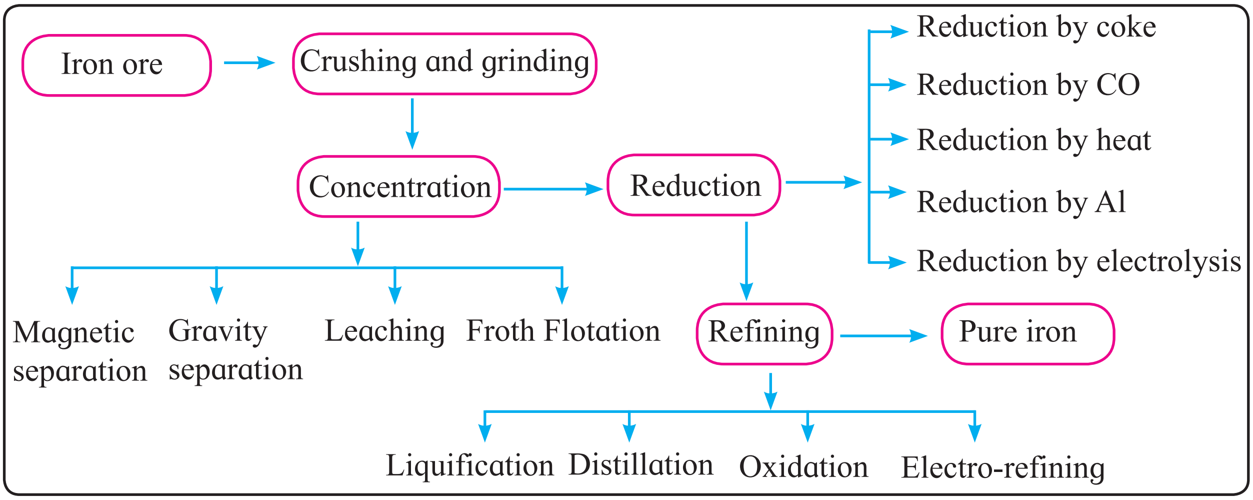
ii. Roasting : The concentrated ore is heated in a current of air. The sulfur and arsenic impurities present in the ore get converted into their oxides and escape as vapour. Ferrous oxide in the ore is converted to Fe_2O_3.

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

The roasted ore is converted into lumps by sintering.

iii. Reduction (Smelting) : This step is carried out in a blast furnace. Blast furnace is a tall cylindrical steel tower which is lined with refractory bricks.

The height of a typical blast furnace is 25 m and its diameter varies between 5 and 10 m. The furnace works on counter current principle where the charge comes down and



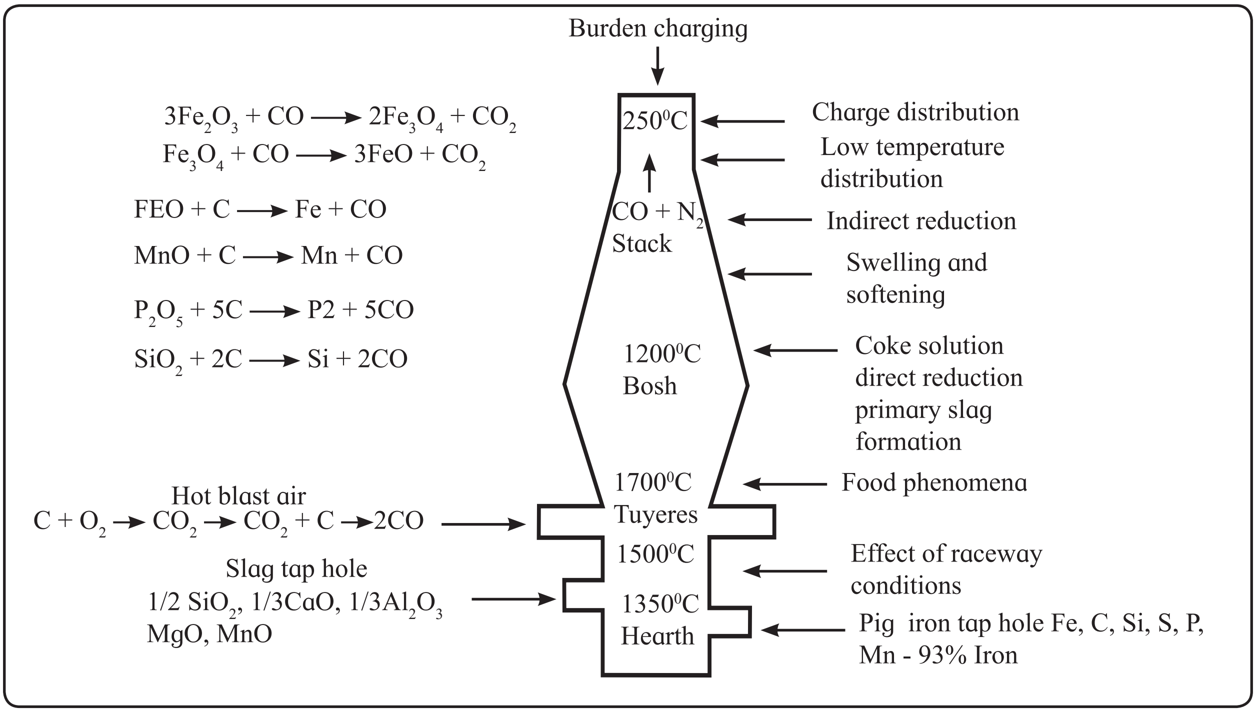


Fig. 8.5 : Blast furnace

hot gases move up the tower. The furnace is comprised of 3 parts - 1. Hearth, 2. Bosh and 3. Stack

The charge contaning ore and lime stone is introduced into the furnace through a cup and cone arrangement. In this arrangement the cone enables uniform distribution of charge and the cup prevents the loss of gases. A blast of preheated air is introduced into the furnance below the bosh. The charge and hot air come in contact with each other and various reactions take place.

Reactions in the blast furnace : There are different temperature zones in the blast furnace. The temperature goes on increasing from top to bottom in the furnace. At the top, the temperature is 500 K. Maximum temperature of the furnace is 2000 K above the tuyers. There are 3 temperature zones in the furnace.

1. Zone of combustion - Combustion of coke with O_2 in the air.

2. Zone of reduction - Reduction of Fe_2O_3 to metallic iron

3. Zone of slag formation - Formation of slag by reaction of gangue with limestone

Chemical reactions taking place in different zones of the blast furnace

1. Zone of combustion : This is 5 - 10 m from the bottom. The hot air blown through the tuyers reacts with coke from the charge to form CO.

$$C + \frac{1}{2} O_2 \longrightarrow CO, \Delta H = -220 \text{ kJ}$$

The reaction is highly exothermic; thus the temperature of this zone is around 2000 K. Some of the CO formed dissociates to form finely divided carbon.

$$2\,CO \longrightarrow 2\,C + O_2$$

The hot gas rich in CO rises upwards in the blast furnace. The charge coming down gets heated and reacts with CO. Thus CO acts as a fuel and also a reducing agent.

2. Zone of Reduction (22-25 m near the top)

Here, the temperature is around 900 K. Fe_2O_3 is reduced to spongy iron by CO

$$Fe_2O_3 + 3\,CO \longrightarrow 2Fe + 3\,CO_2$$

some amount of Fe_2O_3 is reduced to iron by carbon

$$Fe_2O_3 + 3C \longrightarrow 2\,Fe + 3\,CO$$

Table 8.9 : Summary of reactions taking place in blast furnace at different temperature zones

Temp K	Changes taking place	Reaction
500	loss of moisture from ore	
900	Reduction of ore by CO	$Fe_2O_3 + 3CO \longrightarrow 2\,Fe + 3CO_2$
1200	Decomposition of lime	$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
1500	Reduction of ore by C	$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$
2000	Fusion of iron	$CaO + SiO_2 \longrightarrow CaSiO_3$
	Slag formation	$12CaO + 2Al_2O_3 \longrightarrow 4Ca_3AlO_3 + 3\,O_2$

3. Zone of slag formation (20 m unit) : The gangue present in the ore is converted to slag. This slag can be used for making road foundation. Temperature of this zone is 1200 K. The gangue contains silica, alumina and phosphates. A removal of this gangue is effected by adding lime-stone in the charge, which acts as flux. Limestone decomposes to give CaO (quick lime)

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

CaO combines with gangue to form molten slag of calcium silicate and calcium aluminate.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$12\,CaO + 2Al_2O_3 \longrightarrow 4Ca_3\,AlO_3 + 3\,O_2$$

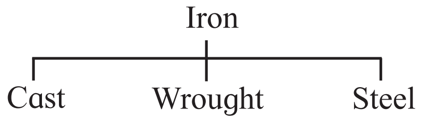
4. Zone of fusion (15 m ht) : MnO_2 and $Ca_3(PO_4)_2$ present in the iron ore are reduced to Mn and P. Some of the silica is also reduced to Si.

The spongy iron coming down in the furnace melt absorbs impurities like C, Si, Mn, P and S. This molten iron collects at the bottom in the furnace. The slag which is lighter floats on the surface of molten iron. Molten slag and iron are collected through separate outlets.

Molten iron is poured into moulds. These solid blocks are called pigs. This iron contains about 4% of carbon. When pig iron is remelted, run into moulds and cooled, it becomes cast iron. The waste gases containing N_2, CO and CO_2 escape through the outlet at the top. These hot gases are used for preheating the blast of air.

5. Refining : Pure iron can be obtained by electrolytic refining of impure iron or other methods given in the flow chart. The choice of extraction technique is governed by the following factors. 1. Nature of ore 2. Availability and cost of reducing agent, generally cheap coke is used. 3. Availability of hydraulic power. 4. Purity of product (metal) required. 5. Value of byproducts for example, SO_2 obtained during roasting of sulphide ores is vital for manufacture of H_2SO_4. Knowledge of electrochemical series provides solutions to many problems.

Commercial forms of Iron



Remember...

1. Iron melts at a very high temperature (1800 K). On addition of carbon its melting point decreases depending upon percentage of carbon.
2. Mechanical properties of steel can be modified by addition of small amounts of suitable elements such as manganese, chromium, sulfur, nickel etc. These elements are called alloying elements and steels are alloy steels.

Differences between cast iron, wrought iron and steel

Cast iron	Wrought iron	Steel
1. Hard and brittle	1. Very soft	1. Neither too hard nor too soft.
2. Contains 4% carbon.	2.Contains less than 0.2% carbon	2. Contains 0.2 to 2% carbon
3. Used for making pipes, manufacturing automotive parts, pots, pans, utensils	3. Used for making pipes, bars for stay bolts, engine bolts and rivetts.	3. Used in buildings infrastructure, tools, ships, automobiles, weapons etc.

Do you know ?

Iron possesses a high degree of magnetism below 1042 K. This is known as ferromagnetism.

8.10 Inner Transition (f-block) Elements: Lanthanoids and Actinoids :

Elements whose f orbitals get filled up by electrons, are called f block elements. These elements are placed separately at the bottom of the periodic table. They are a subset of 6th and 7th periods.

Can you tell ?

- Why f-block elements are called inner transition metals?
- Are there any similarities between transition and inner transition metals?

Since f orbital lies much inside the d orbital, in relation to the transition metals the f block elements are called inner transition elements. These elements have 1 to 14 electrons in their f orbital, 0 or 1 in the penultimate energy level and 2 electrons in the outermost orbital. The lanthanoids are characterized by gradual filling up of 4f and actinides by the 5 f orbitals. There are 14 elements filling the f orbital in each series. The relative energies of the nd and (n-1)f orbitals are very similar and are sensitive to electronic configurations.

Do you know ?

Glenn Seaborg first proposed a revised design of periodic table with a whole new series of elements. When he showed his design to two prominent inorganic chemists of the time, they warned him against publishing it. They told him that tampering with the established periodic table will affect his career. Seaborg went ahead and published it. He later remarked "I did not have any scientific reputation, so I published it anyway". Now we see that elements 89 -102 (filling of 5f orbitals) fit in Seaborg's proposed order.

8.11 Properties of f-block elements

i. Properties are similar to d block elements

ii. Electrons are added to f subshells of (n-2) level

iii. Placed between (n-1)d and ns block elements

Lanthanoids begin with atomic number 57 and end at 71. Although, historically, lanthanoids are termed as **rare earth elements**, they are fairly abundant in earth's crust. For example, thulium is found more in abundance than silver (4.5×10^{-5} vs 0.79×10^{-5} percent by mass). The name rare earth elements was coined because of difficulty in extracting them economically in pure form from other lanthanoids having similar chemical properties. Now, due to newer separation methods like ion exchange resins, the separation of these elements has become easier and more economical.

These metals are soft with moderate densities of about 7 g cm^{-3}. They have high melting (~1000 ^{0}C) and boiling points (~3000 ^{0}C). Similar to groups 1 and 2, lanthanoids in the metallic state are very reactive and resemble alkali and alkaline earth metals in their reactivities than transition metals. For example, they react with water to give the metal hydroxide and hydrogen gas

$$2M(s) + 6\ H_2O\ (l) \longrightarrow 2M(OH)_3(s)\ +\ 3H_2(g)$$

Although, the common oxidation state for lanthanoids is +3, the +2 oxidation state is also important. They all form stable oxides of the type M_2O_3 where M is metal ion. Eu^{2+} and Yb^{2+} are the most stable dipositive metal ions. Higher oxidation states are unusual for lanthanoids with the only exception of cerium which forms a stable +4 species. The energy required to break up the metal lattice is heat of atomization. Lanthanoids have lower heat of atomization than transition metals. This is because with d electrons, transition metals are much harder and require high heat of atomization. Europium and ytterbium have the lowest enthalpies of vaporization and largest atomic radii of lanthanoids, resemble barium. These two elements resemble alkaline earth elements; they dissolve in liquid ammonia to give blue conducting solutions.

Their ionic radii decrease from 117 pm of La to 100 pm for Lu. This is because 5f orbitals do not shield the outer 5s and 5p electrons effectively, leading to increase in effective nuclear charge and decrease in the ionic size. Such large ions have higher coordination number that varies from 6 (most common) to 9, 10 and upto12 in some cases. For example, hydrated lanthanum ion is a nonahydrate, $[La(H_2O)_9]^{3+}$.

All the lanthanoids form hydroxides of the general formula $Ln(OH)_3$(Ln represents any elements of lanthanoid series). These are ionic and basic. Since the ionic size decreases from La^{3+} to Lu^{3+}, the basicity of hydroxides decreases. $La(OH)_3$ is the strongest base while $Lu(OH)_3$ is the weakest base.

Lanthanoids react with nitrogen and halogens to give nitrides and halides of the formulae LnN and LnX_3 repectively. While doing so, lanthanoids lose their outermost 3 electrons to form stable compound in +3 oxidation state. When lanthanoids are heated at elevated temperatures (~ 2800 K) with carbon, the carbides with general formula LnC_2 are obtained.

In +3 oxidation state, many of the lanthanoids are coloured, mostly green, pink and yellow. This is attributed to the electronic transitions among the f orbitals. Like transition metals the electronic spectra of lanthanoids however, do not get affected with different ligands.

8.12 Properties of Lanthanoids

i. Soft metals with silvery white colour and moderate densities of ~ 7 g cm^{-3}. Colour and brightness reduces on exposure to air

ii. Good conductors of heat and electricity.

iii. Except promethium (Pm), all are non-radioactive in nature.

iv. The atomic and ionic radii decrease from lanthanum (La) to lutetium (Lu). This is known as **lanthanoid contraction**.

v. Binding to water is common (i.e.) such that H_2O is often found in products when isolated from aqueous solutions.

vi. Coordination numbers usually are greater than 6, typically 8, 9,... (up to 12 found).

vii. The lanthanoides are strongly paramagnetic. Gadolinium becomes ferromagnetic below 16 ^{0}C (Curie point). The other heavier lathanoids terbium, dysprosium, holmium, erbium, thulium, and ytterbium – become ferromagnetic at much lower temperatures.

viii. Magnetic and optical properties are largely independent of environment (similar spectra in gas/solution/solid).

Table 8.11 : Electronic configuration and atomic ionic radii of lanthanoids

Element	Symbol	Atomic number	Electronic configuration				Atomic radii, pm	Ionic radii (Ln^{+3}, 6-coordinate), pm
			Expected (ground state)	Observed (ground state)	(+2 oxidation state)	(+3 oxidation state)		
Lanthanum	La	57	$[Xe]4f^0 5d^1 6s^2$	$[Xe]4f^0 5d^1 6s^2$	$4f^0$	$4f^0$	187	103
Cerium	Ce	58	$[Xe]4f^2 6s^2$	$[Xe]4f^1 5d^1 6s^2$		$4f^1$	183	102
Praseodymium	Pr	59	$[Xe]4f^3 6s^2$	$[Xe]4f^3 6s^2$	$4f^2$	$4f^2$	182	99
Neodymium	Nd	60	$[Xe]4f^4 6s^2$	$[Xe]4f^4 6s^2$			181	98.3
Promethium	Pm	61	$[Xe]4f^5 6s^2$	$[Xe]4f^5 6s^2$	$4f^4$		181	97
Samarium	Sm	61	$[Xe]4f^6 6s^2$	$[Xe]4f^6 6s^2$	$4f^5$	$4f^5$	180	95.8
Europium	Eu	63	$[Xe]4f^7 6s^2$	$[Xe]4f^7 6s^2$		$4f^6$	199	94.7
Gadolinium	Gd	64	$[Xe]4f^8 6s^2$	$[Xe]4f^7 5d^1 6s^2$	$4f^7$		178	93.8
Terbium	Tb	65	$[Xe]4f^9 6s^2$	$[Xe]4f^9 6s^2$		$4f^8$	177	92.3
Dysprosium	Dy	66	$[Xe]4f^{10} 6s^2$	$[Xe]4f^{10} 6s^2$		$4f^9$	176	91.2
Holmium	Ho	67	$[Xe]4f^{11} 6s^2$	$[Xe]4f^{11} 6s^2$	$4f^{10}$	$4f^{10}$	175	90.1
Erbium	Er	68	$[Xe]4f^{12} 6s^2$	$[Xe]4f^{12} 6s^2$			174	89
Thulium	Tm	69	$[Xe]4f^{13} 6s^2$	$[Xe]4f^{13} 6s^2$	$4f^{12}$	$4f^{12}$	173	88
Ytterbium	Yb	70	$[Xe]4f^{14} 6s^2$	$[Xe]4f^{14} 6s^2$	$4f^{13}$			86.8
Lutetium	Lu	71	$[Xe]4f^{14} 5d^1 6s^2$	$[Xe]4f^{14} 5d^1 6s^2$		$4f^{14}$		86.1

8.12.1 Electronic configuration :

The electronic configuration of lanthanoids is [Xe] $4f^{0-14}$ $5d^{0-2}$ $6s^2$. This is because $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6$ is the electronic configuration of xenon and we can simplify the electronic configuration of lanthanoids by [Xe] $4f^{0-14}5d^{0-2}6s^2$. The lanthanoids involve gradual filling of f-orbitals. The energies of 5d and 4f orbitals are very close. For lanthanum 4f is slightly higher in energy than 5d. The lanthanum has electronic configuration $[Xe]6s^25d^1$ and not $[Xe]6s^24f^1$. Gadolinium (Gd) and lutetium (Lu) have $5d^1$ electron to make f-orbital half-filled and full-filled which render them extra stability. The electronic configuration of lanthanoids have variable occupancy in 4f (0 to 14) orbitals. This can be noticed from Table 8.10. Number of electrons in 6s orbitals remains constant in the ground state. The valence shell electronic configuration of these elements, thus can be represented as: $(n-2)f^{0,2-14}$ $(n-1)d^{0,1,2}$ ns^2

The electronic distribution in different orbitals of elements in their ground and excited states are shown in Table 8.11.

Try this...

Fill in the blanks in Table 8.11.

Ionization Enthalpies

Can you recall ?

- What is ionization enthalpy?
- Some elements have variable oxidation states and some have only two. Can this be justified based on their ionization enthalpies?

The ionization enthalpies of lanthanoids are given in Table 8.12

Table 8.12: First, second, third and fourth ionization enthalpies of lanthanoids in kJ/mol

Lanthanoid	IE_1	IE_2	IE_3
La	538.1	1067	1850.3
Ce	528.0	1047	1949
Pr	523.0	1018	2086
Nd	530.0	1034	2130
Pm	536.0	1052	2150
Sm	543.0	1068	2260
Eu	547.0	1085	2400
Gd	592.0	1170	1990
Tb	564.0	1112	2110
Dy	572.0	1126	2200
Ho	581.0	1139	2200
Er	589.0	1151	2190
Tm	596.7	1163	2284
Yb	603.4	1175	2415
Lu	523.5	1340	2022

Problem : Which of the following will have highest forth ionization enthalpy IE_4? $La^{4\oplus}$, $Gd^{4\oplus}$, $Lu^{4\oplus}$.

Solution : First write electronic configuration of that element/ion. Check for any unpaired electrons present. The energy required for removal of that electron will be less as compared to the energy required to remove an electron from an electron pair.Also compare the energies of the orbitals occupying those electrons. It will be easier to remove an electron from an orbital that is lower in energy than the one with higher in energy. First ionization enthalpy generally decrease across the period.

8.12.2 Oxidation state : +3 oxidation state is common to all elements in which 2 electrons of s- subshell and one from d or f- subshell are removed. The 4f electrons are strongly screened by inner electrons of 5s and 5p electrons. Thus, 4f electrons are not involved in the bonding. Besides these, some lanthanoids show oxidation states +2 and +4. They are formed in case of f^0, f^7 , f^{14} configurations or resulting ions.

For example : $Ce^{4\oplus}$ (f^0) ; $Eu^{2\oplus}$ and $Tb^{4\oplus}$ (f^7) ; $Yb^{2\oplus}$ (f^{14}) Refer Table 8.11.

8.12.3 Colour and Spectra :

Some trivalent ions ($M^{3\oplus}$) are coloured in solid state as well as in solution. The colour of lanthanoid ion is due to f-f transitions which correspond to energy in the visible region of the electromagnetic spectrum. The colour of ions having nf electrons is about the same as those having (14 – n)f electrons. (where n is an integer 1-13).

Ln ion	No. of f-electrons	Colour	
$Pr^{3\oplus}$	$4f^2$	green	(14 -n) f-electrons =14-2 =12
$Tm^{3\oplus}$	$4f^{12}$	green	n f-electrons =12
$Nd^{3\oplus}$	$4f^3$	pink	(14 -n) f-electrons =14-3 =11
$Er^{3\oplus}$	$4f^{11}$	pink	nf-electrons =11

8.12.4 Atomic and ionic radii (Lanthanoid Contraction) : As we move along the lanthanoid series, there is a decrease in atomic and ionic radii (Fig.8.6). This steady decrease in the atomic and ionic radii is called Lanthanoide contraction. As we move from one element to another the nuclear charge increases by one unit and one electron is added. The new electrons are added to the same inner 4f subshell. Thus the 4f electrons shield each other from the nuclear charge poorly owing to their diffused nature. With increasing atomic number and nuclear charge, the effective nuclear charge experienced by each 4f electrons increases. As a result, the whole of 4f electron shell contracts at each successive element.

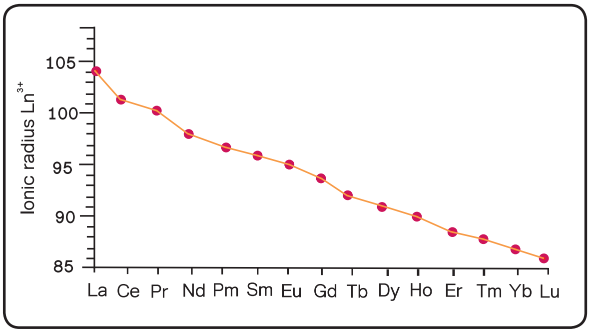


Fig. 8.6 : Ionic radii of lanthanoids in +3 oxidation state

In section 8.3.4 we have learnt about the magnetic behaviour of transition metal complexes.

Use your brain power

- Do you think that lanthanoid complexes would show magnetism?
- Can you calculate the spin only magnetic moment of lanthanoid complexes using the same formula that you used for transition metal complexes?
- Calculate the spin only magnetic moment of La^{3+}. Compare the value with that given in Table 8.13 Is it same or different?

Table 8.13: Effective magnetic moments of lanthanoids in +3 oxidation state

Ln	Ln^{3+} oxidation state	No. of unpaired electrons	Observed magnetic moment, $\mu_{eff\ B.M}$
La	$4f^0$	0	0
Ce	$4f^1$	1	2.3-2.5
Pr	$4f^2$	2	3.4-3.6
Nd	$4f^3$	3	3.5-3.6
Pm	$4f^4$	4	--
Sm	$4f^5$	5	1.4-1.7
Eu	$4f^6$	6	3.3-3.5
Gd	$4f^7$	7	7.9-8.0
Tb	$4f^8$	6	9.5-9.8
Dy	$4f^9$	5	10.4-10.6
Ho	$4f^{10}$	4	10.4-10.7
Er	$4f^{11}$	3	9.4-9.6
Tm	$4f^{12}$	2	7.1-7.6
Yb	$4f^{13}$	1	4.3-4.9
Lu	$4f^{14}$	0	0

8.13 Applications

The lanthanoid compounds are present in every household. It is inside the colour television tubes. When electrons are bombarded on certain mixed lanthanoid compounds, they emit visible light over a small wavelength range. Therefore, the inside surface of a television tube or computer monitor is coated with tiny patches of three different lanthanoid compositions to give three colours that make the colour image.


Promethium


Europium


Actinium


Brekelium

Nobelium


Mendelenium


Sebargium

For example, mixed oxide of europium and yttrium $(Eu,Y)_2O_3$ releases an intense red colour when bombarded with the high energy electrons.The optoelectronics applications use lanthanoid ions as active ions in luminescent materials. The most notable application is the Nd: YAG laser (Nd: YAG = neodymium doped yttrium aluminium garnet). Erbium-doped fibre amplifiers are significant devices in the optical-fibre communication systems. Lanthanoids are used in hybrid cars, superconductors and permanent magnets.

8.14 Actinoids : The last row of elements in the periodic table is the actinoid series. It begins at thorium (Z =72) and ends at lawrencium (Z=103). Most of these elements are not found in nature. They are all radioactive and man-made. The half-lives of the isotopes of thorium (Th-232=1.4 x 10^{10} years) and uranium (U-238=4.5 x 10^9 years) are so long that these elements exist in rocks on earth. The long lived isotopes such as thorium, protactinium, uranium, neptunium, plutonium and americium, are studied in more details. These elements have high densities (~ 15-20 g cm^{-3}), high melting points (~1000 °C) and high boiling points (~3000 °C). Actinoids are less reactive than lanthanoids. For example, they react with hot, but not cold water to give the hydroxide and hydrogen gas. Unlike lanthanoids, they exhibit a range of oxidation numbers in their compounds which varies from +2 to +8. The most common oxidation numbers of the actinoids are shown in Fig. 8.7.

As can be seen from Fig.8.7, the most common oxidation state of early actinoids reflects the loss of all outer electrons which is similar to transition metals than the lanthanoids. A ready loss of 5f electrons by early actinoids indicates that these electrons are much closer in energy to 7s and 6d electrons than the 4f electrons to 6s and 5d electrons as in lanthanoids. All three sets of orbitals that is 6d, 5f and 7s have similar energies. For Th, Pa and Np difference in energy levels is small

Internet my friend

With the help of internet find out the applications of the elements listed in table below. Share this information with your friends

Element	Applications
Lanthanum	
Ytterbium	
Erbium	
Praseodymium	
Samarium	
Promethium	

so electrons occupy either 6d or 5f oribitals. In actinoids series the 5f are orbitals appreciablly lower in energy, thus from Pu onwards 5f shell gets filled in a regular way.

The electronic configuration of actinoids is [Rn] 5f$^{0-14}$ 6d$^{0-2}$ 7s^{2}, where Rn is the electronic configuration of radon. As seen from Fig. 8.7, the most stable oxidation state in actinoids is +3. The highest common oxidation states of early actinoids reflect the loss of all outer electrons which is similar to transition metals than lanthanoids. For example, uranium has electronic configuration of [Rn]7s^{2}5f^{3}6d^{1}. The formation of +6 oxidation state corresponds to an electronic configuration of [Rn]. Similar to lanthanoids, loss of s and d electrons occur before f electrons, in formation of 3+ ions. A ready loss of 5f electrons by early actinoids indicates that these electrons are much closer in energy to 7s and 6d electrons than the 4f electrons are to 6s and 5d electrons in the lanthanoids. In turn, 5f and 6s orbitals expand as they are partially shielded from the nuclear attraction by 7s electrons. As a result all three sets of orbitals i.e. 6d, 5f and 7s have very similar energies. The ionic radius decreases as we move across the series which is known as 'Actinoid contraction'. This is attributed to poor shielding offered by f electrons.

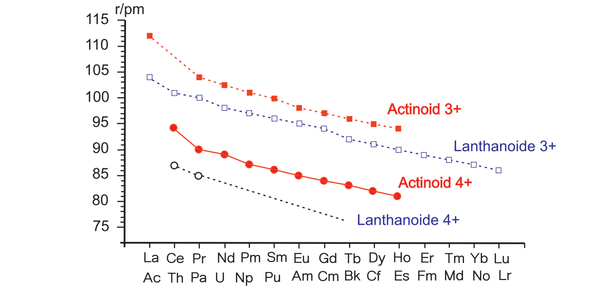


Fig. 8. 8 Figure depicting contraction of ionic radii of lanthanoides and actinoids

8.15 Properties of Actinoids

i. Similar to lanthanoids, they appear silvery white in colour.

ii. These are highly reactive radioactive elements

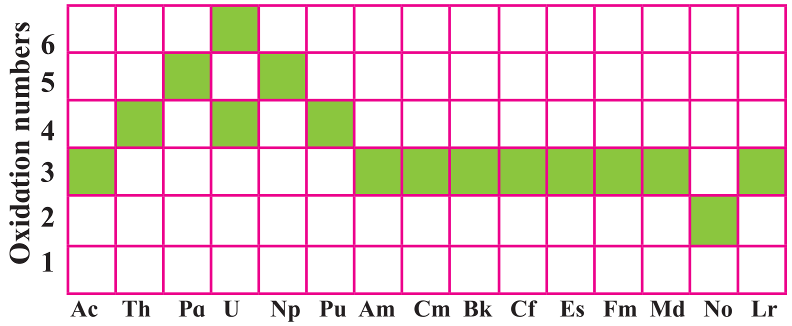


Fig. 8. 7 The most common oxidation numbers of actinoids

iii. Except promethium (Pm), all are non-radioactive in nature

iv. They experience decrease in the atomic and ionic radii from actinium (Ac) to lawrencium (Lw), known as **actinoid contraction**

v. They usually exhibit +3 oxidation state. Elements of first half of the series usually exhibit higher oxidation states.

8.16 Applications of actinoids : We have seen that the half-lives of natural thorium and uranium isotopes are so long that we get very negligible radiation from these elements. We find them in everyday use. For example, Th(IV) oxide, ThO_2 with 1% CeO_2 was used as a major source of indoor lighting before incandescent lamps came into existence only because these oxides convert heat energy from burning natural gas to an intense light. Even today, there is a great demand for these lights for outdoor camping.

Do you know ?

Uranium is another actinoid which is in great demand as it is used in the nuclear reactors. One of the extraction methods for uranium has a very interesting chemistry. The ore containing U(IV) oxide, UO_2, is first treated with Fe(III) ion to give U(VI) oxide, UO_3

$$UO_2\ (s) + H_2O(l) \rightarrow UO_3\ (s) + 2H^{\oplus}\ (aq) + 2e^{\ominus}$$

$$Fe^{3\oplus}\ (aq) + e^{\ominus} \rightarrow Fe^{2\oplus}\ (aq)$$

Addition of H_2SO_4 to this solution produces uranyl sulphate containing $UO_2^{2\oplus}$ cation:

$$UO_3\ (s) + H_2SO_4\ (aq) \rightarrow UO_2SO_4\ (aq) + H_2O\ (l)$$

After purification, ammonia is added to the solution giving bright yellow precipitate of ammonium diuranate, $(NH_4)_2U_7O_7$:

$$2\ UO_2SO_4\ (aq) + 6\ NH_3\ (aq) + 3\ H_2O\ (l) \rightarrow (NH_4)_2U_7O_7\ (s) + 2\ (NH_4)_2SO_4\ (aq)$$

This yellow cake is the marketable form of uranium!

Similarities and differences between lanthanides and actinoids

Similarities	Differences
Both the series show a +3 oxidation state	Lanthanoids show a maximum oxidation state of +4 while actinoids show oxidation states of +3, +4, +5, +6 and +7
In both the series, the f-orbitals are filled gradually	Lanthanoids do not form complexes easily. Actinoids have a greater tendency to form complexes with ligands such as thio-ethers
Ionic radius of the elements in both series decreases with an increase in atomic number	All lanthanoids are non-radioactive except promethium but actinides are radioactive in nature
The electronegativity of all the elements in both the series is low and are said to be highly reactive	Lanthanoids do not form oxocations, but actinides form oxocations such as UO^+, PuO^+, NpO_2^+
The nitrates, perchlorates and sulphates of all the elements are soluble while the hydroxides, fluorides and carbonates are insoluble	Most of the lanthanoids are colourless in nature whereas the actinoids are coloured ions

Table 8.14 Electronic configuration of actinoids and their ionic radii in +3 oxidation state

Element	Symbol	Atomic number	Electronic configuration		*Atomic radii, pm	*Ionic radii ($Ac^{3\oplus}$), pm
			ground state	+3 oxidation state		
Actinium	Ac	89	$[Rn]5f^{0}6d^{1}7s^{2}$	$5f^{0}$	203	126
Thorium	Th	90	$[Rn]5f^{0}6d^{2}7s^{2}$	$5f^{1}$	180	-
Protactinium	Pa	91	$[Rn]5f^{2}6d^{1}7s^{2}$	$5f^{2}$	162	118
Uranium	U	92	$[Rn]5f^{3}6d^{1}7s^{2}$	$5f^{3}$	153	118
Neptunium	Np	93	$[Rn]5f^{4}6d^{1}7s^{2}$	$5f^{4}$	150	116
Plutonium	Pu	94	$[Rn]5f^{6}6d^{0}7s^{2}$	$5f^{5}$	162	115
Americium	Am	95	$[Rn]5f^{7}6d^{0}7s^{2}$	$5f^{6}$	173	114
Curium	Cm	96	$[Rn]5f^{7}6d^{1}7s^{2}$	$5f^{7}$	174	112
Berkelium	Bk	97	$[Rn]5f^{9}6d^{0}7s^{2}$	$5f^{8}$	170	110
Californium	Cf	98	$[Rn]5f^{10}6d^{0}7s^{2}$	$5f^{9}$	186	109
Einsteinium	Es	99	$[Rn]5f^{11}6d^{0}7s^{2}$	$5f^{10}$	186	98
Fermium	Fm	100	$[Rn]5f^{12}6d^{0}7s^{2}$	$5f^{11}$	198	91
Mendelevium	Md	101	$[Rn]5f^{13}6d^{0}7s^{2}$	$5f^{12}$	194	90
Nobelium	No	102	$[Rn]5f^{14}6d^{0}7s^{2}$	$5f^{13}$	197	95
Lawrencium	Lr	103	$[Rn]5f^{14}6d^{1}7s^{2}$	$5f^{14}$	171	88

Table 8.15 : Some comparison between Pre-Transition, Lanthanoids and Transition Metals

Pre-Transition Metals	Lanthanoids	Transition Metals
Essentially monovalent - show group (n+) oxidation state	Essentially in (+3) oxidation state (+2/+4 for certain configurations)	Show variable oxidation states
Periodic trends dominated by effective nuclear charge at noble gas configuration	Lanthanoid contraction of $Ln^{3\oplus}$	Size changes of $M^{n\oplus}$, less marked
Similar properties for a given group	Similar properties	Substantial changes in properties
Always 'hard' (O, X, N donors, preferably negatively charged)	Always 'hard' (O, X, N donors, preferably negatively charged)	heavier metals (increasingly from Fe-Cu) may show a 'soft' character
No ligand field effects	Insignificant ligand field effects	Substantial ligand field effects
Poor coordination properties(C.N. determined by size)	High coordination numbers (C.N. determined by size)	Coordination number 6 is typical maximum (many exceptions)
Flexibility in geometry	Flexibility in geometry	Fixed geometries (ligand field effects)
No magnetism	Show magnetism	Show magnetism

8.17 Postactinoid elements : You have seen that elements with atomic number greater than 92 are called 'Transuranium'. Elements from atomic number 93 to 103 now are included in actinoid series and those from 104 to 118 are called as postactinoid elements. The postactinoid elements that are known so far are transition metals. They are included as postactinoids because similar to actinoid elements, they can be synthesized in the nuclear reactions. So far, nine postactinoid elements have been synthesized. It is difficult to study their chemistry owing their short half-lives. For example, element 112 has a half-life of only 2.8 x 10^{-4} seconds. With half-lives of miliseconds only a little is known about the chemistry of these elements. Rutherfordium forms a chloride, $RfCl_4$, similar to zirconium and hafnium in the +4 oxidation state. Dubnium resembles to both, group 5 transition metal, niobium(V) and actinoid, protactinium(V).

Do you know ?

Traditionally, no element was named after a still-living scientist. This principle was put to an end with naming the element 106 as 'Seaborgium'.

Exercises

1. Choose the most correct option.

i. Which one of the following is dimagnetic

a. $Cr^{2\oplus}$ b. $Fe^{3\oplus}$

c. $Cu^{2\oplus}$ d. $Sc^{3\oplus}$

ii. Most stable oxidation state of Titanium is

a. +2 b. +3

c. +4 d. +5

iii. Components of Nichrome alloy are are

a. Ni, Cr, Fe b. Ni, Cr, Fe, C

c. Ni, Cr d. Cu, Fe

iv. Most stable oxidation state of Ruthenium is

a. +2 b. +4

c. +8 d. +6

v. Stable oxidation states for chromiom are

a. +2, +3 b. +3, +4

c. +4, +5 d. +3, +6

vi. Electronic configuration of Cu and Cu^{+1}

a. $3d^{10}, 4s^0; 3d^9, 4s^0$

b. $3d^9, 4s^1; 3d^9 4s^0$

c. $3d^{10}, 4s^1; 3d^{10}, 4s^0$

d. $3d^8, 4s^1; 3d^{10}, 4s^0$

vii. Which of the following have d^0s^0 configuration

a. $Sc^{3\oplus}$ b. $Ti^{4\oplus}$

c. $V^{5\oplus}$ d. all of the above

viii. Magnetic moment of a metal complex is 5.9 B.M. Number of unpaired electrons in the complex is

a. 2 b. 3

c. 4 d. 5

ix. In which of the following series all the elements are radioactive in nature

a. Lanthanides

b. Actinides

c. d-block elements

d. s-block elements

x. Which of the following sets of ions contain only paramagnetic ions

a. $Sm^{3\oplus}$, $Ho^{3\oplus}$, $Lu^{3\oplus}$

b. $La^{3\oplus}$, $Ce^{3\oplus}$, $Sm^{3\oplus}$

c. $La^{3\oplus}$, $Eu^{3\oplus}$, $Gd^{3\oplus}$

d. $Ce^{3\oplus}$, $Eu^{3\oplus}$, $Yb^{3\oplus}$

xi. Which actinoid, other than uranium, occur in significant amount naturally?

a. Thorium b. Actinium

c. Protactinium d. Plutonium

xii. The flux added during extraction of Iron from teamatite are its?

a. Silica

b. Calcium carbonate

c. Sodium carbonate

d. Alumina

2. Answer the following

i What is the oxidation state of Manganese in (i) MnO_4^{2-} (ii) MnO_4^{-} ?

ii. Give uses of $KMnO_4$

iii. Why salts of $Sc^{3\oplus}$, $Ti^{4\oplus}$, $V^{5\oplus}$ are colourless ?

iv. Which steps are involved in manufacture of potassium dichromate from chromite ore ?

v. Balance the following equation

(i) $KMnO_4 + H_2C_2O_4 \longrightarrow MnSO_4 + K_2SO_4 + H_2O + O_2$

(ii) $K_2Cr_2O_7 + KI + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$

vi. What are the stable oxidation states of plutonium, cerium, manganese, Europium ?

vii. Write probable electronic configuration of chromium and copper.

viii. Why nobelium is the only actinoid with +2 oxidation state?

ix. Explain with the help of balanced chemical equation, why the solution of Ce(IV) is acidic.

x. What is meant by ‘shielding of electrons’ in an atom?

xi. The atomic number of an element is 90. Is this element diamagnetic or paramagnetic?

3. Answer the following

i. Explain the trends in atomic radii of d block elements

ii. Name different zones in the Blast furnace. Write the reactions taking place in them.

iii. What are the differences between cast iron, wrought iron and steel.

iv. Iron exhibits +2 and +3 oxidation states. Write their electronic configuration. Which will be more stable ? Why ?

v. Give the similarites and differences in elements of 3d, 4d and 5d series.

vi. Explain trends in ionisation enthalpies of d block elements.

vii. What is meant by diamagnetic and paramagnetic? Give one example of diamagnetic and paramagnetic transition metal and lanthanoid metal.

viii. Why the ground-state electronic configurations of gadolinium and lawrentium are different than expected?

ix. Write steps involved in metallugical process

x. Cerium and Terbium behaves as good oxidising agents in +4 oxidation state. Explain.

xi. Europium and xtterbium behave as good reducing agents in +2 oxidation state explain.

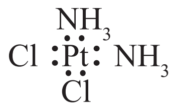
Activity :

Make groups and each group prepares a powerpoint presentation on properties and applications of one element. You can use your imagination to create some innovative ways of presenting data.

You can use pictures, images, flow charts, etc. to make the presentation easier to understand. Don’t forget to cite the reference(s) from where data for presentation is collected (including figures and charts). Have fun!

9. COORDINATION COMPOUNDS

9.1 Introduction : A coordination compound consists of central metal atom or ion surrounded by atoms or molecules. For example, a chemotherapy drug, cisplatin, $Pt(NH_3)_2Cl_2$, is a coordination compound in which the central platinum metal ion is surrounded by two ammonia molecules and two chloride ions. The species surrounding the central metal atom or ion are called ligands. The ligands are linked directly to central metal ion through coordinate bonds. A formation of coordinate bond occurs when the shared electron pair is contributed by ligands. A coordinate bond is conveniently represented by an arrow $\rightarrow$, where the arrow head points to electron acceptor. The central metal atom or ion usually an electron deficient species, accepts an electron pair while the ligands serve as electron donors. Coordination compounds having a metal ion in the centre are common. In cisplatin two ammonia molecules and two chloride ligands utilize their lone pairs of electrons to form bonds with the Pt(II).



The donor nitrogen and chlorine atoms of the ligands are directly attached to and form bonds with platinum.

Can you recall ?

What are Lewis acids and bases ?

Formation of a coordination compound can be looked upon as the Lewis acid-base interaction. The ligands being electron pair donors are Lewis bases. The central metal ion being electron pair acceptor serves as Lewis acid.

9.2 Types of ligands : The ligands can be classified as monodentate and polydentate ligands depending on the number of electron donor atoms they have.

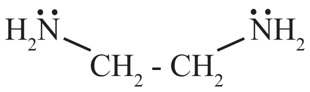
9.2.1 Monodentate ligands : A monodentate ligand is the one where a single donor atom shares an electron pair to form a coordinate bond with the central metal ion. For example: the ligands $Cl^{\ominus}$, $OH^{\ominus}$ or $CN^{\ominus}$ attached to metal have electron pair on Cl, O and N, respectively which are donor atoms :

Use your brain power

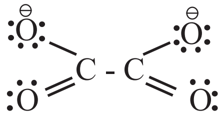
Draw Lewis structure of the following ligands and identify the donor atom in them : NH_3, H_2O

9.2.2 Polydentate ligands : A polydentate ligand has two or more donor atoms linked to the central metal ion. For example, ethylenediamine and oxalate ion. Each of these ligands possesses two donor atoms. These are **bidentate** ligands.

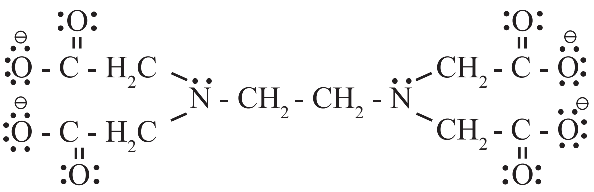
i. Ethylenediamine binds to metal using electron pair on each of its two nitrogens.



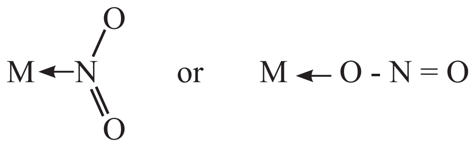
Similarly oxalate ion $(C_2O_4)^{2\ominus}$ utilizes electron pair on each of its negatively charged oxygen atoms upon linking with the metal.



ii. Ethylenediaminetetraacetate ion $(EDTA)^{4\ominus}$ binds to metal ion by electron pairs of four oxygen and two nitrogen atoms. It is a **hexadentate** ligand.



9.2.3 Ambidentate ligand : The ligands which have two donor atoms and use the electron pair of either donor atoms to form a coordinate bond with the metal ion, are ambidentate ligands. For example, the ligand $NO_2^{\ominus}$ links to metal ion through nitrogen or oxygen.



Similarly, $SCN^{\ominus}$ has two donor atoms nitrogen and sulfur either of which links to metal depicted as M ← SCN or M← NCS.

9.3 Terms used in coordination chemistry:

The following terms are used for describing coordination compounds.

9.3.1 Coordination sphere : The central metal ion and ligands linked to it are enclosed in a square bracket. This is called a coordination sphere, which is a discrete structural unit. When the coordination sphere comprising central metal ion and the surrounding ligands together carry a net charge, it is called the complex ion. The ionisable groups shown outside the bracket are the counter ions. For example, the compound $K_4[Fe(CN)_6]$ has $[Fe(CN)_6]^{4-}$ coordination sphere with the ionisable $K^{\oplus}$ ions representing counter ions. The compound ionizes as :

$$K_4[Fe(CN)_6] \longrightarrow 4K^{\oplus} + [Fe(CN)_6]^{4\ominus}$$

Try this...

Can you write ionisation of $[Ni(NH_3)_6]Cl_2$? Identify coordination sphere and counter ions.

9.3.2 Charge number of complex ion and oxidation state of metal ion :

The net charge residing on the complex ion is its charge number. It is algebraic sum of the charges carried by the metal ion and the ligands. The charge carried by the metal ion is its oxidation state (O.S.). The complex $[Fe(CN)_6]^{4\ominus}$ has charge number of -4. It can be utilised to calculate O.S. of Fe. Thus,

charge number of complex = -4

= (O.S. of Fe + charge of ligands)

= (O.S. of Fe + 6 × charge of $CN^{\ominus}$ ion)

= (O.S. of Fe + 6 × (-1))

Therefore, O.S. of Fe = -4 + 6 = +2.

Can you tell ?

A complex is made of Co(III) and consists of four NH_3 molecules and two $Cl^{\ominus}$ ions as ligands. What is the charge number and formula of complex ion ?

9.3.3 Coordination number (C.N.) of central metal ion : Look at the complex $[Co(NH_3)_4Cl_2]^{\oplus}$. Here four ammonia molecules and two chloride ions, that is, total six ligands are attached to the cobalt ion. All these are monodentate since each has only one donor atom. There are six donor atoms in the complex. Therefore, the coordination number of $Co^{3\oplus}$ ion in the complex is six. Thus, the coordination number of metal ion attached to monodentate ligands is equal to number of ligands bound to it.

Consider the bidentate ligand $C_2O_4^{2\ominus}$ or ethylenediamine (en). The complexes, $[Fe(C_2O_4)_3]^{3\ominus}$ and $[Co(en)_3]^{3\oplus}$, have three bidentate ligands each. The total donor atoms in three of ligands is six and the C.N. of $Fe^{3\oplus}$ and $Co^{3\oplus}$ in these complexes is six.

C.N. of metal ion in a complex is the number of ligand donor atoms directly attached to it or the number of electron pairs involved in the coordinate bond.

Use your brain power

Coordination number used in coordination of compounds in somewhat different than that used in solid state. Explain

Can you tell ?

What is the coordination number of Co in $[CoCl_2(en)_2]^{\oplus}$, of Ir in $[Ir(C_2O_4)_2Cl_2]^{3\oplus}$ and of Pt in $[Pt(NO_2)_2(NH_3)_2]$?

9.3.4 Double salt and coordination complex

Combination of two or more stable compounds in stochiometric ratio can give two types of substances, namely, double salt and coordination complexes.

Double salt : A double salt dissociates in water completely into simple ions. For example (i) Mohr's salt, $FeSO_4(NH_4)_2SO_4.6H_2O$ dissociates as :

$$FeSO_4(NH_4)_2SO_4.6H_2O \xrightarrow{\text{water}} Fe^{2\oplus}(aq) + 2NH_4^{\oplus}(aq) + 2SO_4^{2\ominus}(aq)$$

ii. Carnalite $KCl.MgCl_2.6H_2O$ dissociates as

$$KCl.MgCl_2.6H_2O \xrightarrow{\text{water}} K^{\oplus}(aq) + Mg^{2\oplus}(aq) + 3Cl^{\ominus}(aq)$$

Coordination complex : A coordination complex dissociates in water with at least one complex ion. For example, $K_4[Fe(CN)_6]$ dissociates as the complex ion and counter ion.

$$K_4[Fe(CN)_6] \longrightarrow \underset{\text{(counter ion)}}{4K^{\oplus}(aq)} + \underset{\text{(complex ion)}}{[Fe(CN)_6]^{4\ominus}}$$

9.3.5 Werner theory of coordination complexes :

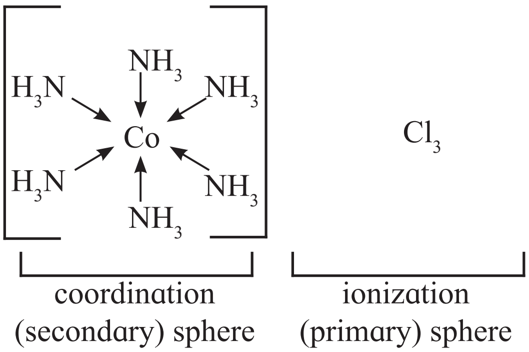
The first attempt to explain nature of bonding in coordination compounds was put forth by Werner. The postulates of Werner theory are as follows.

Postulate (i) Unlike metal salts, the metal in a complex possesses two types of valencies : primary (ionizable) valency and secondary (nonionizable) valency.

Postulate (ii) The ionizable sphere consists of entities which satisfy the primary valency of the metal. Primary valencies are generally satisfied by anions.

Postulate (iii) The secondary coordination sphere consists of entities which satisfy the secondary valencies and are non ionizable. The secondary valencies for a metal ion are fixed and satisfied by either anions or neutral ligands. Number of secondary valencies is equal to the coordination number.

Postulate (iv) The secondary valencies have a fixed spatial arrangement around the metal ion. Two spheres of attraction in the complex $[Co(NH_3)_6]Cl_3$ are shown.



Remember...

When a complex is brought into solution it does not dissociate into simple metal ions. When $[Co(NH_3)_6]Cl_3$ is dissolved in water it does not give the test for $Co^{3\oplus}$ or NH_3. However, on reacting with $AgNO_3$ a curdy white precipitate of AgCl corresponding to 3 moles is observed.

Problem 9.1 : One mole of a purple coloured complex $CoCl_3$ and NH_3 on treatment with excess $AgNO_3$ produces two moles AgCl. Write the formula of the complex if the coordination number of Co is 6.

Solution : One mole of the complex gives 2 moles of AgCl. It indicates that two $Cl^{\ominus}$ ions react with $Ag^{\oplus}$ ions. The complex has two ionisable $Cl^{\ominus}$ ions. The formula of the complex is then $[Co(NH_3)_5Cl]Cl_2$.

Can you tell ?

One mole of a green coloured complex of $CoCl_3$ and NH_3 on treatment with excess of $AgNO_3$ produces 1 mole of AgCl. What is the formula of the complex ? (Given : C.N. of Co is 6)

A complex with coordination number six has **octahedral** structure. When four coordinating groups are attached to the metal ion the complex would either be with **square planar** or **tetrahedral structure**.

9.4 Classification of complexes: The coordination complexes are classified according to types of ligands and sign of charge on the complex ion.

9.4.1 Classification on the basis of types of ligands

i. Homoleptic complexes : Consider $[Co(NH_3)_6]^{3\oplus}$. Here only one type of ligands surrounds the $Co^{3\oplus}$ ion. The complexes in which metal ion is bound to only one type of ligands are homoleptic.

ii. Heteroleptic complexes : Look at the complex $[Co(NH_3)_4Cl_2]^{\oplus}$. There are two types of ligands, NH_3 and Cl attached to $Co^{3\oplus}$ ion. Such complexes in which metal ion is surrounded by more than one type of ligands are heteroleptic.

Use your brain power

Classify the complexes as homoleptic and heteroleptic $[Co(NH_3)_5Cl]SO_4$, $[Co(ONO)(NH_3)_5]Cl_2$ $[CoCl(NH_3)(en)_2]^{2\oplus}$ and $[Cu(C_2O_4)_3]^{3\ominus}$.

9.4.2 Classification on the basis of charge on the complex

i. Cationic complexes : A positively charged coordination sphere or a coordination compound having a positively charged coordination sphere is called cationic sphere complex.

For example: the cation $[Zn(NH_3)_4]^{2\oplus}$ and $[Co(NH_3)_5Cl]SO_4$ are cationic complexes. The latter has coordination sphere $[Co(NH_3)_5Cl]^{2\oplus}$; the anion $SO_4^{2\ominus}$ makes it electrically neutral.

ii. Anionic sphere complexes : A negatively charged coordination sphere or a coordination compound having negatively charged coordination sphere is called anionic sphere complex. For example, $[Ni(CN)_4]^{2\ominus}$ and $K_3[Fe(CN)_6]$ have anionic coordination sphere; $[Fe(CN)_6]^{3\ominus}$ and three $K^{\oplus}$ ions make the latter electrically neutral.

iii. Neutral sphere complexes : A neutral coordination complex does not possess cationic or anionic sphere. $[Pt(NH_3)_2Cl_2]$ or $[Ni(CO)_4]$ have neither cation nor anion but are neutral sphere complexes.

Use your brain power

Classify the complexes as cationic, anionic or neutral. $Na_4[Fe(CN)_6]$, $Co(NH_3)_6Cl_2$, $Cr(H_2O)_2(C_2O_4)_2^{3\ominus}$, $PtCl_2(en)_2$ and $Cr(CO)_6$.

9.5 IUPAC nomenclature of coordination compounds : Tables 9.1, 9.2 and 9.3 summarize the IUPAC nomenclature of coordination compounds.

Rules for naming coordination compounds recommended by IUPAC are as follows:

1. In naming the complex ion or neutral molecule, name the ligand first and then the metal.
2. The names of anionic ligands are obtained by changing the ending -ide to -o and -ate to -ato.
3. The name of a complex is one single word. There must not be any space between different ligand names as well as between ligand name and the name of the metal.
4. After the name of the metal, write its oxidation state in Roman number which appears in parentheses without any space between metal name and parentheses.
5. If complex has more than one ligand of the same type, the number is indicated with prefixes, di-, tri-, tetra-, penta-, hexa- and so on.
6. For the complex having more than one type of ligands, they are written in an alphabetical order. Suppose two ligands with prefixes

Table 9.1 : IUPAC names of anionic and neutral ligands

Anionic ligand	**IUPAC name**	**Anionic ligand**	**IUPAC name**
$Br^{\ominus}$, Bromide	Bromo	$CO_3^{2\ominus}$, Carbonate	Carbonato
$Cl^{\ominus}$, Chloride	Chloro	$OH^{\ominus}$, Hydroxide	Hydroxo
$F^{\ominus}$, Fluoride	Fluoro	$C_2O_4^{2\ominus}$, Oxalate	Oxalato
$I^{\ominus}$ Iodide	Iodo	$NO_2^{\ominus}$, Nitrite	Nitro (For N - bonded ligand)
$CN^{\ominus}$, Cyanide	Cyano	$ONO^{\ominus}$, Nitrite	Nitrito(For O-bonded ligand)
$SO_4^{2\ominus}$, Sulphate	Sulphato	$SCN^{\ominus}$, Thiocyanate	Thiocyanato (For ligand donor atom S)
$NO_3^{\ominus}$, Nitro	Nitrato	$NCS^{\ominus}$, Thiocyanate	Isothiocyanato (For ligand donor atom N)
Neutral ligand	**IUPAC name**	**Neutral ligand**	**IUPAC names**
NH_3, Ammonia	Ammine (Note the spelling)	H_2O, water	Aqua
CO, Carbon monoxide	Cabonyl	en, Ethylene diamine	Ethylenediamine

Table 9.2 : IUPAC names of metals in anionic complexes

Metal	**IUPAC name**	**Metal**	**IUPAC name**
Aluminium, Al	Aluminate	Chromium, Cr	Chromate
Cobalt, Co	Cobaltate	Copper, Cu	Cuprate
Gold, Au	Aurate	Iron, Fe	Ferrate
Manganese, Mn	Maganate	Nickel, Ni	Nickelate
Platinum, Pt	Platinate	Zinc, Zn	Zincate

Table 9.3 : IUPAC names of some complexes

Complex	**IUPAC name**
i. Anionic complexes : a.$[Ni(CN)_4]^{2\ominus}$ b. $[Co(C_2O_4)_3]^{3\ominus}$ c. $[Fe(CN)_6]^{4\ominus}$	Tetracyanonickelate(II) ion Trioxalatocobaltate(III) ion Hexacyanoferrate(II) ion
ii. Compounds containing complex anions and metal cations :	
a. $Na_3[Co(NO_2)_6]$ b. $K_3[Al(C_2O_4)_3]$ c. $Na_3[AlF_6]$	Sodium hexanitrocobaltate(III) Potasium trioxalatoaluminate(III) Sodium hexafluoroaluminate(III)
iii. Cationic complexes : a. $Cu(NH_3)_4^{2\oplus}$ b.$[Fe(H_2O)_5(NCS)]^{2\oplus}$ c.$[Pt(en)_2(SCN)_2]^{2\oplus}$	Tetraamminecopper(II) ion Pentaaquaisothiocyanatoiron(III) ion, Bis(ethylenediamine)dithiocyanatoplatinum(IV).
iv. Compounds containing complex cations and anion :	
a. $[PtBr_2(NH_3)_4]Br_2$ b. $[Co(NH_3)_5CO_3]Cl$ c. $[Co(H_2O)(NH_3)_5]I_3$	Tetraamminedibromoplatinum(IV) bromide, Pentaamminecarbonatocobalt(III) chloride, Pentaammineaquacobalt(III) iodide.
v. Neutral complexes : a. $[Co(NO_2)_3(NH_3)_3]$ b. $Fe(CO)_5$ c. $[Rh(NH_3)_3(SCN)_3]$	Triamminetrinitrocobalt(III) Pentacarbonyliron(0) Triamminetrithiocyanatorhodium(III)

are tetraaqua and dichloro. While naming in alphabetical order, tetraaqua is first and then dichloro.

7. If the name of ligand itself contains numerical prefix then display number by prefixes with bis for 2, tris for 3, tetrakis for 4 and so forth. Put the ligand name in parentheses. For example, (ethylenediamine)$_3$ or (en$_3$) would appear as tris(ethylenediamine) or tris(ethane-1, 2-diamine).
8. The metal in cationic or neutral complex is specified by its usual name while in the anionic complex the name of metal ends with 'ate'.

Try this...

Write the representation of

- Tricarbonatocobaltate(III) ion.
- Sodium hexacyanoferrate(III).
- Potassium hexa cyanoferrate (II)
- Aquachlorobis(ethylenediamine) cobalt(III).
- Tetraaquadichlorochromium(III) chloride.
- Diamminedichloroplatinum(II).

9.6 Effective Atomic Number (EAN) Rule :

An early attempt to explain the stability of coordination compounds was made by Sidgwick who proposed an empirical rule known as effective atomic number (EAN) rule. EAN equals total number of electrons around the central metal ion in the complex. EAN rule states that a metal ion continues to accept electrons pairs till it attains the electronic configuration of the next noble gas. Thus if the EAN is equal to 18 (Ar), 36 (Kr), 54 (Xe), or 86 (Rn) then the EAN rule is obeyed.

EAN can be calculated with the following. Formula

EAN = number of electrons of metal ion + total number of electrons donated by ligands

= atomic number of metal (Z) - number of electrons lost by metal to form the ion (X) + number of electrons donated by ligands (Y).

= Z - X + Y

Cosider $Co[NH_3]_6^{3\oplus}$

Oxidation state of Cobalt is +3, six ligands donate 12 electrons.

$Z = 27; X = 3; Y = 12$

EAN of $Co^{3\oplus} = 27 - 3 + 12 = 36$.

Try this...

Find out the EAN of $Zn(NH_3)_4^{2\oplus}$,$[Fe(CN)_6]^{4\ominus}$

$Cr(CO)_6$ and $[Fe(CN)_6]^{4\ominus}$ are some examples of coordination compounds which obey the EAN rule. Certain other coordination compounds however do not obey the EAN rule. For example, $[Fe(CN)_6]^{3\ominus}$ and $Cu[NH_3]_4^{2\oplus}$ have EAN 35.

Use your brain power

Do the following complexes follow the EAN rule ? $Cr(CO)_4$, $Ni(CO)_4$, $Mn(CO)_5$, $Fe(CO)_5$.

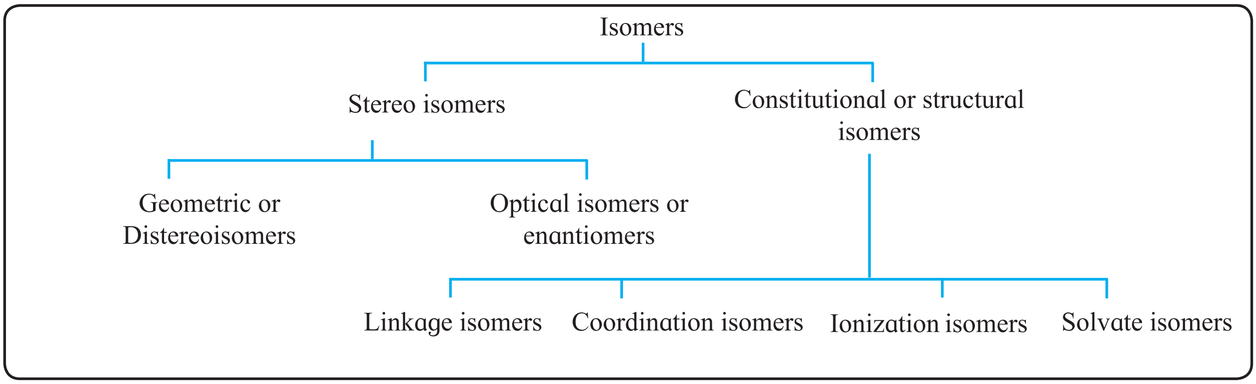


Fig. 9.1 : Classification of isomers in coordination compounds

9.7 Isomerism in coordination compounds :

One of the interesting aspects of coordination chemistry is existence of isomers. Isomers are different compounds that have the same molecular formula. Their chemical reactivities and physical properties such as colour, solubility and melting point are different.

Broadly speaking, isomers are classified into two types namely stereoisomers and constitutional (or structural) isomers as displayed in Fig. 9.1.

9.7.1 Stereoisomers : Stereoisomers have the same links among constituent atoms however the arrangements of atoms in space are different.

There are two kinds of stereoisomers in coordination compounds: (a) geometric isomers or distereoisomers and (b) enantiomers or optical isomers.

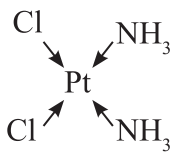
a. Geometric isomers or distereoisomers : These are nonsuperimposable mirror image isomers. These are possible in heteroleptic complexes. In these isomers, there are cis and trans types of arrangements of ligands.

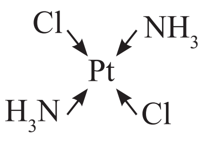
Cis-isomers : Identical ligands occupy adjacent positions.

Trans-isomer : Identical ligands occupy the opposite positions.

Cis and trans isomers have different properties. Cis trans isomerism is observed in square planar and octahedral complexes.

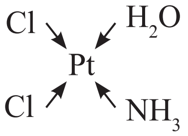
i. Cis and trans isomers in square planar complexes : The square planar complexes of MA_2B_2 and MA_2BC type exist as cis and trans isomers, where A, B and C are monodentate ligands, M is metal. For example : $Pt(NH_3)_2Cl_2$, (MA_2B_2 type)

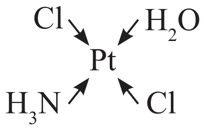

cis isomer


trans isomer

Here the cis isomer is more soluble in water than the trans isomer. The cis isomer named cisplatin is an anticancer drug while the trans isomer is physiologically inactive. The cis isomer is polar with non-zero dipole moment. The trans isomer has zero dipole moment as a result of the two opposite Pt - Cl and two Pt-NH_3 bond moments, which cancel each other.

$[Pt(NH_3)(H_2O)Cl_2]$ (MA_2BC type)

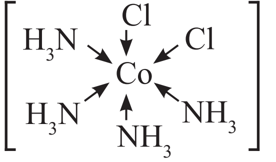

cis isomer

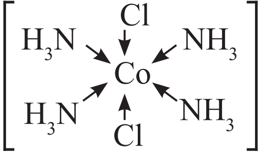

trans isomer

Four coordinate tetrahedral complexes do not show cis and trans isomers.

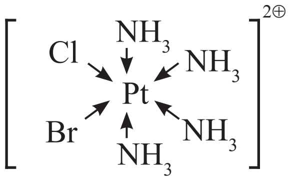
iii. Cis and trans isomers in octahedral complexes : The octahedral complexes of the type MA_4B_2, MA_4BC and $M(AA)_2B_2$ exist as cis and trans isomers. (AA) is a bidentate ligand.

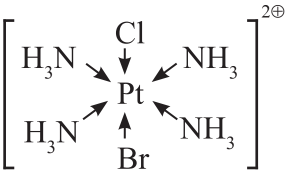
$[Co(NH_3)_4Cl_2]^{\oplus}$, ($MA_4B_2$ type)


cis isomer

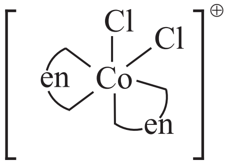

trans isomer

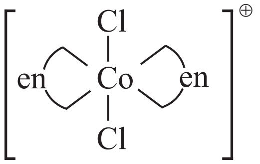
$[Pt(NH_3)_4ClBr]^{2\oplus}$, ($MA_4BC$ type)


cis isomer


trans isomer

$[Co(en)_2Cl_2]^{\oplus}$, ($M(AA)_2B_2$ type)


cis isomer


trans isomer

Try this...

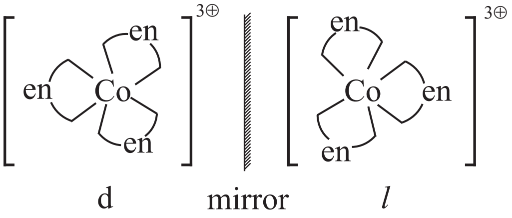
Draw structures of the cis and trans isomers of $[Fe(NH_3)_2(CN)_4]^{\ominus}$

b. Optical isomers (Enantiomers) : The complex molecules or ions that are nonsuperimposable mirror images of each other are enantiomers. The nonsuperimposable mirror images are chiral. (A more elaborate discussion on chirality and optical isomerism is included in Chapter 10.)

Enantiomers have identical properties however differ in their response to the plane-polarized light. The enantiomer that rotates the plane of plane-polarized light to right (clockwise) is called the dextro (d) isomer, while the other that rotates the plane to left (anticlockwise) is called laevo (*l*) isomer.

i. Optical iomers in octahedral complexes

$[Co(en)_3]^{3\oplus}$



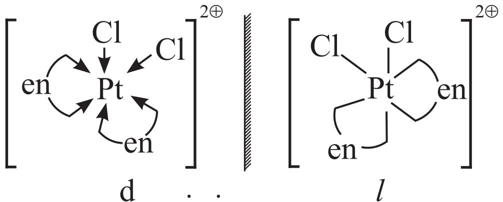
Remember...

Our hands are non superimposable mirror images. When you hold your left hand upto a mirror the image looks like right hand.

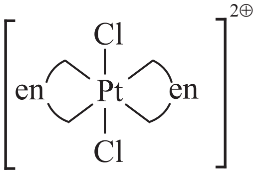
ii. Octahedral complexes existing as both geometric and optical isomers

$[PtCl_2(en)_2]^{2\oplus}$

In this type of complex, only the cis isomer exists as pair of enantiomers



cis isomer



trans isomer

Square planar complexes do not show enantiomers since they have mirror plane and axis of symmetry.

Try this...

1. Draw enantiomers of $[Cr(ox)_3]^{3\ominus}$

2. Draw enantiomers and cis and trans isomers of $[Cr(H_2O)_2(ox)_2]^{\ominus}$ (where ox = $C_2O_4^{2\ominus}$)

9.7.2 Structural isomers (Constitutional isomers) : Structural isomers possess different linkages among their constituent atoms and have, their chemical formulae to be the same.

They can be classified as linkage isomers, ionization isomers, coordination isomers and solvate isomers.

a. Linkage isomers : These isomers are formed when the ligand has two different donor atoms. It coordinates to the metal via different donor atoms. Thus the nitrite ion $NO_2^{\ominus}$ having two donor atoms show isomers as :

$[Co(NH_3)_5(NO_2)]^{2\oplus}$ and $[Co(NH_3)_5(ONO)]^{2\oplus}$

The nitro complex has Co-N bond and the nitrito complex is linked through Co-O bond. These are linkage isomers.

Can you tell ?

Write linkage isomers of $[Fe(H_2O)_5SCN]^{\oplus}$. Write their IUPAC names.

b. Ionization isomers : Ionization isomers involve exchange of ligands between coordination and ionization spheres. For example:

$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$
(I) (II)

In compound I, anion $SO_4^{2\ominus}$, bonded to Co is in the coordination sphere while $Br^{\ominus}$ is in the ionization sphere. In compound II, anion $Br^{\ominus}$ is in the coordination sphere linked to Co while $SO_4^{2\ominus}$ is in the ionisation sphere. These complexes in solution ionize to give different ions.

$$[Co(NH_3)_5SO_4]Br \longrightarrow [Co(NH_3)_5SO_4]^{\oplus} + Br^{\ominus}$$

$$[Co(NH_3)_5Br]SO_4 \longrightarrow [Co(NH_3)_5Br]^{2\oplus} + SO_4^{2\ominus}$$

I and II are examples of ionization isomers.

Can you tell ?

Can you write IUPAC names of isomers I and II?

c. Coordination isomers : Coordination isomers show interchange of ligands between cationic and anionic spheres of different metal ions. For example :

$[Co(NH_3)_6]$ $[Cr(CN)_6]$ $[Cr(NH_3)_6]$ $[Co(CN)_6]$
(cationic) (anionic) (cationic) (anionic)
(I) (II)

In isomer I, cobalt is linked to ammine ligand and chromium to cyanide ligand. In isomer II the ligands coordinating to metals are interchanged. Cobalt coordinates with cyanide ligand and chromium to NH_3 ligand. I and II are examples of coordination isomers.

d. Solvate isomers (Hydrate isomers when water is solvent) : These are similar to ionization isomers. Look at the complexes.

$[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2 .H_2O$
(I) (II)

In compound I the solvent water is directly bonded to Cr. In compound II, H_2O appears as the free solvent molecule. I and II represent solvate (hydrate) isomers.

9.8 Stability of the coordination compounds:

The stability of coordination compounds can be explained by knowing their stability constants. The stability is governed by metal-ligand interactions. In this the metal serves as electron-pair acceptor while the ligand as Lewis base (since it is electron donor). The metal-ligand interaction can be realized as the Lewis acid-Lewis base interaction. Stronger the interaction greater is stability of the complex.

Consider the equilibrium for the metal ligand interaction :

$$M^{a\oplus} + nL^{x\ominus} \rightleftharpoons [ML_n]^{a\oplus + nx\ominus}$$

where a, x, $[a\oplus + nx\ominus]$ denote the charge on the metal, ligand and the complex, respectively. Now, the equilibrium constant K is given by

$$K = \frac{[ML_n]^{a\oplus + nx\ominus}}{[M^{a\oplus}][L^{x\ominus}]^n}$$

Stability of the complex can be explained in terms of K. Higher the value of K larger is the thermodynamic stability of the complex.

The equilibria for the complex formation with the corresponding K values are given below.

$$Ag^{\oplus} + 2CN^{\ominus} \rightleftharpoons [Ag(CN)_2]^{\ominus} \quad K = 5.5 \times 10^{18}$$

$$Cu^{2\oplus} + 4CN^{\ominus} \rightleftharpoons [Cu(CN)_4]^{2\ominus} \quad K = 2.0 \times 10^{27}$$

$$Co^{3\oplus} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3\oplus} \quad K = 5.0 \times 10^{33}$$

From the above data, $[Co(NH_3)_6]^{3\oplus}$ is more stable than $[Ag(CN)_2]^{\ominus}$ and $[Cu(CN)_4]^{2\ominus}$.

9.8.1 Factors which govern stability of the complex :

Stability of a complex is governed by (a) charge to size ratio of the metal ion and (b) nature of the ligand.

a. charge to size ratio of the metal ion

Higher the ratio greater is the stability. For the divalent metal ion complexes their stability shows the trend : $Cu^{2\oplus} > Ni^{2\oplus} > Co^{2\oplus} > Fe^{2\oplus} > Mn^{2\oplus} > Cd^{2\oplus}$. The above stability order is called Irving-William order. In the above list both Cu and Cd have the charge +2, however, the ionic radius of $\mathrm{Cu}^{2\oplus}$ is 69 pm and that of $\mathrm{Cd}^{2\oplus}$ is 97 pm. The charge to size ratio of $\mathrm{Cu}^{2\oplus}$ is greater than that of $\mathrm{Cd}^{2\oplus}$. Therefore the $\mathrm{Cu}^{2\oplus}$ forms stable complexes than $\mathrm{Cd}^{2\oplus}$.

b. Nature of the ligand.

A second factor that governs stability of the complexes is related to how easily the ligand can donate its lone pair of electrons to the central metal ion that is, the basicity of the ligand. The ligands those are stronger bases tend to form more stable complexes.

Use your brain power

The stability constant K of the $[\mathrm{Ag(CN)_2}]^{\ominus}$ is 5.5 × 10^{18} while that for the corresponding $[\mathrm{Ag(NH_3)_2}]^{\oplus}$ is 1.6 × 10^{7}. Explain why $[\mathrm{Ag(CN)_2}]^{2\ominus}$ is more stable.

9.9 Theories of bonding in complexes :

The metal-ligand bonding in coordination compounds has been described by Valence bond theory (VBT) and Crystal field theory (CFT).

9.9.1 Valence bond theory (VBT)

Can you recall ?

What is valence bond theory and the concept of Hybridisation?

The hybridized state is a theoretical step that describes how complexes are formed. VBT is based on the concept of hybridization. The hybrid orbitals neither exist nor can be detected spectroscopically. These orbitals, however, help us to describe structure of coordination compounds. The steps involved in describing bonding in coordination compounds using the VBT are given below.

i. Metal ion provides vacant d orbitals for formation of coordinate bonds with ligands.

ii. The vacant d orbitals along with s and p orbitals of the metal ion take part in hybridisation.

iii. The number of vacant hybrid orbitals formed is equal to the number of ligand donor atoms surrounding the metal ion which equals the coordination number of metal.

iv. Overlap between the vacant hybrid orbitals of the metal and filled orbitals of the ligand leads to formation of the metal-ligand coordinate bonds.

v. The hybrid orbitals used by the metal ion point in the direction of the ligand.

vi. The (n-1)d or nd orbitals used in hybridisation allow the complexes to be classified as (a) outer orbital and (b) inner orbital complexes.

vii. For hybridisation in the outer orbital complex nd orbitals are used, whereas in the inner orbital complexes (n-1)d orbitals are used.

Type of hybridisation decides the structure of the complex. For example when the hybridisation is d^2sp^3 the structure is octahedral.

Steps to understand the metal-ligand bonding include :

i. Find oxidation state of central metal ion

ii. Write valence shell electronic configuration of metal ion.

iii. See whether the complex is low spin or high spin. (applicable only for octahedral complexes with d^4 to d^8 electronic configurations).

iv. From the number of ligands find the number of metal ion orbitals required for bonding.

v. Identify the orbitals of metal ion available for hybridisation and the type of hybridisation involved.

vi. Write the electronic configuration after hybridisation.

vii Show filling of orbitals after complex formation.

viii. Determine the number of unpaired electrons and predict magnetic behaviour of the complex.

Remember...

Complete the missing entries.

Coordination number	Geometry of complex	Hybridization
2		sp
4	Tetrahedral	
4	Square planar	
6		d^2sp^3/ sp^3d^2

Try this...

Give VBT description of bonding in each of following complexes. Predict their magnetic behavior.

a. $[ZnCl_4]^{2\ominus}$

b. $[Co(H_2O)_6]^{2\oplus}$ (high spin)

c. $[Pt(CN)_4]^{2\ominus}$ (square planar)

d. $[CoCl_4]^{2\ominus}$ (tetrahedral)

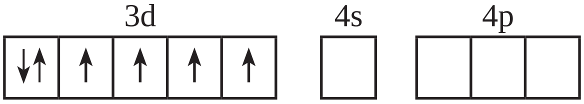
e. $[Cr(NH_3)_6]3^{\oplus}$

9.9.2 Octahedral, complexes

a. $[Co(NH_3)_6]^{3\oplus}$ low spin

i. Oxidation state of Cobalt:$3^{\oplus}$

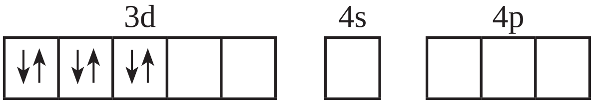
ii. Valence shell electronic configuration of $Co^{3\oplus}$ is represented in box diagram as shown below :



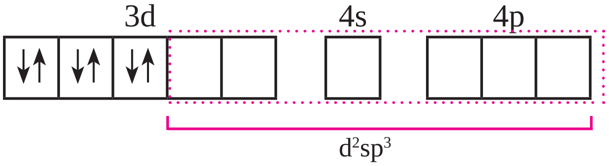
iii. Number of ammine ligands is 6, number of vacant metal ion orbitals required for bonding with ligands must be six.

iv. Complex is low spin, so pairing of electrons will take place prior to hybridisation.

v. Electronic configuration after pairing would be

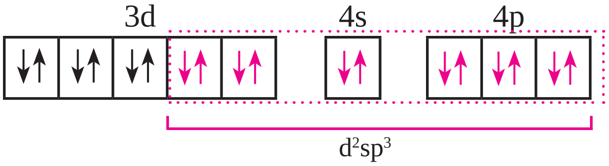


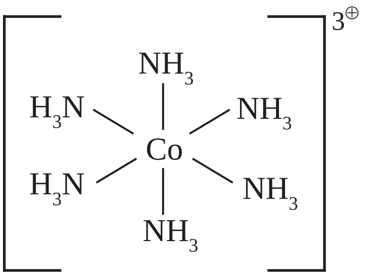
vi. Six orbitals available for hybridisation are two 3d, one 4s, three 4p orbitals



The orbitals for hybridization are decided from the number of ammine ligands which is six. Here (n-1)d orbitals participate in hybridization since it is the low spin complex.

vii. Electronic configuration after complex formation.



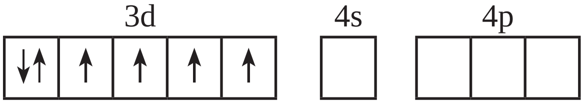


viii. As all electrons are paired the complex is diamagnetic.

b. $[CoF_6]^{3\ominus}$ high spin

i.Oxidation state of central metal Co is 3+

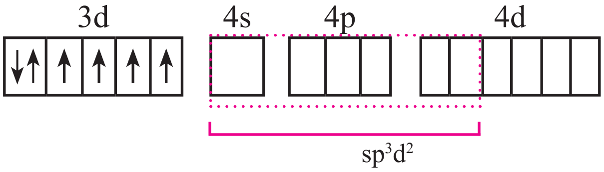
ii.Valence shell electronic configuration of $Co^{3\oplus}$ is



iii. Six fluoride $F^{\ominus}$ ligands, thus the number of vacant metal ion orbitals required for bonding with ligands would be six.

iv. Complex is high spin, that means pairing of electrons will not take place prior to hybridisation. Electronic configuration would remain the same as in the free state shown above.

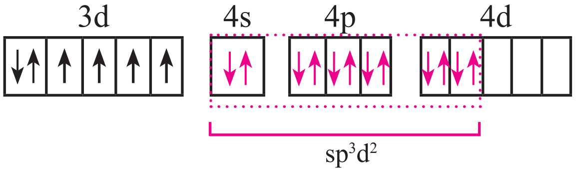
v. Six orbitals available for the hybridisation. Those are one 4s, three 4p, two of 4d orbitals



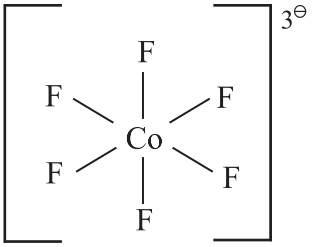
Six metal orbitals after bonding with six $F^{\ominus}$ ligands led to the sp^3d^2 hybridization. The d orbitals participating in hybridisation for this complex are nd.

vi. Six vacant sp^3d^2 hybrid orbital of Co^{3+} overlap with six orbitals of fluoride forming Co - F coordinate bonds.

vii. Configuration after complex formation.



viii. The complex is octahedral and has four unpaired electrons and hence, is paramagnetic.

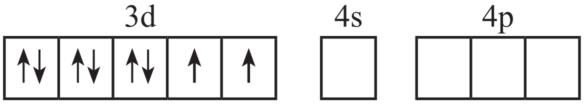


9.9.3 Tetrahedral complex

$[Ni(Cl)_4]^{2\ominus}$

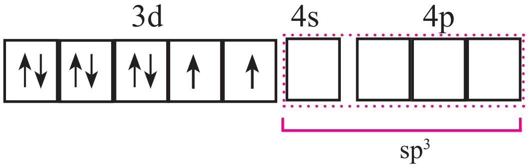
i. Oxidation state of nickel is +2

ii. Valence shell electronic configuration of Ni^{2+}



iii. number of $Cl^{\ominus}$ ligands is 4. Therefore number of vacant metal ion orbitals required for bonding with ligands must be four.

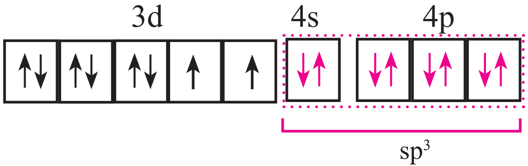
iv. Four orbitals on metal available for hybridisation are one 4s, three 4p. The complex is tetrahedral.



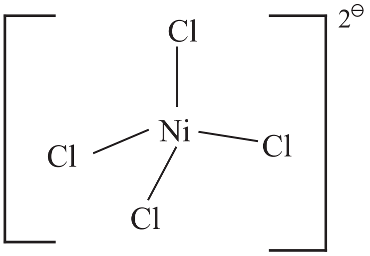
The four metal ion orbitals for bonding with $Cl^{\ominus}$ ligands are derived from the sp^3 hybridization.

vi. Four vacant sp^3 hybrid orbital of $Ni^{2\oplus}$ overlap with four orbitals of $Cl^{\ominus}$ ions.

vii. Configuration after complex formation would be.



viii.The complex has four unpaired electrons and hence, paramagnetic.

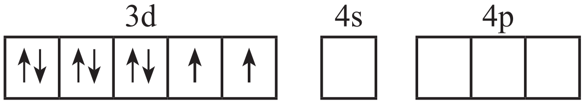


9.9.4 Square planar complex

$[Ni(CN)_4]^{2\ominus}$

i. Oxidation state of nickel is +2

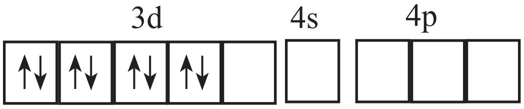
ii. Valence shell electronic configuration of $Ni^{2\oplus}$



iii. Number of $CN^{\ominus}$ ligands is 4, so number of vacant metal ion orbitals required for bonding with ligands would be four.

iv. Complex is square planar so $Ni^{2\oplus}$ ion uses dsp^2 hybrid orbitals.

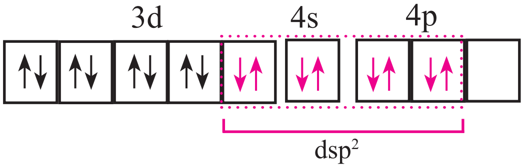
v. 3d electrons are paired prior to the hybridisation and electronic configuration of $Ni^{2\oplus}$ becomes :



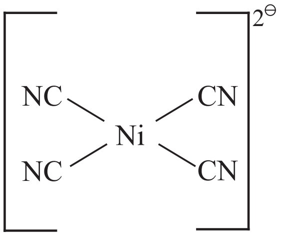
vi. Orbitals available for hybridisation are one 3d, one 4s and two 4p which give dsp^2 hybridization.

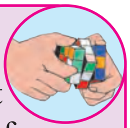
vii. Four vacant dsp^2 hybrid orbitals of $Ni^{2\oplus}$ overlap with four orbitals of $CN^{\ominus}$ ions to form Ni - CN coordinate bonds.

vii. Configuration after the complex formation becomes.



viii.The complex has no unpaired electrons and hence, dimagnetic.





Try this...

Based on the VBT predict structure and magnetic behavior of the $[Ni(NH_3)_6]^{3\oplus}$ complex.

9.9.5 Limitations of VBT

i. It does not explain the high spin or low spin nature of the complexes. In other words, strong and weak field nature of ligands can not be distinguished.

ii. It does not provide any explanation for the colour of coordination compounds.

iii. The structure of the complexes predicted from the VBT would not always match necessarily with those determined from the experiments.

To overcome these difficulties in VBT, the Crystal field theory has been proposed which has widely been accepted.

9.9.6 Crystal Field theory (CFT)

C.F.T. is based on following assumptions

i. The ligands are treated as point charges. The interaction between metal ion and ligand is purely electrostatic or there are no orbital interactions between metal and ligand.

In an isolated gaseous metal ion the five d orbitals, $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, d_{zx} have the same energy i.e. they are degenerate.

ii. When ligands approach the metal ion they create crystal-field around the metal ion. If it were symmetrical the degeneracy of the d orbitals remains intact.

Usually the field created is not symmetrical and the degeneracy is destroyed. The d orbitals thus split into two sets namely, (d_{xy}, d_{yz}, d_{xz}) usually refered by t_{2g} and ($d_{x^2-y^2}$, d_{z^2}) called as e_g. These two sets of orbitals now have different energies. A separation of energies of these two sets of d orbitals is the **crystal field splitting** parameter. This is denoted by Δ_o (O for octahedral).

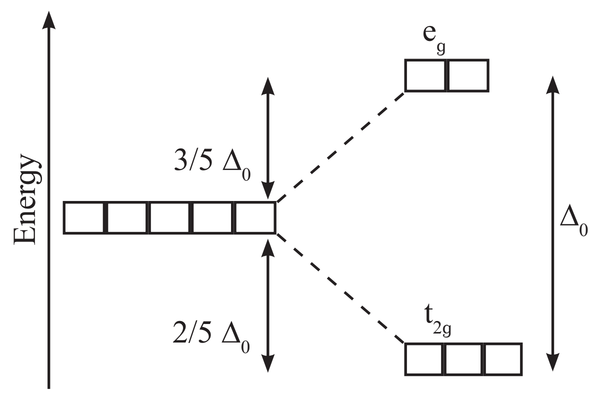
iii. The Δ_o depends on strength of the ligands. The ligands are then classified as (a) strong field and (b) weak field ligands. Strong field ligands are those in which donor atoms are C,N or P. Thus $CN^{\ominus}$, $NC^{\ominus}$, CO, NH_3, EDTA, en (ethylenediammine) are considered to be strong ligands. They cause larger splitting of d orbitals and pairing of electrons is favoured. These ligands tend to form low spin complexes. Weak field ligands are those in which donor atoms are halogens, oxygen or sulphur. For example, $F^{\ominus}$, $Cl^{\ominus}$, $Br^{\ominus}$, $I^{\ominus}$, $SCN^{\ominus}$, $C_2O_4^{2\ominus}$. In case of these ligands the Δ_o parameter is smaller compared to the energy required for the pairing of electrons, which is called as electron pairing energy. The ligands then can be arranged in order of their increasing field strength as

$$I^{\ominus} < Br^{\ominus} < Cl^{\ominus} < S^{2\ominus} < F^{\ominus} < OH^{\ominus} < C_2O_4^{2\ominus} < H_2O < NCS^{\ominus} < EDTA < NH_3, < en < CN^{\ominus} < CO.$$

Let us understand **splitting of d orbitals and formation of octahedral complexes**

In octahedral environment the central metal ion is surrounded by six ligands.

Ligands approach the metal ion along the *x, y, z* axes. As the ligands approach the metal ion the degeneracy of d orbitals is resolved.



e_g - The higher energy set of orbitals (d_{z^2} and $d_{x^2-y^2}$)
t_{2g} - The lower energy set of orbitals (d_{xy}, d_{yz} and d_{zx})
Δ_0 or 10 Dq - The energy separation between the two levels
The e_g orbitals are repelled by an amount of 0.6 Δ_0.
The t_{2g} orbitals to be stabilized to the extend of 0.4 Δ_0.

Fig. 9.2 : Crystal field Splitting in an octahedral complex

With closer approach of ligands along the axes, the doubly degenerate $d_{x^2-y^2}$ and d_{z^2} (e_g) orbitals experience larger repulsion than the triply degenerate t_{2g} orbitals. As shown in Fig. 9.2, the e_g set has higher energy than the t_{2g} set by the amount Δ_o. The Δ_o parameter is equal to 10 Dq units of splitting of t_{2g} and e_g levels. For electronic configurations d^1, d^2, d^3 the electrons occupy t_{2g} orbitals and obey the Hund's rules. For electronic configurations d^1, d^2, d^3 and d^8, d^9, d^{10} the high spin and low spin configurations cannot be distinguished. Only the electronic configurations d^4 to d^7 render the high and low spin complexes.These are depiciated in Fig 9.5.

Table 9.5 : d orbital diagrams for high spin and low spin complexes.

d orbital electronic configuration		High spin	Low spin
d^4	e_g	↑ — —	— —
	t_{2g}	↑ ↑ ↑	↑↓ ↑ ↑
d^5	e_g	↑ ↑	— — —
	t_{2g}	↑ ↑ ↑	↑↓ ↑↓ ↑
d^6	e_g	↑ ↑	— — —
	t_{2g}	↑↓ ↑ ↑	↑↓ ↑↓ ↑↓
d^7	e_g	↑ ↑	↑ —
	t_{2g}	↑↓ ↑↓ ↑	↑↓ ↑↓ ↑↓

9.9.7 Factors affecting Crystal Field Splitting parameter (Δ_0)

a. The magnitude of crystal field splitting depends on strength of the ligands. The strong ligands those appear in spectrochemical series approach closer to the central metal which results in a large crystal field splitting.

b. **Oxidation state of the metal :** A metal with the higher positive charge is able to draw ligands closer to it than that with the lower one. Thus the metal in higher oxidation state results in larger separation of t_{2g} and e_g set of orbitals. The trivalent metal ions cause larger crystal field splitting than corresponidng divalent ones.

9.9.8 Colour of the octahedral complexes

As discussed above, the formation of an octahedral complex is accompanied by splitting of d orbitals into t_{2g} and e_g sets. A separation of these two sets of orbitals is Δ_o, which can be measured from experiments. The Δ_o corresponds to a certain frequency of electromagnetic radiation usually in the visible region. A colour complementary to the absorbed frequency is thus observed. Consider the $[Ti(H_2O)_6]^{3\oplus}$ complex. The central metal ion titanium has electronic configuration 3d and the electron occupies one of the t_{2g} orbitals (Figure 9.3).

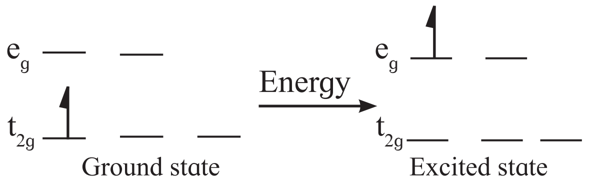


Fig. 9.3 : d - d transition in d' system

The absorption of the wavelength of light corresponding to Δ_o parameter promotes an electron from the t_2g level. Such energy gap in case of the $[Ti(H_2O)_6]^{3\oplus}$ complex is 20,300 cm^{-1} (520 nm, 243 kJ/mol) and a complimentary colour to this is imparted to the complex. A violet color of the $[Ti(H_2O)_6]^{3\oplus}$ complex arises from such d-d transition.

9.9.9 Tetrahedral complexes

A pattern of splitting of d orbitals, which is a key in the crystal field theory, is dependent on the ligand field environment. This is illustrated for the tetrahedral ligand field environment.

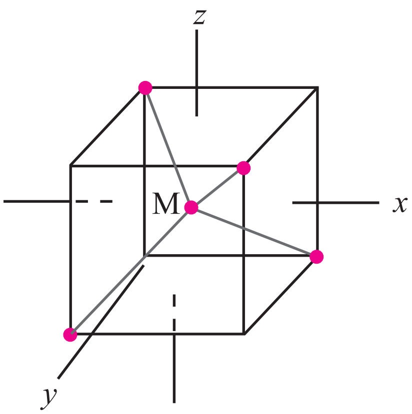


Fig. 9.4 : Tetrahedral structure

The tetrahedral structure having the metal atom M at the centre and four ligands occupying the corners is displayed along with in Fig. 9.4.

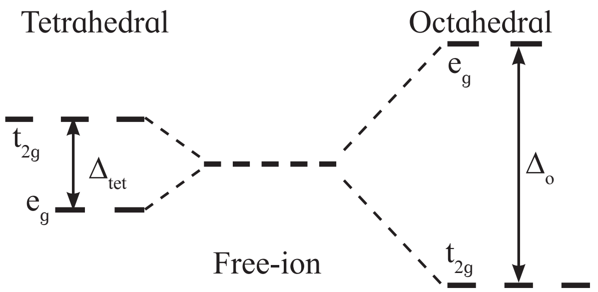
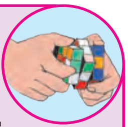


Fig. 9.5 : Splitting of d orbitals in tetrahedral and octahedral complexes

Try this...



Sketch qualitatively crystal field d orbital energy level diagrams for each of the following complexes:

a. $[Ni(en)_3]^{2\oplus}$ b. $[Mn(CN)_6]^{3\ominus}$

c. $[Fe(H_2O)_6]^{2\oplus}$

Predict whether each of the complexes is diamagnetic or paramagnetic.

The $d_{xy,}$ $d_{yz,}$ d_{zx} orbitals with their lobes lying in between the axes point toward the ligands. On the other hand, $d_{x^2-y^2}$ and d_{z^2} orbitals lie in between metal-ligand bond axes. The $d_{xy,}$ d_{yz} and d_{zx} orbitals experience more repulsion from the ligands compared to that by $d_{x^2-y^2}$ and d_{z^2} orbitals.

Due to larger such repulsions the d_{xy}, d_{yz} and d_{zx} orbitals are of higher energy while the $d_{x^2-y^2}$ and d_{z^2} orbitals are of relatively lower energy.

Each electron entering in one of the $d_{xy,}d_{yz}$ and d_{zx} orbitals raises the energy by 4 Dq whereas that accupying $d_{x^2-y^2}$ and d_{z^2} orbitals lowers it by 6 Dq compared to the energy of hypothetical degenerate d orbitals in the ligand field.

A splitting of d orbitals in tetrahedral crystal fields (assumed to be 10 Dq) thus is much less (typically 4/9) compared to that for the octahedral environment. The crystal field splitting of d orbitals in a tetrahedral ligand field is compared with the octahedral one in Fig. 9.5. Thus the pairing of electrons is not favoured in tetrahedral structure. For example, in d^4 configuration an electron would occupy one of the t_2g orbitals. The low spin tetrahedral complexes thus are not found.

Typically metal complexes possessing the cetral metal ion with d^8 electronic configuration, for example, $Ni(CO)_4$, favours the tetrahedral structure.

9.10 Applications of coordination compounds

a. In biology : Several biologically important natural compounds are metal complexes. They play important role in a number of processes occuring in plants and animals.

For example, chlorophyll present in plants is a complex of Mg. Haemoglobin present in blood is a complex of iron.

b. In medicines

i. Pt complex cisplatin is used in the treatment of cancer.

ii. EDTA is used for treatment of lead poisoning.

c. To estimate hardness of water : Hardness of water is due to the presence of Ca^{2+} and Mg$^{2\oplus}$ ions. The ligand EDTA forms stable complexes with Ca$^{2\oplus}$ and Mg$^{2\oplus}$. It can, therefore, be used to estimate hardness.

d. In electroplating : Usually stable coordination complexes on dissolution dissociate to small extent and furnish a controlled supply of metal ions. The metal ions when reduced clump together to form the clusters or nanoparticles. When the coordination complexes are used the ligands in the complex keep the metal atoms well separated from each other. These metal atoms tend to form a protective layer on the surface. Certain cyanide complexes $K[Ag(CN)_2]$ and $K[Au(CN)_2]$ find applications in the electroplating of these noble metals.

Exercises

1. Choose the most correct option.

i. The oxidation state of cobalt ion in the complex $[Co(NH_3)_5Br]SO_4$ is

a. +2 b. +3

c. +1 d. +4

ii. IUPAC name of the complex $[Pt(en)_2(SCN)_2]^{2+}$ is

a. bis (ethylenediamine dithiocyanatoplatinum (IV) ion

b. bis (ethylenediamine) dithiocyantoplatinate (IV) ion

c. dicyanatobis (ethylenediamine) platinate IV ion

d. bis (ethylenediammine)dithiocynato platinate (IV) ion

iii. Formula for the compound sodium hexacynoferrate (III) is

a. $[NaFe(CN)_6]$ b. $Na_2[Fe(CN)_6]$

c. $Na[Fe(CN)_6]$ d. $Na_3[Fe(CN)_6]$

iv. Which of the following complexes exist as cis and trans isomers ?

1. $[Cr(NH_3)_2Cl_4]^{\ominus}$ 2. $[Co(NH_3)_5Br]^{2\oplus}$

3. $[PtCl_2Br_2]^{2\ominus}$ (square planar)

4. $[FeCl_2(NCS)_2]^{2\ominus}$ (tetrahedral)

a. 1 and 3 b. 2 and 3

c. 1 and 3 d. 4 only

v. Which of the following complexes are chiral ?

1. $[Co(en)_2Cl_2]^{\oplus}$ 2. $[Pt(en)Cl_2]$

3. $[Cr(C_2O_4)_3]^{3\ominus}$ 4. $[Co(NH_3)_4Cl_2]^{\oplus}$

a. 1 and 3 b. 2 and 3

c. 1 and 4 d. 2 and 4

vi. On the basis of CFT predict the number of unpaired electrons in $[CrF_6]^{3\ominus}$.

a. 1 b. 2 c. 3 d. 4

vii. When an excess of $AgNO_3$ is added to the complex one mole of AgCl is precipitated. The formula of the complex is

a. $[CoCl_2(NH_3)_4]Cl$

b. $[CoCl(NH3)_4]\ Cl_2$

c. $[CoCl_3(NH_3)_3]$

d. $[Co(NH_3)_4]Cl_3$

viii. The sum of coordination number and oxidation number of M in $[M(en)_2C_2O_4]Cl$ is

a. 6 b. 7 c. 9 d. 8

2. Answer the following in one or two sentences.

i. Write the formula for tetraammineplatinum (II) chloride.

ii. Predict whether the $[Cr(en)_2(H_2O)_2]^{3+}$ complex is chiral. Write structure of its enantiomer.

iv. Name the Lewis acids and bases in the complex $[PtCl_2(NH_3)_2]$.

v. What is the shape of a complex in which the coordination number of central metal ion is 4 ?

vi. Is the complex $[CoF_6]$ cationic or anionic if the oxidation state of cobalt ion is +3 ?

vii. Consider the complexes $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4]$ $[CuCl_4]$. What type of isomerism these two complexes exhibit?

viii. Mention two applications of coordination compounds.

3. Answer in brief.

i. What are bidentate ligands ? Give one example.

ii. What is the coordination number and oxidation state of metal ion in the complex $[Pt(NH_3)Cl_5]^{\ominus}$?

iii. What is difference between a double salt and a complex ? Give an example.

iv. Classify following complexes as homoleptic and heteroleptic

$[Cu(NH_3)_4]SO_4$, $[Cu(en)_2(H_2O)Cl]^{2\oplus}$, $[Fe(H_2O)_5(NCS)]^{2\oplus}$, tetraammine zinc (II) nitrate.

v. Write formulae of the following complexes

a. Potassium amminetrichloroplatinate (II)

b. Dicyanoaurate (I) ion

vi. What are ionization isomers ? Give an example.

vii. What are the high-spin and low-spin complexes ?

viii. $[CoCl_4]^{2\ominus}$ is tetrahedral complex. Draw its box orbital diagram. State which orbitals participate in hybridization.

ix. What are strong field and weak field ligands ? Give one example of each.

x. With the help of crystal field energy-level diagram explain why the complex $[Cr(en)_3]^{3\oplus}$ is coloured ?

4. Answer the following questions.

i. Give valence bond description for the bonding in the complex $[VCl_4]^{\ominus}$. Draw box diagrams for free metal ion. Which hybrid orbitals are used by the metal ? State the number of unpaired electrons.

ii. Draw qualitatively energy-level diagram showing d-orbital splitting in the octahedral environment. Predict the number of unpaired electrons in the complex $[Fe(CN)_6]^{4\ominus}$. Is the complex diamagnetic or paramagnetic? Is it coloured? Explain.

iii. Draw isomers in each of the following

a. $Pt(NH_3)_2ClNO_2$

b. $Ru(NH_3)_4Cl_2$

c. $[Cr(en_2)Br_2]^{\oplus}$

iv. Draw geometric isomers and enantiomers of the following complexes.

a. $[Pt(en)_3]^{4\oplus}$ b. $[Pt(en_2)ClBr]^{2\oplus}$

v. What are ligands ? What are their types ? Give one example of each type.

vi. What are cationic, anionic and neutral complexes? Give one example of each.

vii. How stability of the coordination compounds can be explained in terms of equilibrium constants ?

viii. Name the factors governing the equilibrium constants of the coordination compounds.

Activity :

1. The reaction of chromium metal with H_2SO_4 in the absence of air gives blue solution of chromium ion.

$$Cr(s) + 2H^{\oplus}(aq) \longrightarrow Cr^{2\oplus}(aq) + H_2(s)$$

$Cr^{2\oplus}$ forms octahedral complex with H_2O ligands.

a. Write formula of the complex

b. Describe bonding in the complex using CFT and VBT.

Draw crystal field splitting and valence bond orbital diagrams.

2. Reaction of complex $[Co(NH_3)_3(NO_2)_3$ with HCl gives a complex

$[Co(NH_3)_3H_2OCl_2]^{\oplus}$ in which two chloride ligands are trans to one another.

a. Draw possible stereoisomers of starting material

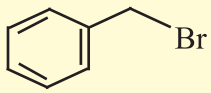
b. Assuming that NH_3 groups remain in place, which of two starting isomers would give the observed product ?

10. HALOGEN DERIVATIVES

Can you recall ?

Identify the functional group in the following compounds.

i.

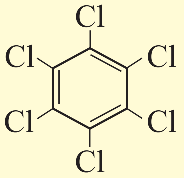


(Benzyl bromide)

ii. CCl_2F_2

(Freon - 12)

iii.

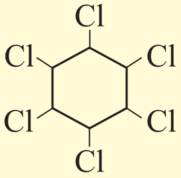


(Hexachlorobenzene)

iv. $Cl - CH = CCl_2$

(Westrosol)

v.



(Hexachlorocyclohexane)

The parent family of organic compounds is hydrocarbon. Replacement of hydrogen atom/s in aliphatic or aromatic hydrocarbons by halogen atom/s results in the formation of halogen derivatives of hydrocarbons.

In this chapter we will study halogen derivatives in a systematic way.

Internet my friend

Find out the structures of two thyroid hormones T3 (triiodothyronine) and T4 (thyroxine). How do these help our body ?

10.1 Classification of halogen derivatives :

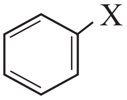
Halogen derivatives of hydrocarbons are classified mainly in two ways.

a. On the basis of hydrocarbon skeleton to which halogen atom is bonded, the halogen derivatives are classified as **haloalkanes**, **haloalkenes**, **haloalkynes and haloarenes**.

$CH_3 - CH_2 - X$ (Haloalkane)

$CH_2 = CH - X$ (Haloalkene)

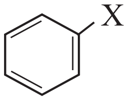
$HC \equiv C - X$ (Haloalkyne)



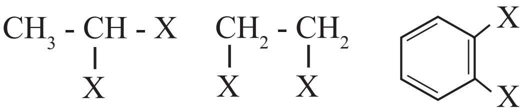
(Haloarene)

b. On the basis of number of halogen atoms, halogen derivatives are classified as mono, di, tri or poly halogen compounds.

$CH_3 - CH_2 - X$



Monohalogen compounds



$CH_3 - \underset{\underset{X}{|}}{CH} - X \qquad \underset{\underset{X}{|}}{CH_2} - \underset{\underset{X}{|}}{CH_2}$

Dihalogen compounds

$\underset{\underset{X}{|}}{CH_2} - \underset{\underset{X}{|}}{CH} - \underset{\underset{X}{|}}{CH_2}$

Trihalogen compounds

We will consider classification of mono halogen derivatives in more detail.

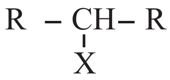
10.1.1 Classification of monohalogen compounds :

Monohalogen compounds are further classified on the basis of position of halogen atom and the type of hybridization of carbon to which halogen is attached.

a. Alkyl halides or haloalkanes : In alkyl halides or haloalkanes the halogen atom is bonded to sp^3 hybridized carbon which is a part of saturated carbon skeleton. Alkyl halides may be primary, secondary or tertiary depending on the substitution state of the carbon to which halogen is attached : (Refer to Std. XI Chemistry Textbook, section 14.3).

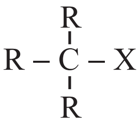
$R-CH_2-X$

Primary halide (1^0 halide)



$R-\underset{X}{CH}-R$

Secondary halide (2^0 halide)

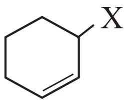


$R-\underset{R}{\overset{R}{C}}-X$

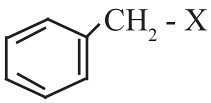
Tertiary halide (3^0 halide)

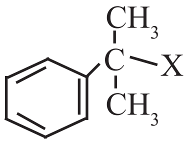
b. Allylic halides : In allylic halides, halogen atom is bonded to a sp^3 hybridized carbon atom next to a carbon-carbon double bond.

$CH_2=CH-CH_2-X$



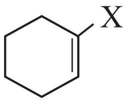
c. Benzylic halide : In benzylic halides halogen atom is bonded to a sp^3 hybridized carbon atom which is further bonded to an aromatic ring.





d. Vinylic halides : In vinylic halides halogen atom is bonded to a sp^2 hybridized carbon atom of aliphatic chain. Vinylic halide is a **haloalkene**.

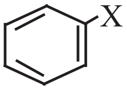
$CH_2=CH-X$



e. Haloalkyne : When a halogen atom is bonded to a sp hybridized carbon atom it is a haloalkyne.

$CH\equiv C-X$

f. Aryl halides or haloarenes : In aryl halides, halogen atom is directly bonded to the sp^2 hybridized carbon atom of aromatic ring.



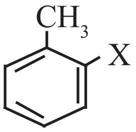
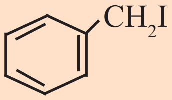
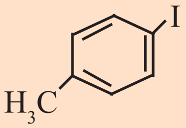
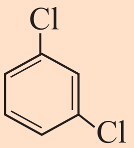


Table 10.1 Names of some halogen derivatives

Formula	Common name	IUPAC name
CH_2Cl_2	Methylene chloride	Dichloromethane
CH_3CH_2Br	Ethyl bromide	Bromoethane
$CH_3CH(Cl)CH_3$	Isopropyl chloride	2-Chloropropane
$(CH_3)_2\ CH-CH_2Br$	Isobutyl bromide	1-Bromo-2-methylpropane
$(CH_3)_3\ C\ Br$	Tert-butyl bromide	2-Bromo-2-methyl-propane
$(CH_3)_3\ C\ CH_2Cl$	Neopentyl chloride	1-Chloro-2, 2-dimethyl propane
$CH_2=CH-Cl$	Vinyl chloride	1-Chloroethene
$CH_2=CH-CH_2Br$	Allyl bromide	3-Bromopropene
$CH\equiv C-Cl$	Chloro acetylene	Chloroethyne
	Benzyl iodide	Iodophenylmethane
	p-Iodotoluene	1-Iodo-4-methyl benzene or 4-Iodotoluene
	m-dichlorobenzene	1, 3-dichlorobenzene

10.2 Nomenclature of halogen derivatives

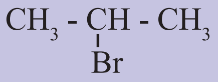
Can you recall ?

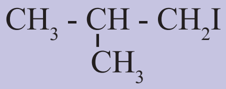
- In IUPAC system of nomenclature does the functional group 'halogen' appear as a suffix or prefix ?
- What are the trivial names of laboratory solvents $CHCl_3$ and CCl_4 ?

The common names of alkyl halides are derived by naming the alkyl group followed by the name of halogen as halide. For example, methyl iodide, tert-butyl chloride. According to IUPAC system of nomenclature (Std. XI Chemistry Textbook Chapter 14, section 14.4.7) alkyl halides are named as **haloalkanes**. Aryl halides are named as **haloarenes** in common as well as IUPAC system. For dihalogen derivative of an arene, prefix o-, m-, p- are used in common name system but in IUPAC system the numerals 1,2 ; 1,3 and 1,4 respectively are used. Common and IUPAC names of some halogen derivatives are given in Table 10.1.

Use your brain power

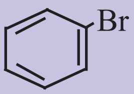
Write IUPAC names of the following.

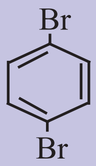
i. 
$CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$

ii. 
$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2I$

iii. $CH_3 - CH = CH - CH_2Cl$

iv. $CH_3 - C \equiv C - CH_2 - Br$

v. 

vi. 

10.3 Methods of preparation of alkyl halides

10.3.1 From alcohol : The most widely used method of preparation of alkyl halide is replacement of hydroxyl group of an alcohol by halogen atom. Alcohols are available in a wide variety. The hydroxyl group may be replaced by halogen atom using (a) halogen acid, (b) phosphorous halide or (c) thionyl chloride.

a. By using halogen acid or hydrogen halide (HX) : The conditions for reaction of alcohol with halogen acid (HX) depend on the structure of the alcohol and particular halogen acid used. The order of reactivity of alcohols with a given haloacid is $3^0>2^0>1^0$. (Refer to section 11.2.1 a)

$$R - OH + HX \xrightarrow[\text{condition}]{\text{suitable}} R - X + H_2O$$

(Alcohol) (Alkyl halide)

Hydrogen chloride is used with zinc chloride (Grooves' process) for primary and secondary alcohols, but tertiary alcohols readily react with concentrated hydrochloric acid in absence of zinc chloride.

$$R - OH + HCl \xrightarrow[ZnCl_2]{\text{anhydrous}} R - Cl + H_2O$$

Do you know ?

Zinc chloride is a Lewis acid and consequently can coordinate with the alcohol, weakening R - O bond. Mixture of concentrated HCl and anhydrous $ZnCl_2$ is called Lucas reagent.

Constant boiling hydrobromic acid (48%) is used for preparing alkyl bromides. Primary alkyl bromides can also be prepared by reaction with NaBr and H_2SO_4. Here HBr is generated *in situ*.

$$R - OH + HBr \xrightarrow[\text{heat}]{NaBr,\ H_2SO_4} R - Br + H_2O$$

Good yield of alkyl iodides may be obtained by heating alcohols with sodium or potassium iodide in 95 % phosphoric acid. Here HI is generated *in situ*.

$$R - OH + HI \xrightarrow{NaI/H_3PO_4} R - I + H_2O$$

Can you tell ?

Why phosphoric acid is preferred to H_2SO_4 to prepare HI *in situ* ?

b. By using phosphorous halide : An alkyl halide may be prepared by action of phosphorous halide on alcohol. Phosphorous tribromide and triiodide are usually generated *in situ* (produced in the reaction mixture) by the action of red phosphorous on bromine and iodine respectively. Phosphorous pentachloride reacts with alcohol to give alkyl chloride.

$$3R - OH + PX_3 \longrightarrow 3R - X + H_3PO_3$$

$$R - OH + PCl_5 \longrightarrow R - Cl + HCl + POCl_3$$

Do you know ?

Some times during replacement of -OH by -X, alcohols tend to undergo rearrangement. This tendency can be minimized by use of phosphorous halides. Straight chain primary alcohols react with phosphorous trihalide to give unrearranged alkyl halides.

c. By using thionyl chloride : Thionyl chloride reacts with straight chain primary alcohols to give unrearranged alkyl chloride. The byproducts obtained are gases. There is **no need to put extra efforts for its separation**. Therefore this method is preferred for preparation of alkyl chloride.

$$R - OH + SOCl_2 \xrightarrow{\Delta} R - Cl + SO_2\uparrow + HCl\uparrow$$

Can you recall ?

Identify the products of the following reactions.

i. $CH_4 + Cl_2 \xrightarrow{h\nu} ?$

ii. $CH_3 - CH = CH_2 \xrightarrow{HCl} ?$

iii. $CH_3 - CH = CH_2 + HBr \xrightarrow{Peroxide} ?$

iv. $CH_2 = CH - CH_3 + Br_2 \xrightarrow{CCl_4} ?$

10.3.2 From hydrocarbon

Alkyl halides are formed from saturated as well as unsaturated hydrocarbons by various reactions. Halogenation of alkanes is not suitable for preparation of alkyl halides as a mixture of mono and poly halogen compounds is formed.

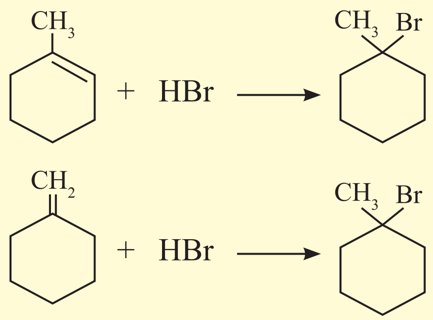
Addition of hydrogen halide to alkene

Alkyl halides are formed on addition of hydrogen halide to alkenes. Refer to Std XI Chemistry Textbook Chapter 15, section 15.2.4 for all the details including **order of reactivity of HX**, **Markownikov rule** and **peroxide effect**.

Problem 10.1 : How will you obtain 1-bromo-1-methylcyclohexane from alkene?

Write possible structures of alkene and the reaction involved.

Solution :



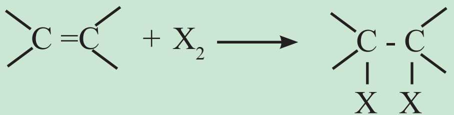
Use your brain power

Rewrite the following reaction by filling the blanks :

- $CH_3 - CH = CH_2 + HBr \longrightarrow$ ....+....... (major)(minor)
- $(CH_3)_2C{=}CHCH_3{+}HBr \xrightarrow{peroxide}$ ....+....... (major)(minor)
- $CH_3 - CH = CH_2{+}HBr \xrightarrow{peroxide}$ ....+....... (major)(minor)

Do you know ?

Alkenes form additon product, vicinal dihalide, with chlorine or bromine usually in inert solvent like CCl_4 at room temperature.



(X = Cl, Br)

Do you know ?

When alkenes are heated with Br_2 or Cl_2 at high temperature, hydrogen atom of allylic carbon is substituted with halogen atom giving allyl halide.

$$CH_2 = CH - CH_3 + Cl_2 \longrightarrow CH_2 = CH - CH_2Cl + HCl$$

10.3.3 Halogen exchange :

10.3.3 Halogen exchange : Alkyl iodides are prepared conveniently by treating alkyl chlorides or bromides with sodium iodide in methanol or acetone solution. The sodium bromide or sodium chloride precipitates from the solution and can be separated by filtration.

$$R - Cl + NaI \xrightarrow{\text{acetone}} R - I + NaCl \downarrow$$

The reaction is known as **Finkelstein reaction**.

Alkyl fluorides are prepared by heating alkyl chlorides or bromides with metal fluorides such as AgF, Hg_2F_2, AsF_3, SbF_3 etc.

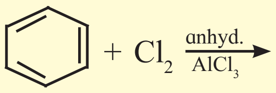
$$R - Cl + AgF \longrightarrow R - F + AgCl \downarrow$$

The reaction is known as **Swartz reaction**.

10.3.4 Electrophilic substitution :

Can you recall ?

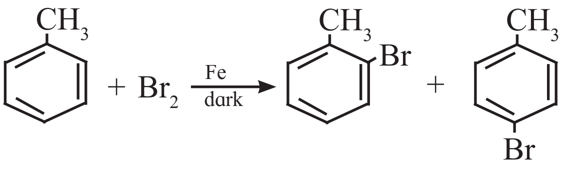
- Identify the product of the following reaction.



- Name the type of halide produced in the above reaction.
- What type of reactions are shown by benzene ?

Aryl chlorides and bromides can be prepared by direct halogenation of benzene and its derivatives through electrophilic substitution. It may be conveniently carried out in dark at ordinary temperature in presence of suitable Lewis acid catalyst like Fe, $FeCl_3$ or anhydrous $AlCl_3$.

When toluene is brominated in presence of iron, a mixture of ortho and para bromo toluene is obtained.



(o - Bromotoluene) (p-Bromotoluene)

+ HBr

Aromatic electrophilic substitution with iodine is reversible. In this case use of HNO_3/HIO_4 removes HI by oxidation to I_2, equilibrium is shifted to right and iodo product is formed. F_2 being highly reactive, fluoro compounds are not prepared by this method.

10.3.5 Sandmeyer's reaction :

Aryl halides are most commonly prepared by replacement of nitrogen of diazonium salt. (For details refer to Chapter 13 section 13.6).

10.4 Physical properties :

Physical properties of alkyl halides are considerably different from those of corresponding alkanes. The boiling point of alkyl halides is determined by polarity of the C-X bond as well as the size of halogen atoms.

10.4.1 Nature of intermolecular forces:

Halogens (X = F, Cl, Br and I) are more electronegative than carbon.

Carbon atom that carries halogen develops a partial positive charge while the halogen carries a partial negative charge. Thus carbon-halogen bond in alkyl halide is a polar covalent bond. Therefore alkyl halides are moderately polar compounds.

Size of the halogen atom increases from fluorine to iodine. Hence the C-X bond length increases. The C-X bond strength decreases with an increase in size of halogen. This is because as the size of p-orbital of halogen increases the p-orbital becomes more diffused and the extent of overlap with orbital of carbon decreases. Some typical bond lengths, bond enthalpies and dipole moments of C-X bond are given in Table 10.2.

Table 10.2 : Bond parameters of C-X bond

Bond	Bond length/ (pm)	Bond enthalpy/ (kJ mol^{-1})	Dipole moment/ debye
$CH_3 - F$	139	452	1.847
$CH_3 - Cl$	178	351	1.860
$CH_3 - Br$	193	293	1.830
$CH_3 - I$	214	234	1.636

10.4.2 Boiling point : Boiling points of alkyl halides are considerably higher than those of corresponding alkanes due to higher polarity and higher molecular mass. Within alkyl halides, for a given alkyl group, the boiling point increases with increasing atomic mass of halogen, because magnitude of van der Waals force increases with increase in size and mass of halogen.

Thus boiling point of alkyl halide decreases in the order RI > RBr > RCl > RF

For example, :

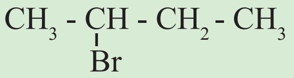
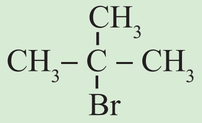
Haloalkane	CH_3F	CH_3Cl	CH_3Br	CH_3I
Boiling point (K)	194.6	248.8	276.6	315.4

For the given halogen, boiling point rises with increasing carbon number.

For example,

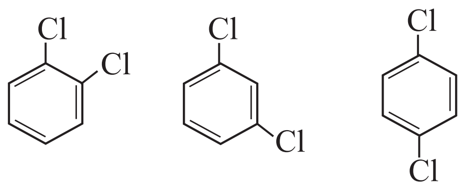
Haloalkane	Boiling point (K)
CH_3Cl	248.8
CH_3CH_2Cl	285.5
$CH_3CH_2CH_2Cl$	320.0
$CH_3CH_2CH_2CH_2Cl$	351.5

For isomeric alkyl halides, boiling point decrease with increased branching as surface area decreases on branching and van der Waals forces decrease. For example :

Haloalkane	Boiling point (K)
$CH_3CH_2CH_2CH_2Br$	375
 $CH_3-\underset{\mid}{\underset{Br}{CH}}-CH_2-CH_3$	364
 $CH_3-\overset{CH_3}{\overset{\mid}{\underset{\underset{Br}{\mid}}{C}}}-CH_3$	346

10.4.3 Solubility : Though alkyl halides are moderately polar, they are insoluble in water. It is due to inability of alkyl halides to form hydrogen bonds with water. Attraction between alkyl halide molecules is stronger than attraction between alkyl halide and water. Alkyl halides are soluble in non-polar organic solvents.

Aryl halides are also insoluble in water but soluble in organic solvents. If aryl halides are not modified by presence of any other functional group, they show properties similar to corresponding alkyl halides. The isomeric dihalobenzenes have nearly the same boiling points, but melting points of these isomers show variation. Melting point of para isomer is quite high compared to that of ortho or meta isomer. This is because of its symmetrical structure which can easily pack closely in the crystal lattice. As a result intermolecular forces of attraction are stronger and therefore greater energy is required to overcome its lattice energy.



b.p./K	453	446	448
m.p./K	256	249	323

Problem 10.2 Arrange the following compounds in order of increasing boiling points : bromoform, chloromethane, dibromomethane, bromomethane.

Solution : The comparative boiling points of halogen derivatives are mainly related with van der Waals forces of attraction which depend upon the molecular size. In the present case all the compounds contain only one carbon. Thus the molecular size depends upon the size of halogen and number of halogen atoms present.

Thus increasing order of boiling point is,

$CH_3Cl < CH_3Br < CH_2Br_2 < CHBr_3$

10.5 Optical isomerism in halogen derivatives :

Can you recall ?

- What is the relationship between two compounds having the same molecular formula?
- What is meant by stereoisomerism ?

Isomers having the same bond connectivities, that is, structural formula are called stereoisomers. Knowledge of optical isomerism, which is a kind of stereoisomerism will be useful to understand nucleophilic substitution reactions of alkyl halides (see 10.6.3).

10.5.1 Chiral atom and molecular chirality

Try this...

- Make a three - dimensional model of 2 - chlorobutane.
- Make another model which is a mirror image of the first model.
- Try to superimpose the two models on each other.
- Do they superimpose on each other exactly ?
- Comment on whether the two models are identical or not.

Let us, now, jot down the atoms/groups attached to each carbon in 2 - chlorobutane.

$$\overset{1}{C}H_3 - \overset{2}{C}HCl - \overset{3}{C}H_2 - \overset{4}{C}H_3$$

C-1 : - H, -H, -H, $-\overset{2}{C}HCl-\overset{3}{C}H_2-\overset{4}{C}H_3$

C-2 : -H, -Cl, $-\overset{1}{C}H_3$, $-\overset{3}{C}H_2-\overset{4}{C}H_3$

C-3 : -H, -H, $-\overset{4}{C}H_3$, $-\overset{2}{C}HCl-\overset{1}{C}H_3$

C-4 : -H, -H, -H, $-\overset{3}{C}H_2-\overset{2}{C}HCl-\overset{1}{C}H_3$

It can be seen that the four groups bonded to C-2 are all different from each other. **Carbon atom in a molecule which carries four different groups/atoms is called chiral carbon atom**. Thus, the C-2 in 2-chlorobutane is a chiral carbon. Chiral atom in a molecule is marked with asterisk (*). For example, CH_3-*CHCl-CH_2-CH_3.

When a molecule contains one chiral atom, it acquires a unique property. Such a molecule can not superimpose perfectly on its mirror image. It is called **chiral** molecule. A chiral molecule and its mirror image are not identical (see Fig. 10.1).

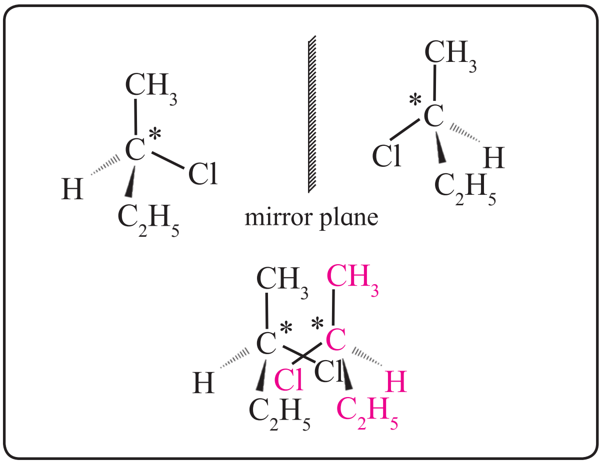


Fig. 10.1 : Nonsuperimposable mirror images

A chiral molecule and its mirror image both have the same structural formula and, of course, the same molecular formula. The spatial arrangement of the four different groups around the chiral atom, however, is different. In other words, a chiral molecule and its mirror image are stereoisomers of each other. (Refer to Std. XI Chemistry Textbook, Chapter 14).

The relationship between a chiral molecule and its mirror image is similar to the relationship between left and right hands. Therefore it is called **handedness** or **chirality**. (Origin : Greek word : Cheir means hand)

The stereoisomerism in which the isomers have different spatial arrangements of groups/ atoms around a chiral atom is called **optical isomerism**. The optical isomers differ from each other in terms of a measurable property called **optical activity**.

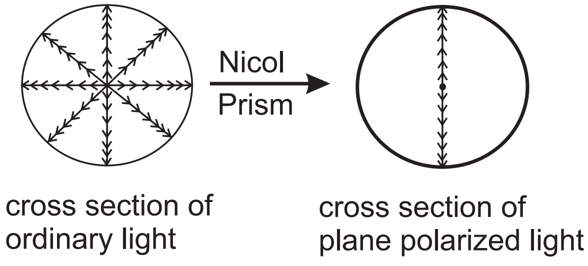
To understand optical activity, we must know what is **plane polarized light**.

Remember...

The phenomenon of optical isomerism in organic compounds was observed first and its origin in molecular chirality was recognized later.

10.5.2 Plane polarized light : An ordinary light consists of electromagnetic waves having oscillations of electric and magnetic field in all possible planes perpendicular to direction of propagation of light.

When ordinary light is passed through Nicol's prism, oscillations only in one plane emerge out. Such a **light having oscillations only in one plane perpendicular to direction of propagation of light is known as plane polarized light**.



Do you know ?

Nicol prism is a special type of prism made from pieces of calcite, a crystalline form of $CaCO_3$, arranged in a specific manner. Nicol prism is also called polarizer.

10.5.3 Optical activity : When an aqueous solution of certain organic compounds like sugar, lactic acid is placed in the path of plane polarized light, the transmitted light has oscillations in a different plane than the original. In other words, the incident light undergoes rotation of its plane of polarization. The plane of polarization rotates either to the right (clockwise) or to the left (anticlockwise). This property of a substance by which it **rotates plane of polarization of incident plane polarized light is known as optical activity**. The compounds which rotate the plane of plane polarized light are called **optically active compounds** and those which do not rotate it are optically inactive compounds. Optical activity of a substance is expressed numerically in terms of **optical rotation**. The angle through which a substance rotates the plane of plane polarized light on passing through it is called optical rotation. In accordance with the direction of optical rotation an optically active substance is either dextrorotatory or laevorotatory. A compound which rotates the plane of plane polarized light towards right is called **dextrorotatory** and designated by symbol **d-** or by **(+)** sign. A compound which rotates plane of plane polarized light towards left is called **laevorotatory** and designated by symbol ***l*-** or by **(-)** sign.

Isomerism in which isomeric compounds have different optical activity is known as **optical isomerism**. French scientist Louis Pasteur first recognized that optical activity is associated with certain type of 3-dimensional structure of molecules. Pasteur introduced the term **enantiomers** for the optical isomers having equal and opposite optical rotation.

Figure 10.2 indicates a few objects in our day to day life which exhibit superimposable and non-superimposable mirror image relationship.

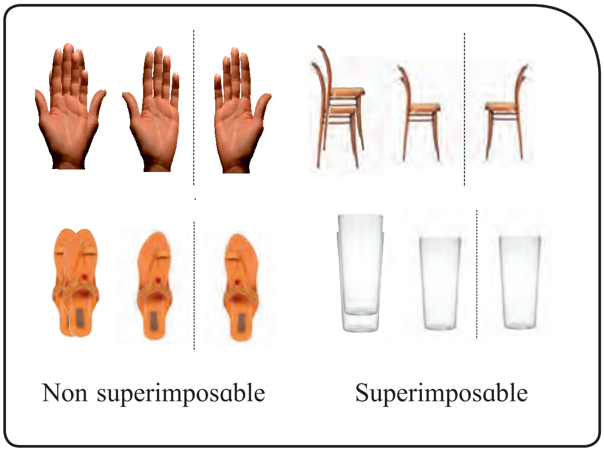


Fig. 10.2 : Superimposable and nonsuperimposable mirror image

Remember...

- Optical activity is an experimentally observable property of compounds. Chirality is a description of molecular structure. Optical activity is the consequence of chirality.
- Molecules which contain one chiral atom are chiral, that is, they are nonsuperimposable on their mirror image.
- The two non-superimposable mirror image structures are called **pair of enantiomers**.
- Enantiomers have **equal and opposite optical rotation**. Thus, enantiomers are a kind of optical isomers.

10.5.4 Enantiomers : The optical isomers which are non-superimposable mirror image of each other are called **enantiomers** or **enantiomorphs** or **optical antipodes**. For example, 2 - chlorobutane exists as a pair of enantiomers (Fig. 10.1).

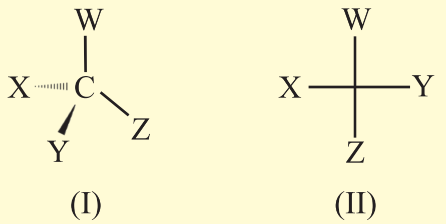
Enantiomers have identical physical properties (Such as melting point, boiling points, densities, refractive index) except the sign of optical rotation. The magnitude of their optical rotation is equal but the sign of optical rotation is opposite. They have identical chemical properties except towards optically active reagent.

An equimolar mixture of enantiomers (dextrorotatory and laevorotatory) is called **racemic modification or racemic mixture**. A racemic modification is optically inactive because optical rotation due to molecules of one enatiomer is cancelled by equal and opposite optical rotation due to molecules of the other enantiomer. A racemic modification is designated as ***(dl)*** or by **(±)** sign.

10.5.5 Representation of configuration of molecules :

Can you recall ?

- Identify the type of following 3-D representation (I) and (II) of a molecule and state significance of the lines drawn.



a. Fischer projection formula (cross formula) : Two representations are used to represent configuration of chiral carbon and the 3-dimensional structure of optical isomers on plane paper. These are (a) wedge formula and (b) Fischer projection formula (also called cross formula) (Std. XI Chemistry Textbook Chapter 14 section 14.2.3).

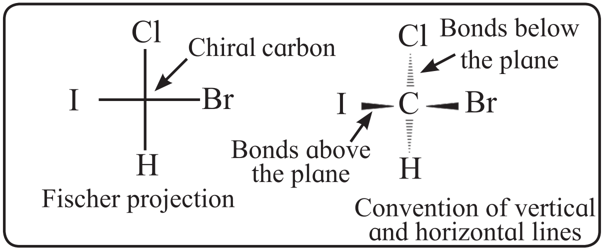
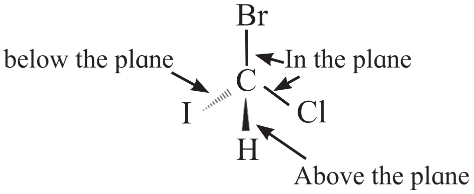


Fig. 10.3 Fischer projection formula

a. Wedge formula : When a tetrahedral carbon is imagined to be present in the plane of paper all the four bonds at this carbon cannot lie in the same plane. The bonds in the plane of paper are represented by normal lines, the bonds projecting above the plane of paper are represented by solid wedges (or simply by bold lines) while bonds going below the plane of paper are represented by broken wedges (or simply by broken lines).



Try this...

1. Draw structures of enantiomers of lactic acid  $(CH_3\text{-}\underset{\displaystyle OH}{\underset{|}{C}}H\text{-}COOH)$ using Fischer projection formulae.
2. Draw structures of enantiomers of 2-bromobutane using wedge formula.

10.6 Chemical properties :

10.6.1 Laboratory test of haloalkanes :

Haloalkanes are of neutral type in aqueous medium. On warming with aqueous sodium or potassium hydroxide the covalently bonded halogen in haloalkane is converted to halide ion.

$$R - X + OH^{\ominus} \xrightarrow{\Delta} R - OH + X^{\ominus}$$

When this reaction mixture is acidified by adding dilute nitric acid and silver nitrate solution is added a precipitate of silver halide is formed which confirms presence of halogen in the original organic compound.

$$Ag^{\oplus}\ (aq) + X^{\ominus}\ (aq) \longrightarrow AgX\downarrow\ (s)$$

10.6.2 Nucleophilic substitution reactions of haloalkanes :

When a group bonded to a carbon in a substrate is replaced by another group to get a product with no change in state of hybridization of that carbon the reaction is called **substitution reaction**. The C-X bond in alkyl halides is a polar covalent bond and the carbon in C-X bond is positively polarized. In other words, the **C-X carbon** is an **electrophilic centre**. It has, therefore, a tendency to react with a nucleophile. (Refer to Std. XI Chemistry Textbook Chapter 14.) Alkyl halides react with a variety of nucleophiles to give **nucleophilic substitution reactions (S_N)**. The reaction is represented in general form as shown below.

Can you recall ?

- What is meant by substitution reaction ?
- Can you identify substitution reaction from the following ?

  (i) $CH_3 - CH_2 - OH + HCl \xrightarrow{ZnCl_2} CH_3 - CH_2 - Cl + H_2O$

  (ii) $CH_2 = CH_2 + HI \longrightarrow CH_3 - CH_2 - I$
- Is the carbon carrying halogen in alkyl halide, an electrophilic or a nucleophilic centre ?

$$Nu^{\ominus} + -\overset{|}{\underset{|}{C}}{}^{\delta\oplus} - X^{\delta\ominus} \longrightarrow -\overset{|}{\underset{|}{C}} - Nu + X^{\ominus}$$

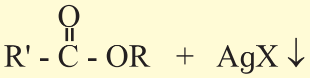
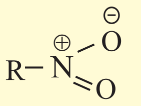
When a substrate reacts fast it is said to be reactive. The reactivity of alkyl halides in S_N reaction depends upon two factors, namely, the substitution state (1^0, 2^0 or 3^0) of the carbon and the nature of the halogen. The order of reactivity influenced by these two factors is as shown below.

tertiary alkyl halide (3^0) > secondary alkyl halide (2^0) >primary alkyl halide (1^0) and

R - I > R - Br > R - Cl

Examples of some important nucleophilic substitution reactions of alkyl halides are shown in Table 10.3.

10.3 Nucleophilic substitution reactions of alkyl halides

Sr. No.	Alkyl halide	Reagent	Substitution product
1.	R - X +	NaOH(aq) $\xrightarrow{\Delta}$ (or KOH)	R - OH + NaX (alcohol) (or KX)
2.	R - X +	$\overset{\oplus}{Na}\overset{\ominus}{O}R' \xrightarrow{\Delta}$ (sodium alkoxide)	R - O - R' + NaX (ether)
3.	R - X +	 $R' - \overset{O}{\overset{\parallel}{C}} - \overset{\ominus}{O}\overset{\oplus}{Ag} \xrightarrow{\Delta}$ (silver carboxylate)	 $R' - \overset{O}{\overset{\parallel}{C}} - OR + AgX \downarrow$ (ester)
4.	R - X +	NH_3(alc.) $\xrightarrow[\text{pressure}]{\Delta}$ (excess)	$R - NH_2$ + HX (primary amine)
5.	R - X +	KCN (alc.) $\xrightarrow{\Delta}$	R - CN + RX (nitrile)(alkyl cyanide)
6.	R - X +	AgCN (alc.) $\xrightarrow{\Delta}$	$R - N \equiv C$ + AgX ↓ (isocyanide)
7.	R - X +	$\overset{\oplus}{K}\overset{\ominus}{O} - N = O \longrightarrow$ (potassium nitrite)	R - O - N = O + KX (alkyl nitrite)
8.	R - X +	Ag - O - N = O ⟶ (silver nitrite)	 + AgX ↓ (nitroalkane)

Do you know ?

Cyanide ion is capable of attacking through more than one site (atom).

$$\overset{\ominus}{:}C \equiv \ddot{N}: \longleftrightarrow :C = \ddot{N}\overset{\ominus}{:}$$

Such nucleophiles are called ambident nucleophiles. KCN is predominantly ionic ($K^{\oplus}C^{\ominus} \equiv \dot{N}$) and provides cyanide ions. Both carbon and nitrogen are capable of donating electron pair. C-C Bond being stronger than C-N bond, attack occurs through carbon atom of cyanide group forming alkyl cyanides as major product. However AgCN ($Ag-C \equiv \dot{N}$) is mainly covalent compound and nitrogen is free to donate pair of electron. Hence attack occurs through nitrogen resulting in formation of isocyanide.

Another ambident nucleophile is nitrite ion, which can attack through 'O' or 'N'.

$$\overset{\ominus}{:}\ddot{O} - \ddot{N} = \ddot{O}$$

Can you tell ?

Alkyl halides when treated with alcoholic solution of silver nitrite give nitroalkanes whereas with sodium nitrite they give alkyl nitrites Explain.

10.6.3 Mechanism of S_N reaction :

Can you recall ?

- What is meant by order and molecularity of a reaction ?
- What is meant by mechanism of chemical reaction ?

It can be seen from the Table 10.3 that in a nucleophilic substitution reactions of alkyl halides the halogen atom gets detached from the carbon and a new bond is formed between that electrophilic carbon and nucleophile. The covalently bonded halogen is converted into halide ion ($X^{\ominus}$). It means that the two electrons constituting the original covalent bond are carried away by the halogen along with it. The halogen atom of alkyl halide is, therefore, called **'leaving group'** in the context of this reaction. Leaving group is the group which leaves the carbon by taking away the bond pair of electrons. The substrate undergoes two changes during a S_N reaction. The original C-X bond undergoes heterolysis and a new bond is formed between the carbon and the nucleophile using two electrons of the nucleophile. These changes may occur in one or more steps. The description regarding the sequence and the way in which these two changes take place in S_N reaction is called mechanism of S_N reaction. The mechanism is deduced from the results of study of kinetics of S_N reactions. Two mechanisms are observed in various S_N reactions. These are denoted as S_N1 and S_N2 mechanisms.

a. S_N2 Mechanism : The reaction between methyl bromide and hydroxide ion to give methanol follows a second order kinetics, that is, the rate of this reaction depends on concentration of two reacting species, namely, methyl bromide and hydroxide. Hence it is called **subtitution nucleophilic bimolecular, S_N2**.

$$CH_3Br + OH^{\ominus} \longrightarrow CH_3OH + Br^{\ominus}$$

$$\text{rate} = k\,[CH_3Br]\,[OH^{\ominus}]$$

Rate of a chemical reaction is influenced by the chemical species taking part in the slowest step of its mechanism. In the above reaction only two reactants are present and both are found to influence the rate of the reaction. This means that the reaction is a single step reaction which can also be called the slow step. This further implies that the two changes, namely, bond breaking and bond forming at the carbon take place simultaneously. This S_N2 mechanism is represented as shown in Fig. 10.4.

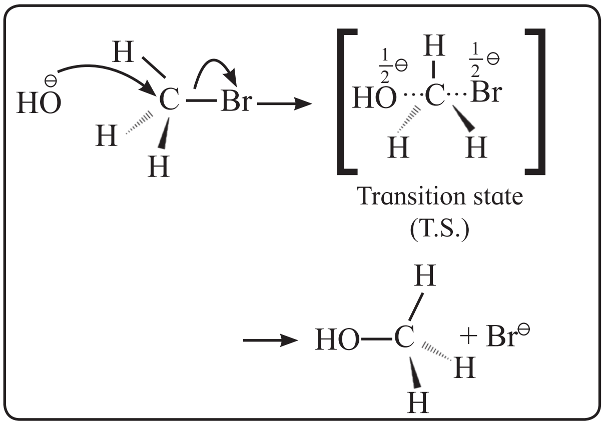


Fig. 10.4 : S_N2 mechanism

Salient features of S_N2 mechanism :

i. **Single step mechanism** with simultaneous bond breaking and bond forming.

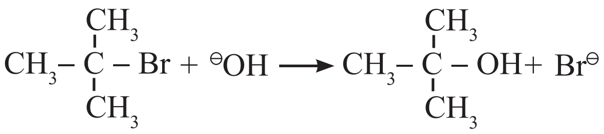
ii. **Backside attack of nucleophile :** The nucleophile attacks the carbon undergoing substitution from the side opposite to that of the leaving group. This is to avoid steric repulsion (repulsion due to bulkyness of the groups) and electrostatic repulsion between the incoming nucleophile and the leaving group.

iii. In the transition state (T.S.) the nucleophile and leaving groups are bonded to the carbon with partial bonds and carry partial negative charge. (Thus, the total negative charge is diffused.)

iv. The T.S. contains **pentacoordinate carbon** having three σ (sigma) bonds in one plane making bond angles of 120^0 with each other and two partial covalent bonds along a line perpendicular to this plane.

v. When S_N2 reaction is brought about at chiral carbon (in an optically active substrate), the product is found to have opposite configuration compared to that of the substrate. In other words, S_N2 reaction is found to proceed with inversion of configuration. This is like flipping of an umbrella (See Fig. 10.4). It is known as **Walden inversion**. The inversion in configuration is the result of backside attack of the nucleophile.

b. S_N1 Mechanism : The reaction between tert-butyl bromide and hydroxide ion to give tert-butyl alcohol follows a first-order kinetics, that is the rate of this reaction depends on concentration of only one species, which is the substrate molecule, tert-butyl bromide. Hence it is called **substitution nucelophilic unimolecular, S_N1**.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Br + {}^{\ominus}OH \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH + Br^{\ominus}$$

$$\text{rate} = k\,[(CH_3)_3CBr]$$

It can be seen in this reaction that concentration of only substrate appears in the rate equation; concentration of the nucleophile does not influence the reaction rate. In other words, tert-butyl bromide reacts with hydroxide by a two step mechanism. In the slow step C-X bond in the substrate undergoes heterolysis and in the subsequent fast step the nucleophile uses its electron pair to form a new bond with the carbon undergoing change. This S_N1 mechanism is represented as shown in Fig. 10.5.

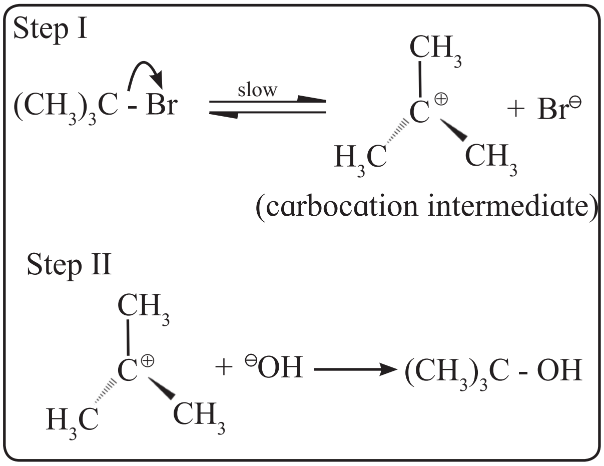


Fig. 10.5 : S_N1 mechanism

Salient features of S_N1 mechanism :

i. **Two step** mechanism.

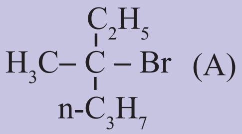
ii. **Heterolyis** of C-X bond in the slow and reversible first step to form **planar carbocation intermediate**.

iii. **Attack of the nucleophile** on the carbocation intermediate in the fast second step to form the product.

iv. When S_N1 reaction is carried out at chiral carbon in an optically active substrate, the product formed is nearly racemic. This indicates that S_N1 reaction proceeds **mainly** with **racemization**. This means both the enantiomers of product are formed in almost equal amount. Racemization in S_N1 reaction is the result of formation of planar carbocation intermediate (Fig. 10.5). Nucleophile can attack planar carbocation from either side which results in formation of both the enantiomers of the product.

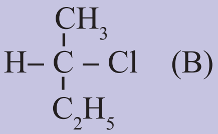
Use your brain power

- Draw the Fischer projection formulae of two products obtained when compound (A) reacts with $OH^{\ominus}$ by S_N1 mechanism.



$$H_3C-\overset{\displaystyle C_2H_5}{\underset{\displaystyle n\text{-}C_3H_7}{C}}-Br \quad (A)$$

- Draw the Fischer projection formula of the product formed when compound (B) reacts with $OH^{\ominus}$ by S_N2 mechanism.



$$H-\overset{\displaystyle CH_3}{\underset{\displaystyle C_2H_5}{C}}-Cl \quad (B)$$

10.6.4 Factors influencing S_N1 and S_N2 mechanism :

a. Nature of substrate : S_N2 : The T.S. of S_N2 mechanism is pentacoordinate and thus crowded (See Fig. 10.4). As a result S_N2 mechanism is favoured in primary halides and least favoured in tertiary halides.

S_N1 : A planar carbocation intermediate is formed in S_N1 reaction. It has no steric crowding. Bulky alkyl groups can be easily accommodated in planar carbocation See (Fig. 10.5). As a result S_N1 mechanism is most favoured in tertiary halides and least favoured in primary halides. (Formation of planar carbocation intermediate results in a

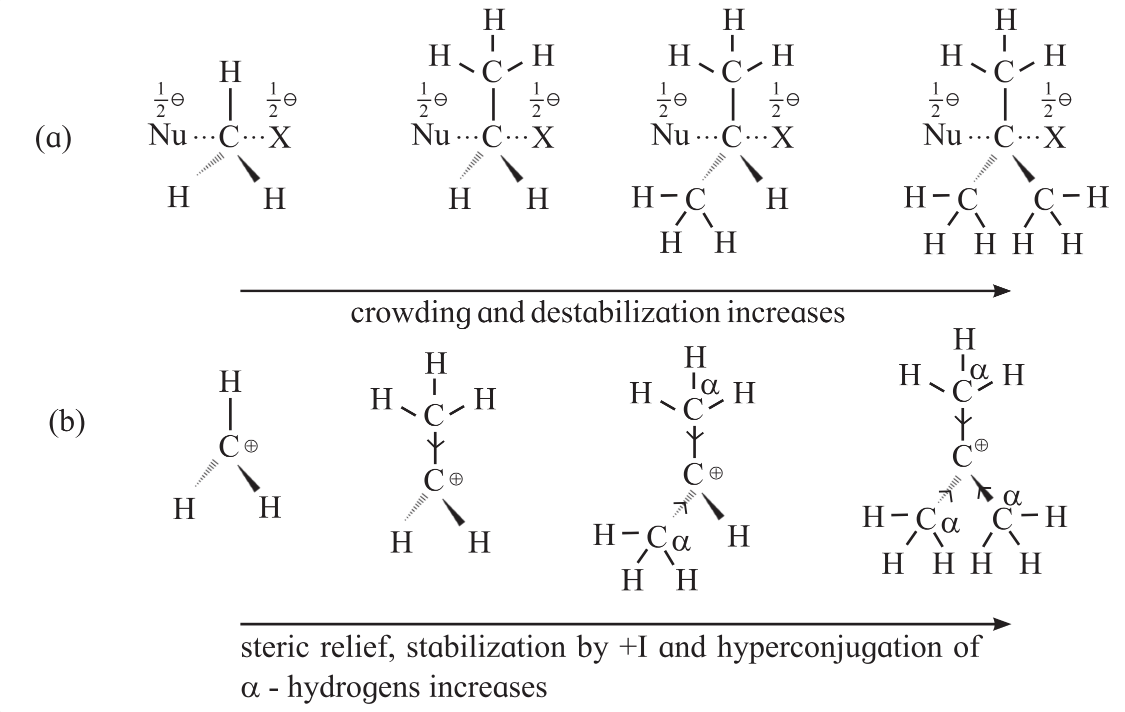


Fig. 10.6 : Influence of substrate in S_N1 and S_N2 (a) Transition states (T.S.) in S_N2 (b) Carbocation intermediates in S_N1

relief from steric crowding present in the tertiary halide substrate).

Secondly the carbocation intermediate is stabilized by +I effect of alkyl substituents and also by hyperconjugation effect of alkyl substituents containing α-hydrogens. As a result, S_N1 mechanism is most favoured in tertiary halides and least favoured in primary halides. This can be represented diagramatically as shown below.

$$\xrightarrow{S_N1 \text{ rate increases}}$$

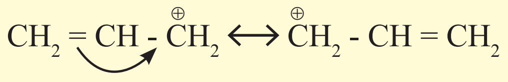
$$CH_3 - X \qquad 1^0 \quad 2^0 \quad 3^0$$

$$\xleftarrow[S_N2 \text{ rate increases}]{}$$

Tertiary halides undergo nucleophilic substitution by S_N1 mechanism while primary halides follow S_N2 mechanism. Secondary halides react by either of the mechanism or by mixed mechanism depending upon the exact conditions.

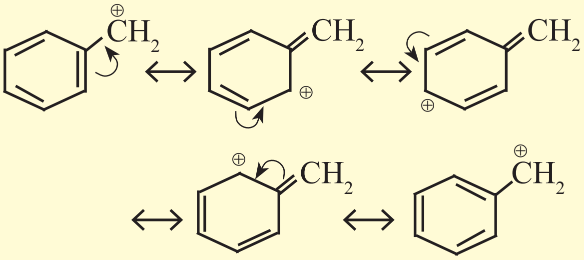
Problem 10.4 : Primary allylic and primary benzylic halides show higher reactivity by S_N1 mechanism than other primary alkyl halides. Explain.

Solution : S_N1 reaction involves formation of carbocation intermediate. The allylic and benzylic carbocation intermediate formed are resonance stabilized, and hence S_N1 mechanism is favoured.



$$CH_2 = CH - \overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH_2$$

Resonance stabilization of allylic carbocation



Resonance stabilization of benzylic carbocation

b. Nucleophilicity of the reagent :

Can you recall ?

- Give some examples of nucleophiles that are electrically neutral.
- Give some examples of anionic nucleophiles.
- What is the difference between a base and a nucleophile ?

A nucleophile is a species that uses its electron pair to form a bond with carbon. Nucleophilic character of any species is expressed in its electron releasing tendency, which can be corelated to its strength as Lewis base.

A more powerful nucleophile attacks the substrate faster and favours S_N2 mechanism. The rate of S_N1 mechanism is independent of the nature of nucleophile. Nucleophile does not react in slow step of S_N1. It waits till the carbocation intermediate is formed, and reacts fast with it.

Do you know ?

1. A negatively charged nucleophile is more powerful than its conjugate acid. For example $R\text{-}O^{\ominus}$ is better nucleophile than R-OH.
2. When donor atoms are from same period of periodic table, nucleophilicity decreases from left to right in a period. For example $H_2\ddot{O}$ is less powerful nucleophile than NH_3.
3. When donor atoms are from same group of the periodic table, nucleophilicity increases down the group. For example, $I^{\ominus}$ is better nucleophile than $Cl^{\ominus}$.

c. Solvent polarity : S_N1 mechanism proceeds via formation of carbocation intermediate. A good ionizing solvent, polar solvent, stabilizes the ions by solvation. Solvation of carbocation is relatively poor and solvation of anion is particularly important. Anions are solvated by hydrogen bonding solvents, that is, protic solvents. Thus S_N1 reaction proceeds more rapidly in polar protic solvents than in aprotic solvents.

Polar protic solvents usually decrease the rate of S_N2 reaction. In the rate determining step of S_N2 mechanism substrate as well as nucleophile is involved. A polar solvent stabilizes nucleophile (one of the reactant) by solvation. Thus solvent deactivates the nucleophile by stabilizing it. Hence aprotic solvents or solvents of low polarity will favour S_N2 mechanism.

Problem 10.5 : Which of the following two compounds would react faster by S_N2 mechanism and Why ?

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2Cl$

1-Chlorobutane

$CH_3\text{-}\underset{\displaystyle Cl}{\underset{|}{C}H}\text{-}CH_2\text{-}CH_3$

2-Chlorobutane

Solution : In S_N2 mechanism, a pentacoordinate T.S. is involved. The order of reactivity of alkyl halides towards S_N2 mechanism is,
Primary > Secondary > Tertiary, (due to increasing crowding in T.S. from primary to tertiary halides. 1-Chlorobutane being primary halide will react faster by S_N2 mechanism, than the secondary halide 2-chlorobutane.

Can you recall ?

- How are alkenes prepared from alkyl halides ?
- Which is stronger base from the following ?

i. aq. KOH   ii. alc. KOH

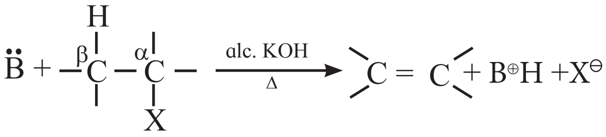
10.6.5 Elimination reaction : Dehydrohalogenation

When alkyl halide having at least one β-hydrogen is boiled with alcoholic solution of potassium hydroxide, it undergoes elimination of hydrogen atom from β-carbon and halogen atom from α - carbon resulting in the formation of an alkene.

Remember...

The carbon bearing halogen is commonly called α-carbon (alpha carbon) and any carbon attached to α-carbon is β-carbon (beta carbon). Hydrogens attached to β-carbon are β-hydrogens.

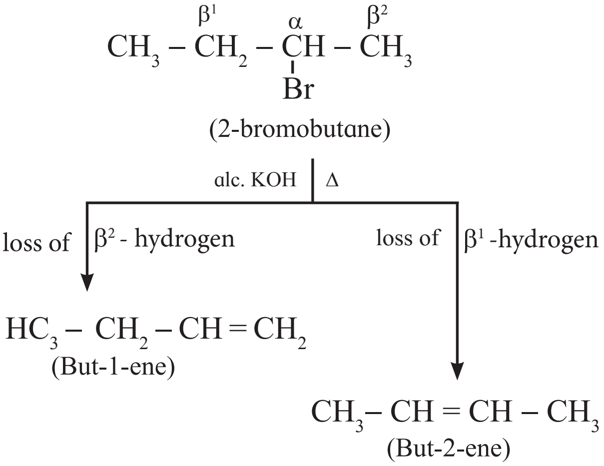
This reaction is called β-elimination (or 1,2 - elimination) reaction as it involves elimination of halogen and a β - hydrogen atom.



(base) (alkyl halide) (alkene)

As hydrogen and halogen is removed in this reaction it is also known as **dehydrohalogenation** reaction.

If there are two or more non-equivalent β-hydrogen atoms in a halide, then this reaction gives a mixture of products. Thus, 2-bromobutane on heating with alcoholic KOH gives mixture of but-1-ene and but-2-ene.



The different products of elimination do not form in equal proportion. After studying a number of elimination reactions, Russian chemist Saytzeff formulated an empirical rule given below.

In dehydrohalogenation reaction, the preferred product is that alkene which has greater number of alkyl groups attached to doubly bonded carbon atoms.

Therefore, in the above reaction but-2-ene is the preferred product, and is formed as the major product. It turned out that more highly substituted alkenes are also more stable alkenes. Hence **Saytzeff elimination is preferred formation of more highly stabilized alkene during an elimination reaction.** The stability order of alkyl substituted alkenes is :

$$R_2C = CR_2 > R_2C = CHR > R_2C = CH_2,$$
$$RCH = CHR > RCH = CH_2$$

Do you know ?

Elimination versus substitution:

Alkyl halides undergo sunstitution as well as elimination reaction. Both reactions are brought about by basic reagent, hence there is always a competition between these two reactions. The reaction which actually predominates depends upon following factors.

a. Nature of alkyl halides : Tertiary alkyl halides prefer to undergo elimination reaction where as primary alkyl halides prefer to undergo substitution reaction.

b. Strength and size of nucleophile : Bulkier electron rich species prefers to act as base by abstracting proton, thus favours elimination. Substitution is favoured in the case of comparatively weaker bases, which prefer to act as nucleophile

c. Reaction conditions : Less polar solvent, high temperature fovours elimination where as low tempertaure, polar solvent favours substitution reaction.

10.6 Reaction with active metals

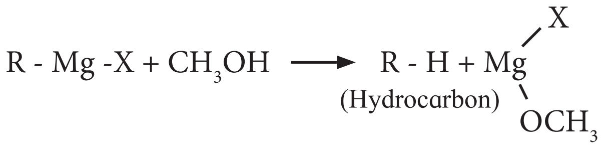
Active metals like sodium, magnesium cadmium readily combine with alkyl chlorides, bromides and iodides to form compounds containing carbon-metal bonds. These are known as organometallic compounds.

a. Reaction with magnesium : When alkyl halide is treated with magnesium in dry ether as solvent, it gives alkyl magnesium halide. It is known as Grignard reagent.

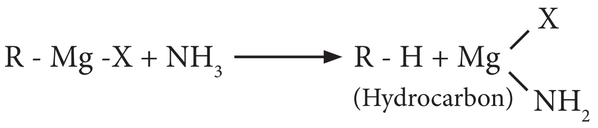
$$R\text{-}X + Mg \xrightarrow{\text{dry ether}} R - Mg - X$$

alkyl magnesium halide
(Grignard reagent)

Grignard reagents are very reactive compounds. They react with water or compounds containing hydrogen attached to electronegative element.



$$R - Mg - X + CH_3OH \longrightarrow \underset{\text{(Hydrocarbon)}}{R - H} + Mg\begin{matrix} X \\ OCH_3 \end{matrix}$$



$$R - Mg - X + NH_3 \longrightarrow \underset{\text{(Hydrocarbon)}}{R - H} + Mg\begin{matrix} X \\ NH_2 \end{matrix}$$

Do you know ?

Carbon-magnesium bond in Grignard reagent is a polar covalent bond. The carbon pulls electrons from the electropositive magnesium. Hence carbon in Grignard reagent has negative polarity and acts as a nucleophite

$$\overset{\delta^{\ominus}}{R} - \overset{\delta^{\oplus}}{Mg} : \ddot{\underset{..}{X}} :$$

Victor Grignard received Nobel Prize in 1912 for synthesis and study of organo-magnesium compounds. Grignard reagent is a very versatile reagent used by organic chemist. Vinyl and aryl halides also form Grignard reagent.

b. Wurtz reaction : Alkyl halides react with metallic sodium in dry ether as solvent, and form higher alkanes containing double the number of carbon atoms present in alkyl halide. This reaction is called Wurtz reaction. (Refer to Std. XI Chemistry Textbook sec. 1.5.3)

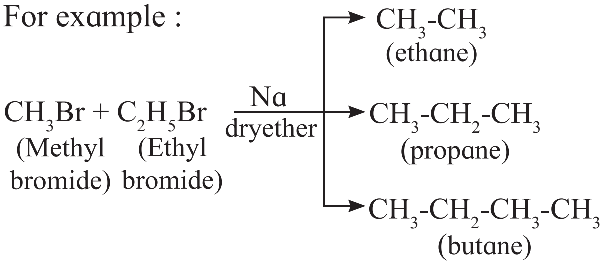
$$2\ R\text{-}X + 2\ Na \xrightarrow[\text{ether}]{\text{dry}} R - R + 2\ NaX$$

$$2C_2H_5\ Br + 2Na \xrightarrow[\text{ether}]{\text{dry}} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 + 2\ NaBr$$

(Ethyl bromide) (Butane)

When a mixture of two different alkyl halides is used, all the three possible alkanes are formed.

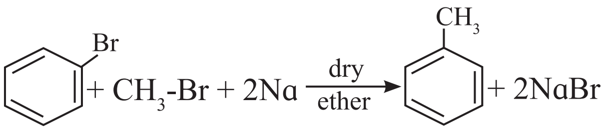
For example :



10.6.1 Reaction of haloarenes :

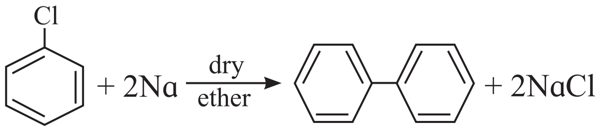
a. Reactions of haloarene with metals

The reaction of aryl halide with alkyl halide and sodium metal in dry ether to give substituted aromatic compounds is known as **Wurtz- Fittig reaction**. This reaction is an extension of Wurtz reaction and was carried out by Fittig. This reaction allows alkylation of aryl halides.



(Bromobenzene) (Toluene)

In case only aryl halide takes part in the reaction, the product is biphenyl and the reaction is known as **Fittig reaction**.



(Chlorobenzene) (Biphenyl)

b. Nucleophilic substitution S_N of haloarenes:

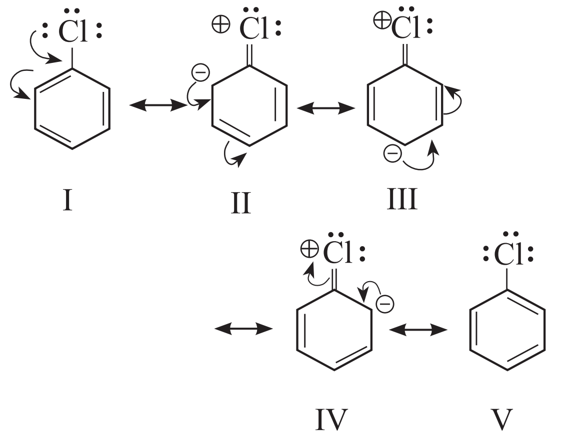
Can you recall ?

- What is resonance?
- Draw resonance structures of bromobenzene.
- Identify the type of hybridization of carbon to which halogen is attached in haloarene.

Aryl halides show low reactivity towards nucleophilic substitution reactions. The low reactivity of aryl halides is due to :

i. Resonance effect and
ii. sp^2 hybrid state of C .

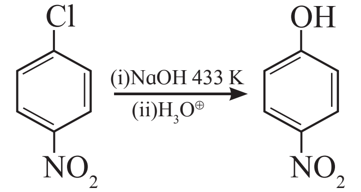
i. One of the lone pairs of electrons on halogen atom is in conjugation with π -electrons of the ring. For example the following different resonance structures can be written for chlorobenzene.



Resonance structures II, III and IV show double bond character to carbon-chlorine bond. Thus carbon-chlorine bond in chlorobenzene is stronger and shorter than chloroalkane molecule, C-Cl bond length in chlorobenzene is 169 pm as compared to C-Cl bond length in alkyl chloride 178 pm. Hence it is difficult to break. Phenyl cation produced due to self-ionization of haloarene will not be stabilised by resonance, which rules out possibility of S_N1 mechanism. Back side attack of nucleophile is blocked by the aromatic ring, which rules out S_N2 mechanism.

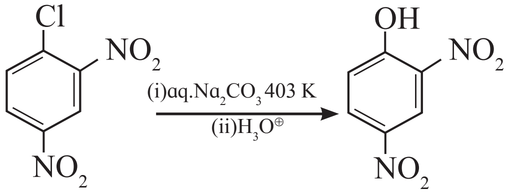
Thus nuclophilic substitution reaction involving cleavage of C-X bond in haloarene proceeds with difficulty. However, the presence of certain groups at certain positions of the ring, markedly activate the halogen of aryl halides towards substitutuion. For example, presence of electron withdrawing group at ortho and/or para postion greatly increases the reactivity of haloarenes towards subsitution of halogen atom. Greater the number of electron withdrawing groups at o/p position, greater is the reactivity. Electron withdrawing group at meta position has practically no effect on reactivity.

i.



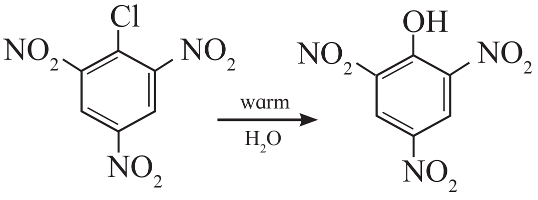
(p-nitrochlorobenzene) (p-nitrophenol)

ii.



(2,4-dinitrochlorobenzene) (2,4 - dinitrophenol)

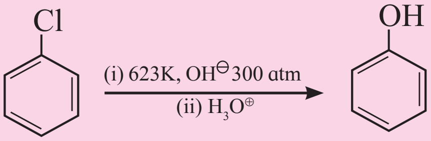
iii.



(2,4,6-trinitrochlorobenzene) (2,4,6 - trinitrophenol)

Can you tell ?

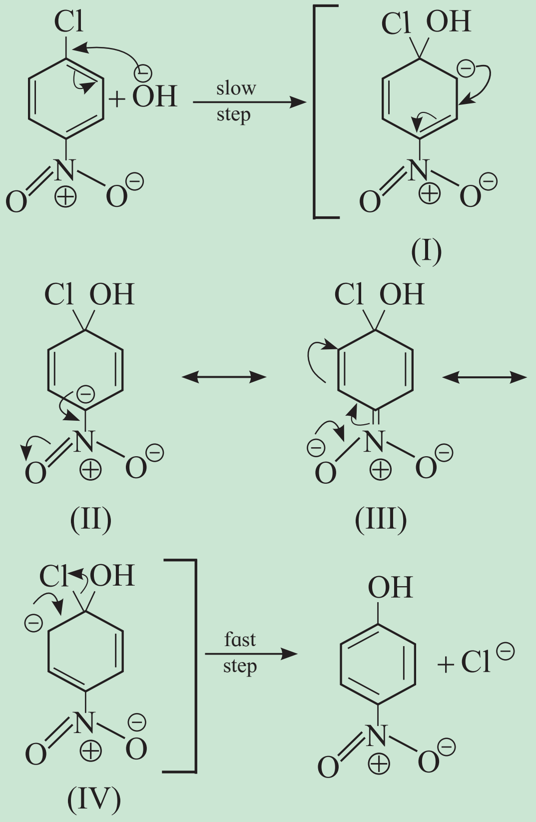
Conversion of chlorobenzene to phenol by aqueous sodium hydroxide requires high temperture of about 623K and high pressure. Explain.



Chlorobenzene Phenol

Do you know ?

Occurrence of nucleophilic substitution in p-nitrochlorobenzene can be explained on the basis of resonance stabilization of the intermediate.



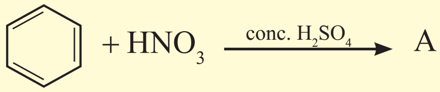
The resonance structure (III) shows that the electron withdrawing nitro group (-NO_2) in the p-position extends the conjugation. As a result, the intermediate carbanion is better stabilized which favours nucleophilic substitution reaction.

c. Electrophilic substitution (SE) in arylhalides

Can you recall ?

- What is an electrophile?
- Give some examples of electrophiles
- What type of reactions are observed in benzene?

- Identify the product A of following reaction.



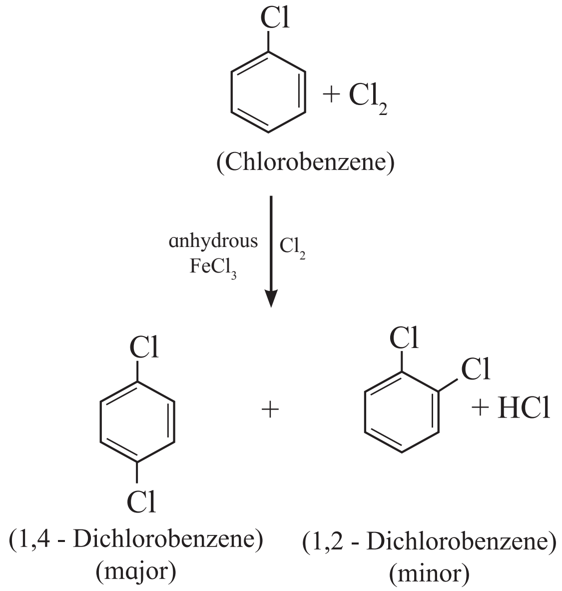
Aryl halides undergo electrophilic substitution reaction slowly as compared to benzene.

In resonance structures of chlorobenzene (see section 10.6.5) elelctron density is relatively more at ortho and para position. Therefore incoming electrophilic group is more likely to attack at these positions. But due to steric hinderance at ortho position, para product usually predominates. In haloarenes, halogen atom has strong electron withdrawing inductive effect (-I). This deactivates the ring and electrophilic substitution reaction occurs slowly.

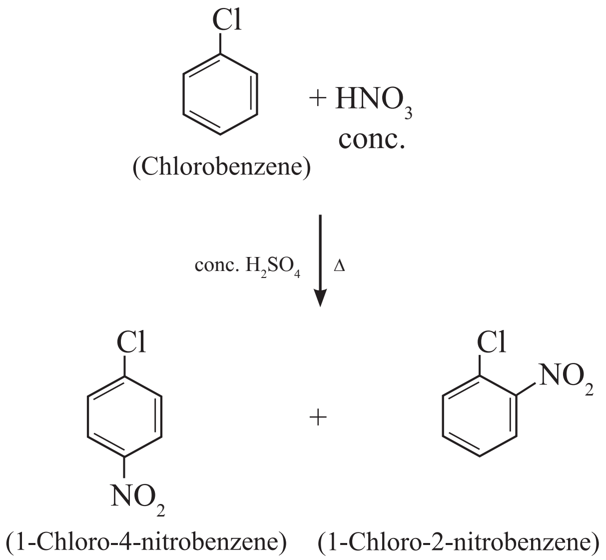
Remember...

The -I effect of Cl is more powerful than its +R effect. Therefore Cl is o-/p- directing but ring deactivating group.

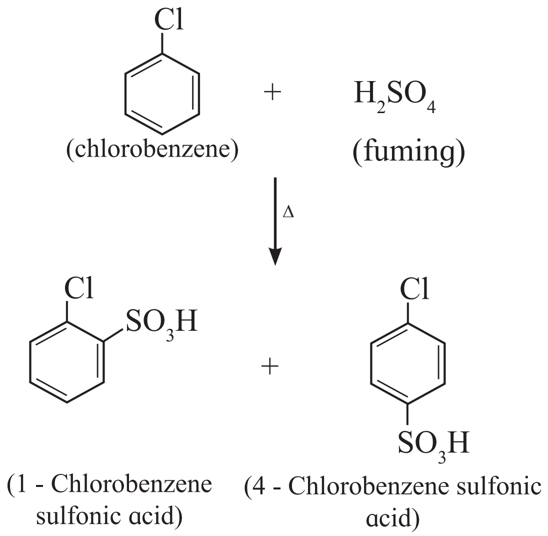
i. Halogenation : It is carried out by reacting haloarene with halogen in presence of ferric salt as Lewis acid catalyst.



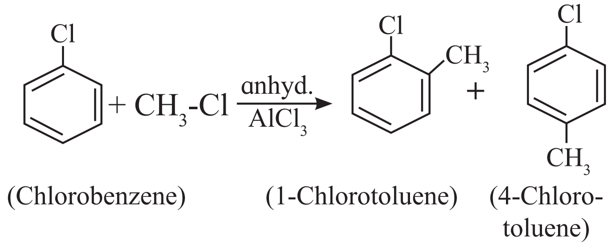
ii. Nitration : It is carried out by heating haloarene with conc. HNO_3 in presence of conc. H_2SO_4.

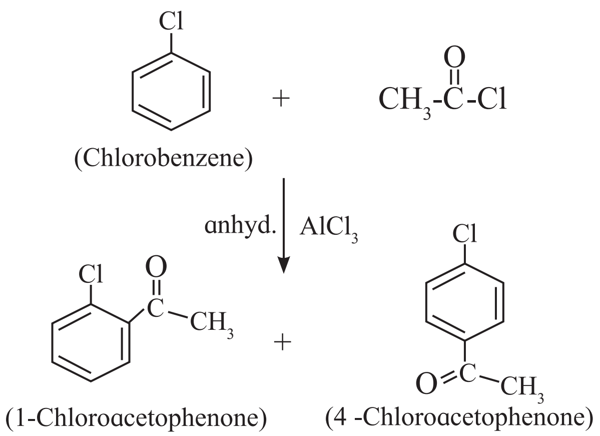


iii. Sulfonation : It is carried out by heating haloarene with fuming H_2SO_4.



iv. Friedel Craft's reaction : It is carried out by treating haloarene with alkyl chloride or acyl chloride in presence of anhydrous $AlCl_3$ as a catalyst.





10.7 Uses and Environmental effects of some polyhalogen compounds

10.7.1 Dichloromethane/ methylene chloride (CH_2Cl_2) : It is a colourless volatile liquid with moderately sweet aroma. It is used as a solvent, and used as a propellant in aerosols.

Over exposure to dichloromethane causes dizziness, fatigue, nausea, headaches, numbness, weakness. It is highly dangerous if it comes in direct contact with eyes as it damages cornea.

10.7.2 Chloroform / trichloromethane ($CHCl_3$) : It is a colourless liquid with peculiar sweet smell. It is used to prepare chloroflurомethane, a refrigerant R-22. It is used as a solvent for extraction of natural products like gums, fats, resins. It is used as a source of dichlorocarbene. Chloroform causes depression of central nervous system. Inhaling chloroform for a short time causes fatigue, dizziness and headache. Long exposure to chloroform may affect liver. Chloroform when exposed to air and light forms a poisonous compound phosgene so it is stored in dark coloured air tight bottles.

10.7.3 Carbon tetrachloride / tetrachloromethane (CCl_4) :

It is a colourless liquid with sweet smell. It is very useful solvent for oils, fats, resins. It serves as a source of chlorine. It is used as a cleaning agent. It is highly toxic to liver. Exposure to high concentration of CCl_4 can affect central nervous system and it is suspected to be carcinogenic. Prolonged exposure may cause death. It is a green house gas.

10.7.4 Idoform or triiodomethane (CHI_3):

It is a yellow crystalline substance with disagreeable smell. It is used in medicine as a healing agent and antiseptic in dressing of wounds, however its use is limited.

It causes irritation to skin and eyes. It may cause respiratory irritation or breathing difficulty, dizziness, nausea, depression of central nervous system, visual disturbance.

10.7.5 Freons : These are organic compounds of chlorine and fluorine, chlorofluorocarbons, CFC's are commonly used as refrigerants. The most common representative is dichlorodifluromethane (Freon-12) others include chlorodifluromethane (R-22), trichlorofluromethane (R-11) and so on.

They are used as refrigerants in fridge and airconditioning, propellants in aerosol and solvents. They are used as blowing agents in making foams and packing materials.

Chloroflurocarbons are responsible for ozone depletion of ozone in stratosphere. Regular large inhalation of freons results in breathing problems, organ damage, loss of consciousness.

Do you know ?

How do CFC distroy the ozone layer in the atmosphere ?

When ultraviolet radiation (UV) strikes CFC (CFCl3) molecules in the upper atmosphere, the carbon-chlorine bond breaks and produces highly reactive chlorine atom (Cl).

$$CFCl_3 \longrightarrow CFCl_2 + Cl$$

This reactive chlorine atom decomposes ozone (O3) molecule into oxygen molecule (O2).

$$O_3 + Cl \longrightarrow O_2 + ClO$$

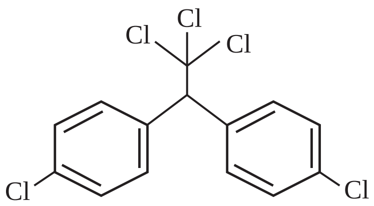
$$ClO + O \longrightarrow O_2 + Cl$$

One atom of chlorine can destroy upto 100,000 ozone molecules.

10.7.6 Dichlorodiphenyltrichloroethane (DDT) : It is colourless, tasteless and odorless crystalline compound having insecticidal property.

It kills insects such as houseflies, mosquitoes and body lice. It was used for controlling maleria and typhus.

Exposure to high doses of DDT may cause vomiting, tremors or shakiness. Laboratory animal studies showed adverse effect of DDT on liver and reproduction. DDT is a pressistent organic pollutant, readily absorbed in soils and tends to accumulate in the ecosystem. When dissolved in oil or other lipid, it is readily absorbed by the skin. It is resistant to metabolism. It accumulates in fatty tissues. There is a ban on use of DDT due to all these adverse effects .



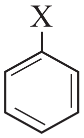
Do you know ?

DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.

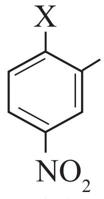
Exercises

1. Choose the most correct option.

i. The correct order of increasing reactivity of C-X bond towards nucleophile in the following compounds is



(I)



(II)

$(CH_3)_3C\text{-}X$ (III)

$(CH_3)_2CH\text{-}X$ (IV)

a. I < II < III < IV

b. II < I < III < IV

c. III < IV < II < I

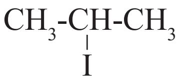
d. IV < III < I < II

ii. $CH_3\text{-}CH{=}CH_2 \xrightarrow[\text{peroxide}]{HI}$

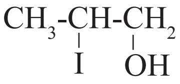
The major product of the above reaction is,

a. $I\text{-}CH_2\text{-}CH{=}CH_2$

b. $CH_3\text{-}CH_2\text{-}CH_2I$

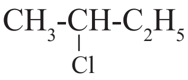
c. 

$CH_3\text{-}\underset{\substack{|\\ I}}{CH}\text{-}CH_3$

d. 

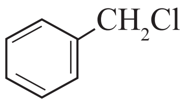
$CH_3\text{-}\underset{\substack{|\\ I}}{CH}\text{-}\underset{\substack{|\\ OH}}{CH_2}$

iii. Which of the following is likely to undergo racemization during alkaline hydrolysis ?

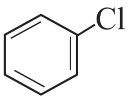


$CH_3\text{-}\underset{\substack{|\\ Cl}}{CH}\text{-}C_2H_5$

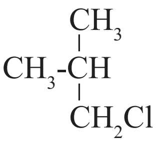
(I)



(II)



(III)



$CH_3\text{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_2Cl}}{CH}}$

(IV)

a. Only I

b. Only II

c. II and IV

d. Only IV

iv. The best method for preparation of alkyl fluorides is

a. Finkelstein reaction

b. Swartz reaction

c. Free radical fluorination

d. Sandmeyer's reaction

v. Identify the chiral molecule from the following.

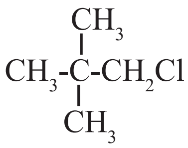
a. 1-Bromobutane

b. 1,1- Dibromobutane

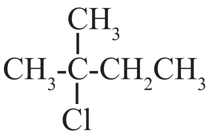
c. 2,3- Dibromobutane

d. 2-Bromobutane

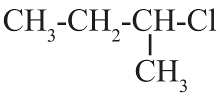
vi. An alkyl chloride on Wurtz reaction gives 2,2,5,5-tetramethylhexane. The same alkyl chloride on reduction with zinc-copper couple in alchol give hydrocarbon with molecular formula C_5H_{12}. What is the structure of alkyl chloride

a. 

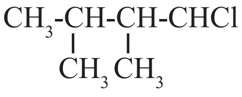
$CH_3\text{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}\text{-}CH_2Cl$

b. 

$CH_3\text{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ Cl}}{C}}\text{-}CH_2CH_3$

c. 

$CH_3\text{-}CH_2\text{-}\underset{\substack{|\\ CH_3}}{CH}\text{-}Cl$

d. 

$CH_3\text{-}\underset{\substack{|\\ CH_3}}{CH}\text{-}\underset{\substack{|\\ CH_3}}{CH}\text{-}CHCl$

vii. Butanenitrile may be prepared by heating

a. propanol with KCN

b. butanol with KCN

c. n-butyl chloride with KCN

d. n-propyl chloride with KCN

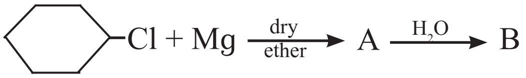
viii. Choose the compound from the following that will react fastest by S_N1 mechanism.

a. 1-iodobutane

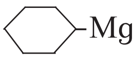
b. 1-iodopropane

c. 2-iodo-2 methylbutane

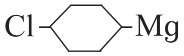
d. 2-iodo-3-methylbutane

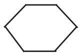
ix.


The product 'B' in the above reaction sequence is,

a. 

b. 

c. 

d. 

x. Which of the following is used as source of dichlorocarbene

a. tetrachloromethane

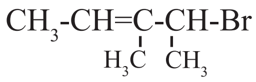
b. chloroform

c. iodoform

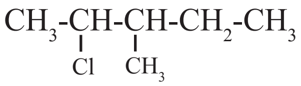
d. DDT

2. Do as directed.

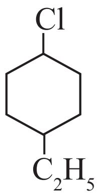
i. Write IUPAC name of the following compounds

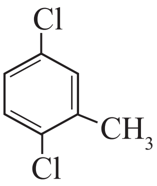
a. 

$CH_3\text{-}CH\text{=}\underset{H_3C}{\underset{|}{C}}\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}Br$

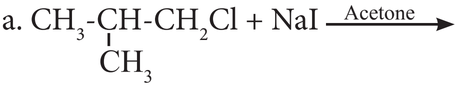
b. 

$CH_3\text{-}\underset{Cl}{\underset{|}{CH}}\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3$

c. 

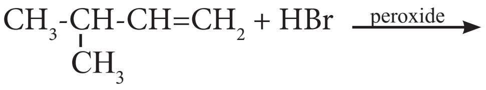
d. 

ii. Write structure and IUPAC name of the major product in each of the following reaction.

a. 

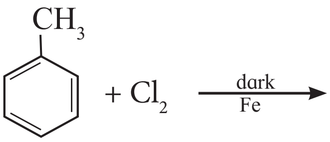
$CH_3\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH_2Cl + NaI \xrightarrow{Acetone}$

b. $CH_3\text{-}CH_2Br + SbF_3 \longrightarrow$

c. 

$CH_3\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH\text{=}CH_2 + HBr \xrightarrow{peroxide}$

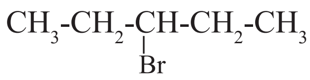
d. 

e. 

iii. Identify chiral molecule/s from the following.

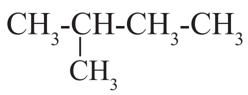
a. 

$CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3$

b. 

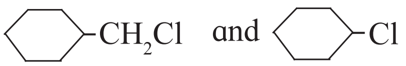
$CH_3\text{-}CH_2\text{-}\underset{Br}{\underset{|}{CH}}\text{-}CH_2\text{-}CH_3$

c. $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2Br$

d. 

$CH_3\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH_3\text{-}CH_3$

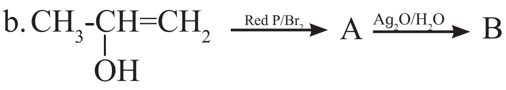
iv. Which one compound from the following pairs would undergo S_N2 faster from the?

a. 

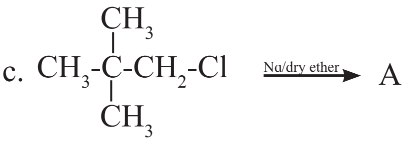
b. $CH_3CH_2CH_2I$ and $CH_3CH_2CH_2Cl$

v. Complete the following reactions giving major product.

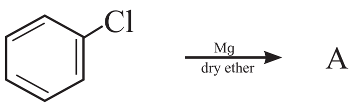
a. $CH_3\text{-}CH\text{=}CH_2 \xrightarrow[peroxide]{HBr} A \xrightarrow{alc.\ KOH} B$

b. 

$CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{=}CH_2 \xrightarrow{Red\ P/Br_2} A \xrightarrow{Ag_2O/H_2O} B$

c. 

$CH_3\text{-}\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}\text{-}CH_2\text{-}Cl \xrightarrow{Na/dry\ ether} A$

d. 

vi. Name the reagent used to bring about the following conversions.

a. Bromoethane to ethoxyethane

b. 1-Chloropropane to 1 nitropropane

c. Ethyl bromide to ethyl isocyanide

d. Chlorobenzene to biphenyl

vii. Arrange the following in the increase order of boiling points

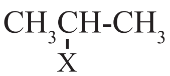
a. 1-Bromopropane

b. 2- Bromopropane

c. 1- Bromobutane

d. 1-Bromo-2-methylpropane

viii. Match the pairs.

Column I	**Column II**
a.  $CH_3\underset{\mid \atop X}{C}H\text{-}CH_3$	i. vinyl halide
b. $CH_2{=}CH\text{-}CH_2X$	ii. alkyl halide
c. $CH_2{=}CH\text{-}X$	iii. allyl halide
	iv. benzyl halide
	v. aryl halide

3. Give reasons

i. Haloarenes are less reactive than halo alkanes.

ii. Alkyl halides though polar are immiscible with water.

iii. Reactions involving Grignard reagent must be carried out under anhydrous condition.

iv. Alkyl halides are generally not prepared by free radical halogenation of alkanes.

4. Distinguish between - S_N1 and S_N2 mechanism of substitution reaction ?

5. Explain - Optical isomerism in 2-chlorobutane.

6. Convert the following.

i. Propene to propan-1-ol

ii. Benzyl alcohol to benzyl cyanide

iii. Ethanol to propane nitrile

iv. But-1-ene to n-butyl iodide

v. 2-Chloropropane to propan-1-ol

vi. tert-Butyl bromide to isobutyl bromide

vii. Aniline to chlorobenzene

viii. Propene to 1-nitropropane

7. Answer the following

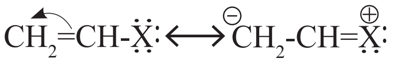
i. HCl is added to a hydrocarbon 'A' (C_4H_8) to give a compound 'B' which on hydrolysis with aqueous alkali forms tertiary alcohol 'C' ($C_4H_{10}O$). Identify 'A' , 'B' and 'C'.

ii. Complete the following reaction sequences by writing the structural formulae of the organic compounds 'A', 'B' and 'C' .

a. 2-Bromobutane $\xrightarrow{\text{alc.KOH}} A \xrightarrow[Br_2]{} B \xrightarrow[NaNH_2]{} C$

b. Isopropyl alcohol $\xrightarrow[PBr_3]{\Delta} A \xrightarrow[NH_3\text{ excess}]{} B$

iii. Observe the following and answer the questions given below.



$CH_2{=}CH\text{-}\ddot{\underset{..}{X}}{:} \longleftrightarrow \overset{\ominus}{C}H_2\text{-}CH{=}\overset{\oplus}{\ddot{\underset{..}{X}}}{:}$

a. Name the type of halogen derivative

b. Comment on the bond length of C-X bond in it

c. Can react by S_N1 mechanism? Justify your answer.

Activity :

1. Collect detailed information about Freons and their uses.

2. Collect information about DDT as a persistent pesticide.

Reference books

i. Organic chemistry by Morrison, Boyd, Bhattacharjee, 7th edition, Pearson

ii. Organic chemistry by Finar, Vol 1, 6th edition, Pearson

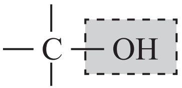
11. ALCOHOLS, PHENOLS AND ETHERS

Can you recall ?

1. What is the name and formula of 2nd member of homologous series of alcohols?
2. What is the structural formula of functional group of ether?
3. What is the name of the compound having -OH group bonded to benzene ring?

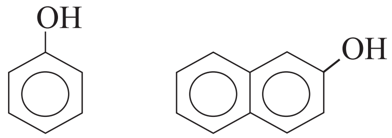
11.1 Introduction :

Alcohols are organic compounds whose molecules contain hydroxyl group, (-OH) attached to a saturated carbon atom.

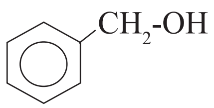


$$-\overset{|}{\underset{|}{C}}-\boxed{OH}$$

Hydroxyl group can also be present in aromatic compounds. There are two types of aromatic hydroxy compounds: **phenols** and **aromatic alcohols.** Phenols contain a hydroxyl group directly attached to the carbon atom of benzene ring. When the hydroxyl group is present in the side chain of aromatic ring, the compound is termed as aromatic alcohol.



Phenols



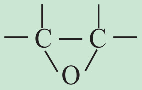
Aromatic alcohol

Ethers are compounds which contain an oxygen atom bonded to two alkyl groups or two aryl groups or one alkyl and one aryl group. Ethers are organic oxides. Ethers are considered as anhydrides of alcohols.

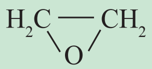
R-O-R', R-O-Ar, Ar-O-Ar'.

Do you know ?

Epoxide are cyclic ethers in which the ethereal oxygen is a part of a three membered ring.



(Ethylene oxide)



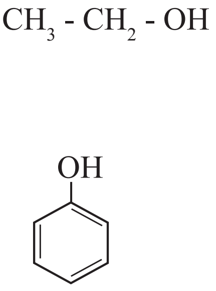
(1,2-Epoxyethane)

11.2 Classification :

Let us first consider classification of alcohols, phenols and then ethers.

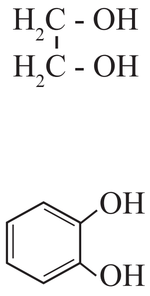
11.2.1 Mono, di, tri and polyhydric compounds :

Alcohols and phenols are classified as mono, di-, tri, or polyhydric compounds on the basis of one, two, three or more hydroxyl groups present in their molecules as :



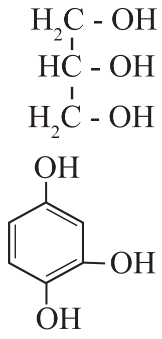
CH_3-CH_2-OH

Monohydric alcohols/phenols



$$\begin{array}{l}H_2C-OH\\ \quad|\\ H_2C-OH\end{array}$$

Dihydric alcohols/ phenols



$$\begin{array}{l}H_2C-OH\\ \quad|\\ HC-OH\\ \quad|\\ H_2C-OH\end{array}$$

Trihydric alcohols/phenols

Monohydric alcohols are further classified on the basis of hybridisation state of the carbon atom to which hydroxyl group is attached.

a. Alcohols containing sp^3C - OH bond : In these alcohols -OH group is attached to a sp^3 hybridised carbon atom of alkyl group. These alcohols are further classified as primary (1^0), secondary (2^0) and tertiary (3^0) alcohols in which -OH group is attached to primary, secondary and teriary carbon atom respectively. (see Fig. 11.1), also refer to Std. XI Chemistry Textbook Chapter 14, sec. 14.3.2)

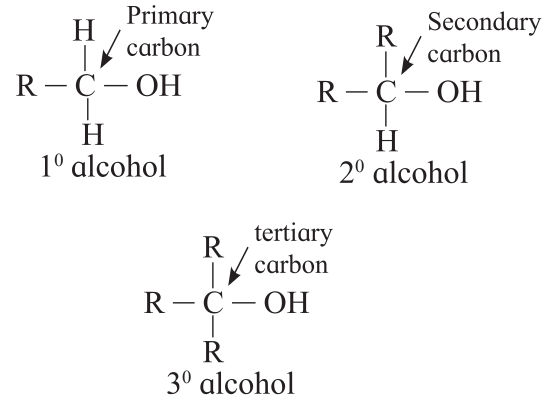


Fig. 11.1 : Primary, secondary and tertiary alcohols

Each of these three types of alcohols can also be either allylic or benzylic if the sp^3 carbon carrying -OH is further bonded to sp^2 carbon.

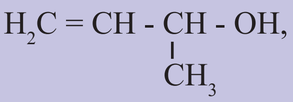
- **Allylic alcohols** : In this type of alcohols -OH group is attached to sp^3 hybridised carbon atom which is further bonded to a carbon-carbon double bond. Allylic alcohol may be primary, secondary or tertiary.
- **Benzylic alcohols** : In this type of alcohols -OH group is attached to sp^3 hybridised carbon atom which is further bonded to an aromatic ring. Benzylic alcohol may be primary, secondary or tertiary.

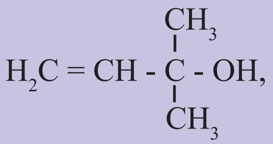
Use your brain power

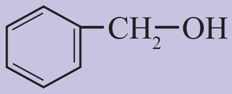
Classifiy the following

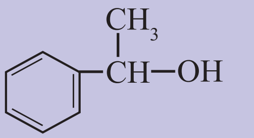
alcohols as 1^0 / 2^0 / 3^0 and allylic/ benzylic

$H_2C = CH - CH_2 - OH$,


$H_2C = CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} - OH$,


$H_2C = CH - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - OH$,





b. Alcohols contianing sp^2C-OH bonds :

In these alcohols -OH group is attached to a sp^2 hybridised carbon atom which is part of a carbon-carbon double bond. These alcohols are known as **vinylic alcohols**. For example

$CH_2 = CH - OH$ (Vinyl alcohol)

11.2.2 Classification of Ethers : Ethers are classified as **symmetrical ethers** (**simple ethers**) or **unsymmetrical ethers** (**mixed ethers**) depending on whether the two alkyl/ aryl groups bonded to oxygen atom are same or different respectively. For example :

$$R - O - R / Ar - O - Ar$$

$$CH_3 - O - CH_3$$

symmetrical ethers (simple ethers)

$$R - O - R' / Ar - O - Ar'$$

$$CH_3 - O - C_2H_5,\ C_6H_5 - O - CH_3$$

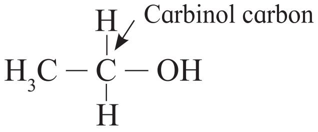
unsymmetrical ethers (mixed ethers)

11.3 Nomenclature :

11.3.1 Alcohols : There are three systems of nonmenclature of monohydric alcohols.

a. Common/trivial names : The common or trivial names of alcohols are obtained by adding word alcohol after the name of alkyl group bonded to -OH. Names of higher alkyl groups also include prefixes like normal, iso, secondary, tertiary (see. Table 11.1).

b. Carbinol system : In this system alcohols are considered as derivatives of **methyl alcohol** which is called **carbinol**. The alkyl group attached to the carbon carrying -OH group are named in alphabetical order. Then the suffix carbinol is added. For example :



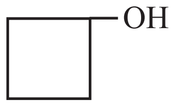
$H_3C - \overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}} - OH$

Methyl carbinol

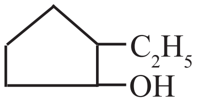
Use your brain power

Name t-butyl alcohol using carbinol system of nomenclature.

c. IUPAC system : Acoriding to IUPAC system (Std XI Chemistry Text book, Chapter 14), alcohols are named as **alkanols**. The ending 'e' in the name of the parent alkane, alkene or alkyne is replaced by the suffix 'ol'. For naming polyhydric alcohol, 'e' in the ending of alkane is retained, the ending 'ol' is added and number of -OH groups is indicated by prefix di, tri, etc., before 'ol'. The positions of -OH groups are indicated by appropriate locants. For example ethane -1,2-diol (see. Table 11.1). Similarly cyclic alcohols are named by using prefix cyclo to the parent alkane and considering -OH group attached to C-1 carbon atom.



Cyclobutanol



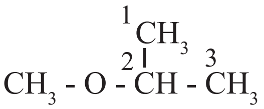
2- Ethylcyclopentanol

11.3.2 Nomenclature of phenols :

The hydroxyl derivative of benzene is called phenol. The IUPAC system name of phenol is benzenol. The common name phenol is also accepted by IUPAC. The common names have prefixes ortho, meta and para in subsituted phenols. IUPAC system uses the locant 2-, 3-, 4-, etc. to indicate the positions of substituents (see Table 11.2).

11.3.3 Nomenclature of Ethers :

In the **common system** of nomenclature, the ethers are named by writing names of the alkyl groups attached to the oxygen atom in alphabetical order and word ether is added. If two alkyl groups are same, prefix di- is used. According to the **IUPAC system** of nomenclature, ethers are named as **alkoxyalkanes** (see Table 11.3). The larger alkyl group is considered to be the parent alkane. The name of the smaller alkane is prefixed by the name of alkoxy group and its locant. For example :



$CH_3-O-\overset{\overset{1}{C}H_3}{\overset{2\,|}{C}H}-\overset{3}{C}H_3$

2-Methoxypropane

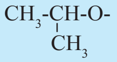
Some alkoxy group	
CH_3-CH_2O-	Ethoxy
CH_3-CH_2-CH_2-O-	n-Propoxy
 $CH_3-\underset{CH_3}{CH}-O-$	Isopropoxy

Table 11.1 Common/Trivial and IUPAC Names of some alcohols

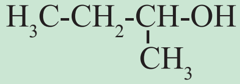
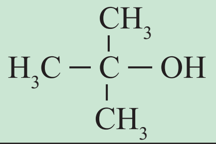
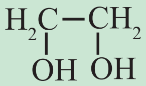
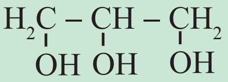
Structural formula	Common/ Trivial Name	IUPAC Name
H_3C-OH	Methyl alcohol	Methanol
H_3C-CH_2-OH	Ethyl alcohol	Ethanol
$H_3C-CH_2-CH_2-OH$	n -Propyl alcohol	Propan -1-ol
 $H_3C-CH_2-\underset{CH_3}{CH}-OH$	sec-Butyl alcohol	Butan -2-ol
 $H_3C-\underset{CH_3}{CH}-CH_2-OH$	Isobutyl alcohol	2- Methylpropanol
 $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH$	tert-Butyl alcohol	2-Methylpropan-2-ol
 $\underset{OH}{H_2C}-\underset{OH}{CH_2}$	Ethylene glycol	Ethane-1, 2-diol
 $\underset{OH}{H_2C}-\underset{OH}{CH}-\underset{OH}{CH_2}$	Propylene glycerol	Propane-1,2,3-triol
$H_3CCH=CHCH_2OH$	Crotonyl alcohol	But-2-en-1-ol

Table 11.2 Common and IUPAC names of some phenols

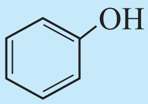
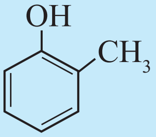
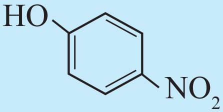
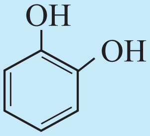
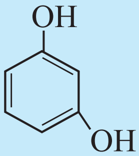
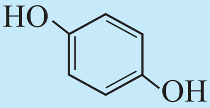
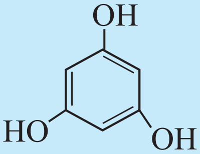
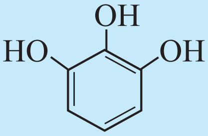
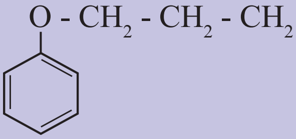
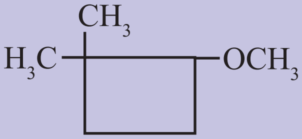
Structural formula	Common name	IUPAC Name
	Phenol	Benzenol/Phenol
	o- Cresol	2-Methylphenol
	p-Nitrophenol	4-Nitrophenol
	Catechol	Benzene-1,2-diol
	Resorcinol	Benzene-1,3-diol
	Hydroquinone/ quinol	Benzene -1,4-diol
	Phloroglucinol	Benzene-1,3,5-triol
	Pyrogallol	Benzene-1,2,3-triol

Table 11.3 Common and IUPAC Names of some Ethers

Structural formula	Common Name	IUPAC Name
$H_3C - O - CH_3$	Dimethyl ether	Methoxymethane
$H_3C - O - CH_2 - CH_3$	Ethyl methyl ether	Methoxyethane
$H_3C - O - CH_2 - CH_2 - CH_3$	Methyl n-propyl ether	1-Methoxypropane
$C_6H_5 - O - CH_3$	Methyl phenyl ether (Anisole)	Methoxybenzene
	Phenyl n-propyl ether	1- Propoxybenzene
	-	2- Methoxy-1,1-dimethylcyclobutane

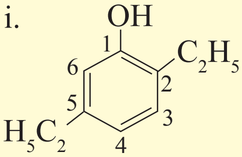
Problem 11.1 : Draw structures of following compounds.

i. 2,5-Diethylphenol ii. Prop-2-en-1-ol

iii. 2-methoxypropane iv. Phenylmethanol

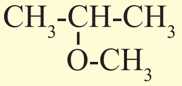
Solutuion :

i.



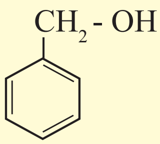
ii. $\overset{3}{H_2C} = \overset{2}{CH} - \overset{1}{CH_2} - OH$

iii.



$CH_3-\underset{\underset{O-CH_3}{|}}{CH}-CH_3$

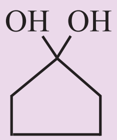
iv.



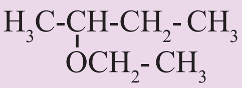
Try this...

Write IUPAC names of the following compounds.

i.

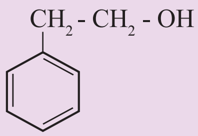


ii.

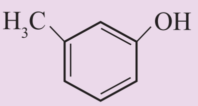


$H_3C-\underset{\underset{OCH_2-CH_3}{|}}{CH}-CH_2-CH_3$

iii.



iv.



11.4 Alcohols and Phenols :

11.4.1 Prepartion of alcohols :

a. From alkyl halide by hydrolysis with aqueous alkali or moist silver oxide (refer to section 10.6.2)

b. By acid catalyzed hydration of alkenes :

Alkene reacts with sulfuric acid to produce alkyl hydrogen sulfate, which on hydrolysis gives alcohol (Refer to Std XI Chemistry Textbook, section 15.2.4). This reaction follows **Markownikoff's rule**.

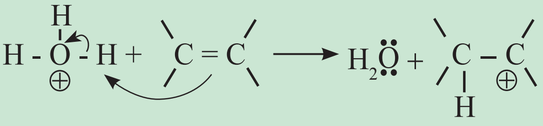
c. Hydroboration - Oxidation of alkenes :

With diborane (B_2H_6) alkene undergoes addition reaction (Hydroboration) to give to trialkylborane (R_3B), which on oxidation with hydrogen peroxide in alkaline medium gives alcohol. (Refer to Std. XI Chemistry Textbook section 15.2.4). This is an **antimarkownikoff hydration** of alkene.

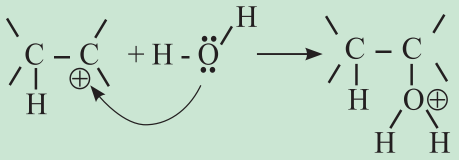
Do you know ?

The mechanism of acid catalyzed hydration of alkene involves the following three steps:

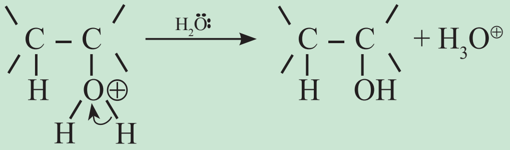
Step 1: Formation of carbocation intermediate.



Step 2: Nucleophilic attack of $H_2\ddot{O}$ on $C^{\oplus}$

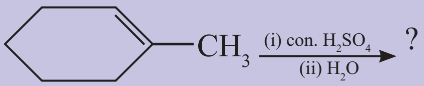


Step 3: Deprotonation



Use your brain power

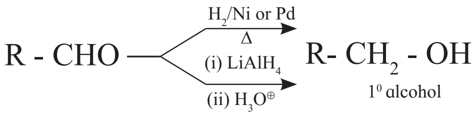
Predict the major product of the following reactions :

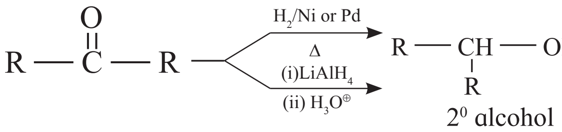
- $CH_3 - CH = CH_2 \xrightarrow[(ii)H_2O_2,\ ^{\ominus}OH]{(i)B_2H_6 - THF} ?$
- 

d. By reduction of carbonyl compounds :

i. By reduction of aldehydes and ketones :

Aldehydes on reduction by H_2/Ni or $LiAlH_4$ give primary alcohols (1^0). Similarly ketones on reduction with H_2/Ni or $LiAlH_4$ give secondary alcohols (2^0).

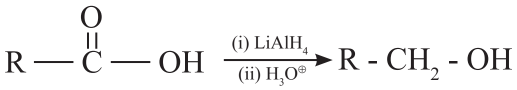




$$R-\overset{\overset{\large O}{\|}}{C}-R \xrightarrow[\Delta]{H_2/Ni \text{ or } Pd} R-\underset{\underset{\large R}{|}}{CH}-OH \qquad R-\overset{\overset{\large O}{\|}}{C}-R \xrightarrow[(ii)\ H_3O^{\oplus}]{(i) LiAlH_4} R-\underset{\underset{\large R}{|}}{CH}-OH$$

2^0 alcohol

ii. By reduction of carboxylic acids : Caboxylic acids require strong reducing agent $LiAlH_4$ to form primary alcohols.



$$R-\overset{\overset{\large O}{\|}}{C}-OH \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} R-CH_2-OH$$

However $LiAlH_4$ is an expensive reagent. Therefore, commercially acids are first transformed into esters which on catalytic hydrogenation give primary alcohols.

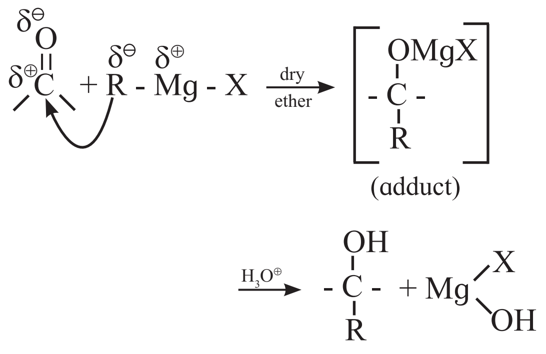
$$R-COOH + R'OH \overset{H^{\oplus}}{\rightleftharpoons} R-COOR' + H_2O$$

$$RCOOR' + 2H_2 \xrightarrow[\Delta]{Ni/Pd} R-CH_2OH + R'OH$$

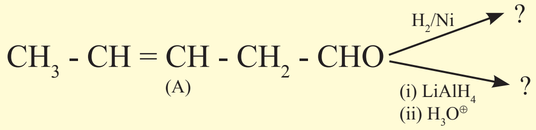
Remember...

The advantage of $LiAlH_4$ over H_2/Ni is that it does not reduce the isolated olefinic bond and hence it can reduce unsaturated aldehyde and ketones to unsaturated alcohols.

e.By addition of Grignard reagent to aldeheydes and ketones : Grignard reagent reacts with aldehyde or ketone to form an adduct which on hydrolysis with dilute acid gives the corresponding alcohols.



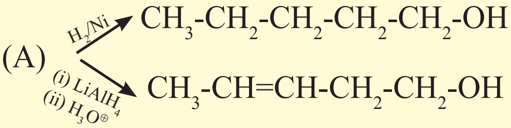
Problem 11.2 : Predict the products for the following reaction.



$$CH_3-CH=CH-CH_2-CHO \xrightarrow{H_2/Ni} ? \qquad CH_3-CH=CH-CH_2-CHO \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} ?$$

(A)

Solution : The substrate (A) contains an isolated $>C=C<$ and an aldehyde group. H_2/Ni can reduce both these functional groups while $LiAlH_4$ can reduce only -CHO of the two, Hence



$$(A) \xrightarrow{H_2/Ni} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$$

$$(A) \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}OH$$

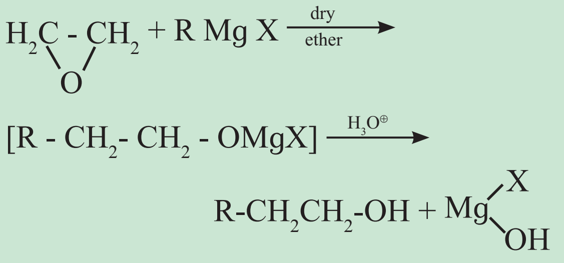
This reaction is useful in synthesis of a variety of alcohols (see Table 11.4).

Table 11.4 Preparation of alcohols by Grignard reagent

Aldehyde/ ketone	Grignard reagent	Final product	Type of alcohol
H - CHO (formaldehyde)	R - Mg Br	$R-CH_2OH$	1^0
R' - CHO (aldehyde)	R - Mg Br	$R-\underset{\underset{\large R'}{\vert}}{CH}-OH$	2^0
R' - CO - R" (ketone)	R - Mg Br	$R-\overset{\overset{\large R''}{\vert}}{\underset{\underset{\large R'}{\vert}}{C}}-OH$	3^0

Do you know ?

Epoxide reacts with Girgnard reagent followed by acidic hydolysis to give primary alcohols



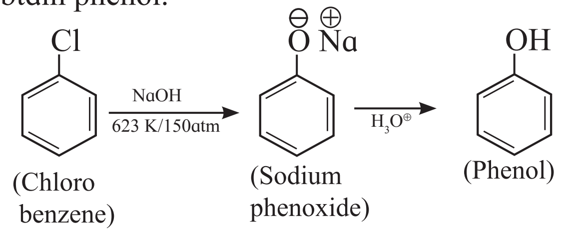
$$H_2C-CH_2 \text{ (O bridged)} + R\,Mg\,X \xrightarrow[\text{ether}]{\text{dry}}$$

$$[R-CH_2-CH_2-OMgX] \xrightarrow{H_3O^{\oplus}}$$

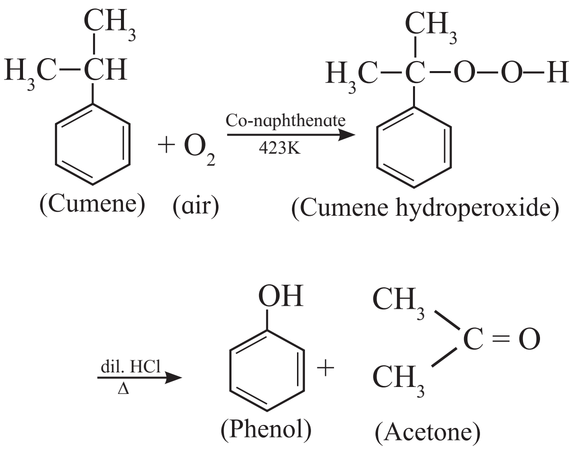
$$R\text{-}CH_2CH_2\text{-}OH + Mg\begin{matrix}X\\OH\end{matrix}$$

11.4.2 Preparation of phenol :

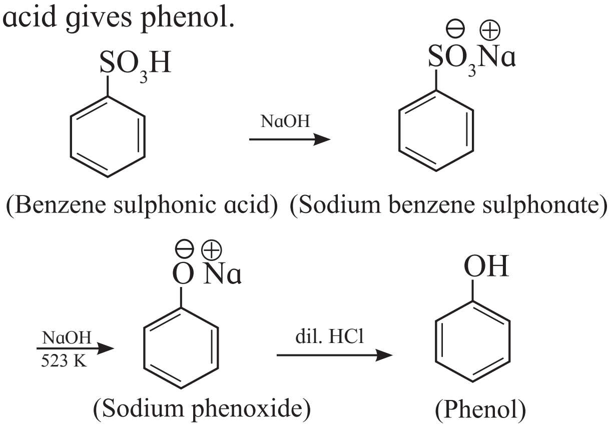
a. From chlorobenzene (Dow Process) : Chlorobenzene is fused with NaOH at high temperature and pressure (623K and 150atm) followed by treatment with dilute HCl to obtain phenol.



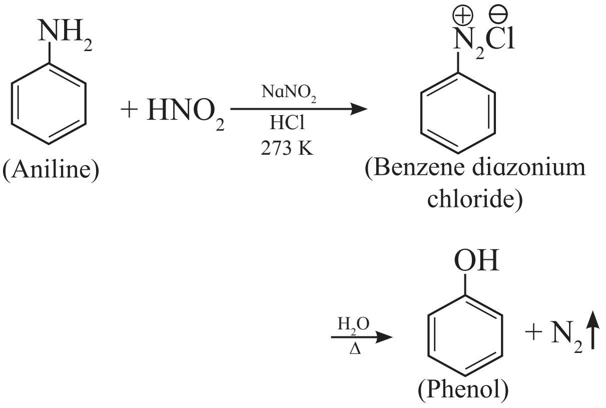
b. From Cumene : This is the commercial method of preparation of phenol. Cumene (isopropylbenzene) on air oxidation in presence of Co-naphthenate gives cumene hydroperoxide, which on decomposition with dilute acid gives phenol with acetone as a valuable by product.



c. From benzene sulfonic acid : Benzene sulfonic acid on neutralization by NaOH gives sodium benzene sulfonate, which on fusion with solid NaOH at 573 K gives sodium phenoxide, followed by reaction with dilute acid gives phenol.

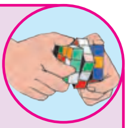


d. From aniline : Aniline is treated with nitrous acid [$NaNO_2$ + HCl] at low temparature to obtain benzene diazonium chloride, which on hydrolysis gives phenol (Also refer to chapter 13 for this reaction).



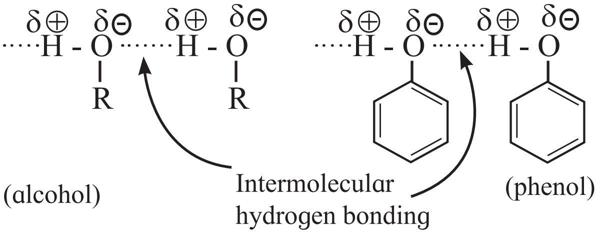
11.4.3 Physical Properties of alcohols and phenols

Try this...



Arrange O-H, C-H and N-H bonds in increasing order of their bond polarity.

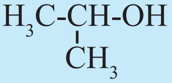
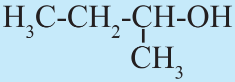
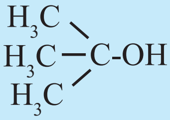
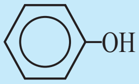
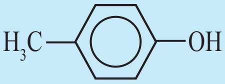
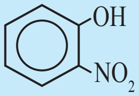
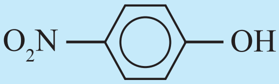
a. Nature of intermolecular forces : Alcohols and phenols are very polar molecules due to presence of -OH groups. The polar -OH groups are held together by the strong intermolecular forces, namely hydrogen bonding.



b. Physical State : Lower alcohols are colourless, toxic liquids having characterstic alcoholic odour. Pure phenol is colourless, toxic, low melting solid having characterstic carbolic or phenolic odour.

c. Boiling Points : The boiling points of alcohols and phenols increase with increase in their molecular mass (Table 11.5).

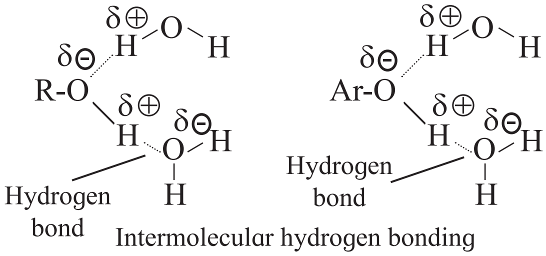
Table 11.5 M.P/B.P and solubilities of some alcohols and phenols

Name	Formula	M.P. (^{0}C)	B.P. (^{0}C)	Solubility (g/100g H_2O)
Methyl alcohol	$H_3C\text{-}OH$	-97	65	0.793
Ethyl alcohol	$H_3C\text{-}CH_2\text{-}OH$	-115	78	0.789
n-Propyl alcohol	$H_3C\text{-}CH_2\text{-}CH_2\text{-}OH$	-126	97	0.804
Isopropyl alcohol	 $H_3C\text{-}\underset{\mid \atop CH_3}{CH}\text{-}OH$	-86	83	0.789
n-Butyl alcohol	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$	-90	118	0.810
Isobutyl alcohol	 $H_3C\text{-}\underset{\mid \atop CH_3}{CH}\text{-}CH_2\text{-}OH$	-108	108	0.802
sec-Butyl alcohol	 $H_3C\text{-}CH_2\text{-}\underset{\mid \atop CH_3}{CH}\text{-}OH$	-114	99.5	0.806
tert-Butyl alcohol		25.5	83	0.789
Phenol		41	182	9.3
p-Cresol		35	202	2.3
o-Nitrophenol		45	217	0.2
p-Nitrophenol		114	-	1.7

Problem 11.3 : The boiling point of n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol and tert-butyl alcohol are 118^{0}C, 108^0 C. 99^{0}C and 82^{0}C respectively. Explain.

Solution : As branching increases intermolecular van der Waal's force become weaker and the boiling point decreases. Therefore n-butyl alcohol has highest boiling point 118^{0}C and tert-butyl alcohol has lowest boiling point 83^{0}C. Isobutyl alcohol is a primary alcohol and hence its boiling points is higher than that of sec-butyl alcohol.

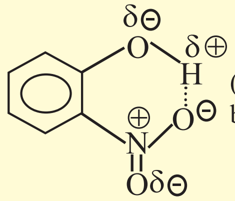
d. Solubility : Phenols and lower alcohols (having upto three carbons) show appreciable solubility in water due to their ability to form intermolecular hydrogen bonding with water molecule (See Table 11.5).



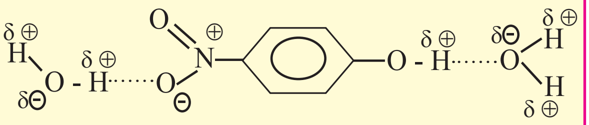
Intermolecular hydrogen bonding of R-OH and Ar-OH with water

Problem 11.4 : The solubility of o-nitrophenol and p-nitrophenol is 0.2 g and 1.7 g/100 g of H_2O respectively Explain the difference.

Solution :



(intramolecular hydrogen bonding in o-nitrophenol)



(intermolecular hydrogen bonding in p-nitrophenol and water)

p-Nitrophenol has strong intermolecular hydrogen bonding with solvent water. On the other hand, o-nitrophenol has strong intramolecular hydrogen bonding and therefore the intermolecular attraction towards solvent water is weak. The stronger the intermolecular attraction between solute and solvent higher is the solubility. Hence p-nitrophenol has higher solubility in water than that of o-nitrophenol.

11.4.4 Chemical properties of Alcohols and Phenols

a. Laboratory tests of alcohols and phenols :

i. Litmus test : Water soluble alcohols and phenols can be tested with litmus paper. Aqueous solution of alcohols is neutral to litmus (neither blue nor red litmus change colour). Aqueous solutions of phenols turn blue litmus red. Thus, phenols have acidic character.

ii. Reaction with bases :

- Acid strength of phenols being very low, phenols cannot react with $NaHCO_3$ but react with NaOH.

$$Ar - OH + NaHCO_3(aq) \longrightarrow \text{No reaction}$$

Phenols dissolve in aqueous NaOH by forming water soluble sodium phenoxide and are reprecipitated/regenerated on acidification with HCl.

$$Ar - OH + NaOH(aq) \longrightarrow Ar\text{-}O^{\ominus}Na^{\oplus}(aq) + H_2O(l)$$

$$Ar - O^{\ominus}Na^{\oplus}(aq) + HCl(aq) \longrightarrow Ar - OH\downarrow + NaCl(aq)$$

Do you know ?

Sodium bicarbonate, sodium hydroxide, sodium metal are increasingly strong bases. Weak and strong acids can be distinguished from each other qulitatively by testing their reactivity towards bases of different strengths. A weak acid does not react with a weak base, it requires a stronger base instead. Hence phenols react with NaOH but not with $NaHCO_3$. A strong acid shows high reactivity towards weak as well as strong base. For example : HCl is a strong acid. Its reacts with both $NaHCO_3$ and NaOH as shown below:

$$HCl(aq)+NaHCO_3(aq) \longrightarrow H_2O(l)+ NaCl(aq)+ CO_2\uparrow$$

$$HCl(aq)+NaOH(aq) \longrightarrow NaCl(aq)+H_2O(l)$$

- Alcohols show no acidic character in aqueous solution, thus, alcohols do not react with either aqueous $NaHCO_3$ or aqueous NaOH. Very weak acidic character of alcohol is revealed in the reaction with active metal. When alcohols are treated with very strong base like alkali metal Na or K they react to give sodium or potassium alkoxide with liberation of hydrogen gas.

$$2R - OH + 2Na \longrightarrow 2R\text{-}O^{\ominus}Na^{\oplus} + H_2\uparrow$$

Liberation of H_2 gas is used to detect the presence of alcoholic -OH group in a molecule.

iii. Characteristic test for phenols : Phenols reacts with neutral ferric chloride solution to give deep (purple/violet/green) colouration of ferric phenoxide.

$$3Ar - OH + \underset{\text{(neutral)}}{FeCl_3} \longrightarrow \underset{\text{(deep colour)}}{(Ar\text{ -}O)_3\text{—}Fe} + 3HCl$$

iv. Distinguishing test for alcohols (Lucas test) : Primary, secondary and tertiary alcohols can be distinguished from each other in the laboratory using Lucas reagent (conc. HCl and $ZnCl_2$). The reaction involved is :

$$R - OH \xrightarrow[ZnCl_2]{HCl} R - Cl$$

Alcohols are soluble in Lucas reagent but the product alkyl chloride is not. Hence, the clear solution becomes turbid when product starts forming. Tertiary alcohols reacts fast and the reagent turns turbid instantaneously. Secondary alcohols turn the reagent turbid slowly. Primary alcohols turn the reagent turbid only on heating.

b. Reactions due to breaking of O -H bond.

i. Acidic character of alcohols and phenols :

From the laboratory tests it is understood that in aqueous medium phenols show weak acidic character while alcohols are neutral. It is clear, therefore, that the reactivity of alcohols and phenols towards ionization of O-H bond in them is different. The reason behind this difference lies in the extent of stabilization of their respective conjugate bases by electronic effects as shown below.

- Ionization of alcohols is represented by the following equilibrium

$$\underset{\text{(alcohol)}}{R - OH} + H_2O \rightleftharpoons \underset{\text{(alkoxide)}}{R \rightarrow O^{\ominus}} + H_3O^{\oplus}$$

Electron donating inductive effect (+I effect) of alkyl group destabilizes the alkoxide ion (the conjugate base of alcohol). As a result alcohol does not ionize much in water, and behaves like neutral compound in aqueous medium.

- Ionization of phenol is represented by the equilibrium shown in Fig. 11.1.

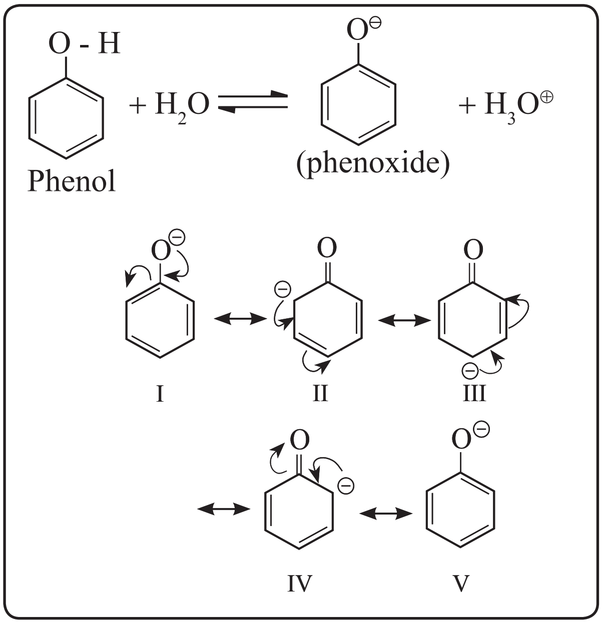


Fig. 11.1 Ionization of phenol and resonance stabilization phenoxide ion

Phenoxide ion, the conjugate base of phenol, is resonance stabilized by delocalization of the negative charge. Therefore phenol ionizes in aqueous medium to a moderate extent, and thereby shows a weak acidic character.

Problem 11.5 : Arrange the following compounds in decreasing order of acid strength and justify.

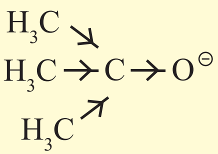
i. CH_3-CH_2-OH ii. $(CH_3)_3C$-OH

iii. C_6H_5-OH iv. p-NO_2-C_6H_4-OH

Solution : Compounds (iii) and (iv) are phenols and therefore are more acidic than the alcohols (i) and (ii). The acidic strenghts of compounds depend upon stabilization of the corresponding conjugate bases. Hence let us compare electronic effects in the conjugate bases of these compounds :

Alcohols :

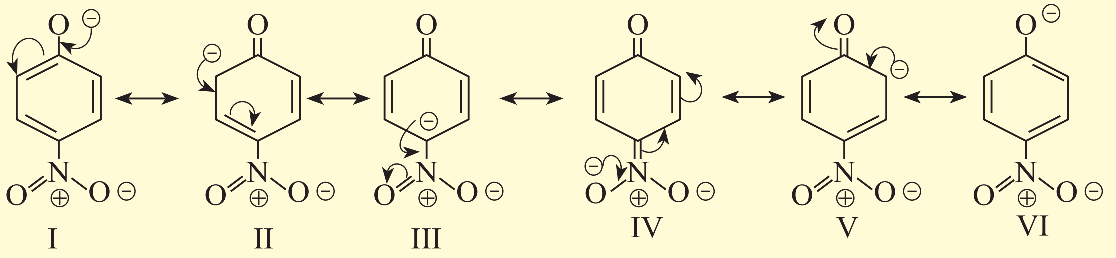
$CH_3 \rightarrow CH_2 \rightarrow O^{\ominus}$ (Conjugate base of (i)) and



$$(H_3C \rightarrow)_3 C \rightarrow O^{\ominus}$$

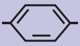
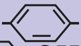
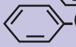
(Conjugate base of (ii))

The conjugate base of the alcohol (i) is destabilized by +I effect of one alkyl group, where as conjugate base of the alcohol (ii) is destabilized by +I effect of three alkyl groups. Hence (ii) is weaker acid than (i)



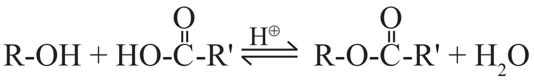
Phenols : The conjugate base of p-nitrophenol (iv) is better resonance stabilized due to six resonance structures compared to the five resonance structures of conjugate base of phenol (iii) (see Fig. 11.1). The resonance structure VI has -ve charge on only electronegative oxygens. Hence the phenol (iv) is stronger acid than (iii). Thus the decreasing order of acid strength is (iv) > (iii) > (i) > (ii)

Use your brain power

What are the electronic effects exerted by $-OCH_3$ and -Cl ? predict the acid strength of H_3C-O--OH and Cl --OH relative to parent phenol -OH .

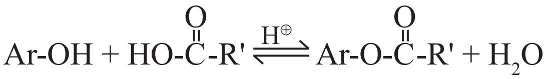
ii. Esterification : Alcohols and phenols form esters by reaction with carboxylic acid, acid halides and acid anhydrides. The reaction between alcohol or phenol with a carboxylic acid to form an ester is called **esterification**.

Esterification of alcohol or phenol is carried out in the presence of concentrated sulphuric acid. The reaction is reversible and can be shifted in the forward direction by removing water as soon as it is formed.



$$\text{R-OH} + \text{HO-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-R'} \xrightleftharpoons{H^{\oplus}} \text{R-O-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-R'} + H_2O$$

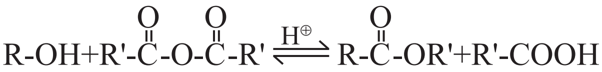
(alcohol) (acid) (ester)



$$\text{Ar-OH} + \text{HO-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-R'} \xrightleftharpoons{H^{\oplus}} \text{Ar-O-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-R'} + H_2O$$

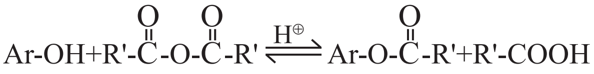
(phenol) (acid) (ester)

Alcohols and phenols react with acid anhydrides in presence of acid catalyst to form ester.



$$\text{R-OH+R'-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-O-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-R'} \xrightleftharpoons{H^{\oplus}} \text{R-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-OR'+R'-COOH}$$

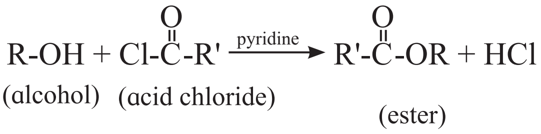
(alcohol) (anhydride) (ester) (acid)



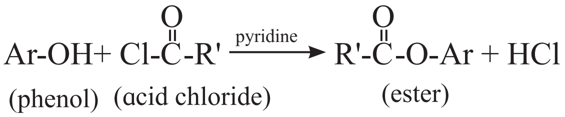
$$\text{Ar-OH+R'-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-O-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-R'} \xrightleftharpoons{H^{\oplus}} \text{Ar-O-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{-R'+R'-COOH}$$

(phenol) (anhydride) (ester) (acid)

The reaction of alcohol and phenols with acid chloride is carried out in the presence of pyridine (base), which neutralizes HCl.

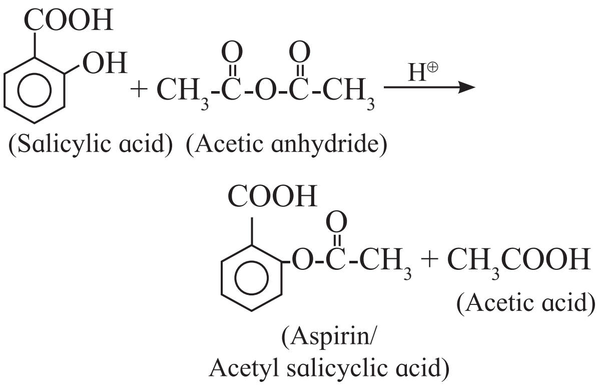


$$\text{R-OH} + \text{Cl-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'} \xrightarrow{\text{pyridine}} \text{R'-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OR} + \text{HCl}$$



$$\text{Ar-OH} + \text{Cl-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'} \xrightarrow{\text{pyridine}} \text{R'-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O-Ar} + \text{HCl}$$

Acetyl derivatives : The CH_3-CO- group is called **acetyl group**. The acetate esters of alcohols or phenols are also called 'acetyl derivatives' of alcohols or phenols repectively. The number of alcoholic or phenolic -OH groups in the given compound can be deduced from the number of acetyl groups introduced in it as a result of acetylation. Aspirin, a well known generic medicine, is an acetyl derivative of salicylic acid formed by its acetylation using acetic anhydride.



c. Reaction due to breaking of C-O bond in alcohols :

i. Reaction with hydrogen halides : Alcohols reacts with hydrogen halides to form alkylhalides (refer to Chapter 10 section 10.3.1) In general, tertiary alcohols react rapidly with hydrogen halides; secondary alcohols react somewhat slower; and primary alcohols, even more slowly. The order of reactivity of hydrogen halides is

$$\text{HI} > \text{HBr} > \text{HCl}$$

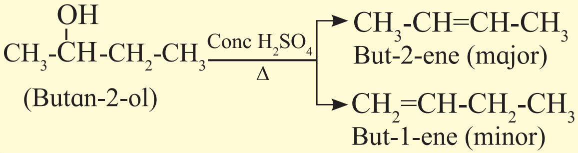
HCl reacts only in the presence of anhydrous $ZnCl_2$. No catalyst is required in the case of HBr and HI.

ii. Reaction with phosphorous halide : Alcohols react with phosphorous pentahalide (PX_5) and phosphorous trihalide (PX_3) to form alkyl halides. (refer to Chapter 10 section 10.3.1).

iii. Dehydration of alcohols to alkenes : Alcohol when treated with concerntrated sulphuric acid or phosphoric acid or alumina undergoes dehydration to form alkene and water. (refer to Std. XI Chemistry Textbook section 15.2) The reaction gives more substituted alkene as the major product, in accordance with **Saytzeff rule**.

Problem 11.6 : Write the reaction showing major and minor products formed on heating butan-2-ol with concentrated sulfuric acid.

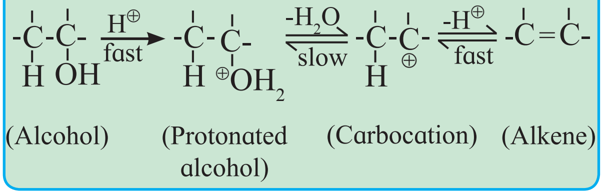
Solution : In the reaction described butan-2-ol undergoes dehydration to give but-2-ene (major) and but-1-ene (minor) in accordance with Saytzeff rule.



Do you know ?

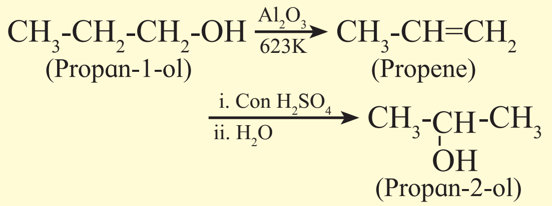
According to the common accepted mechanism dehydration involves following three steps.

1. Formation of protonated alcohols R-$\overset{\oplus}{O}H_2$
2. Its slow dissociation into carbocation
3. Fast removal of hydrogen ion to form alkene.



Problem 11.7 : Write and explain reactions to convert propan-1-ol into propan-2-ol ?

Solution : The dehydration of propane-1-ol to propene is the first step. Markownikoff hydration of propene is the second step to get the product propan-2-ol. This is brought about by reaction with concerntrated H_2SO_4 followed by hydrolysis.



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow[623K]{Al_2O_3} CH_3\text{-}CH{=}CH_2$$

(Propan-1-ol) (Propene)

$$\xrightarrow[\text{ii. } H_2O]{\text{i. Con } H_2SO_4} CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_3$$

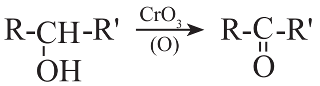
(Propan-2-ol)

iv. Oxidation of alcohols :

Can you recall ?

What are the various definitions of oxidation ?

On reaction with oxidising agent primary and secondary alcohols undergo dehydrogenation to form carbonyl compounds, namely aldehydes and ketones respectively Seondary alcohol on oxidation with chromic anhydride (CrO_3) forms ketone.



$$R\text{-}\underset{OH}{\underset{|}{CH}}\text{-}R' \xrightarrow[(O)]{CrO_3} R\text{-}\underset{O}{\underset{\|}{C}}\text{-}R'$$

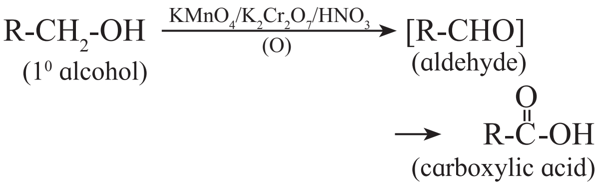
(2^0alcohol) (ketone)

Primary alcohol on oxidation with CrO_3 forms aldehyde. However, a better reagent to bring about this oxidation is PCC (pyridinium chlorochromate).

$$R\text{-}CH_2\text{-}OH \xrightarrow[(O)]{PCC} R\text{-}CHO$$

(1^0 alcohol) (aldehyde)

When common oxidizing agents like nitric acid, potassium permanganate or potassium dichromate are used to oxidise primary alcohol, the oxidation does not stop at aldehyde stage, but the aldehyde formed is further oxidized to carboxylic acid containing the same number of carbon atoms.



$$R\text{-}CH_2\text{-}OH \xrightarrow[(O)]{KMnO_4/K_2Cr_2O_7/HNO_3} [R\text{-}CHO] \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

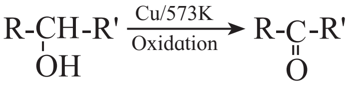
(1^0 alcohol) (aldehyde) (carboxylic acid)

Tertiary alcohols are difficult to oxidise. On oxidation with strong oxidising agents at high temperature tertiary alcohol undergoes breaking of C-C bonds and gives a mixture of carboxylic acids containing less number of carbon atoms than the starting 3° alcohol.

Heating with Cu : When vapours of various types of alcohols are passed over hot copper the following reactions are observed.

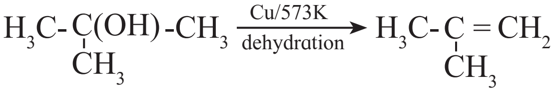
$$R\text{-}CH_2\text{-}OH \xrightarrow[\text{Oxidation}]{Cu/573K} R\text{-}CHO$$

(1^0 alcohol) (aldehyde)



$$R\text{-}\underset{OH}{\underset{|}{CH}}\text{-}R' \xrightarrow[\text{Oxidation}]{Cu/573K} R\text{-}\underset{O}{\underset{\|}{C}}\text{-}R'$$

(2^0 alcohol) (ketone)



$$H_3C\text{-}\underset{CH_3}{\underset{|}{C}}(OH)\text{-}CH_3 \xrightarrow[\text{dehydration}]{Cu/573K} H_3C\text{-}\underset{CH_3}{\underset{|}{C}}=CH_2$$

(3^0 alcohol) (alkene)

Problem 11.8 : An organic compound gives hydrogen on reaction with sodium metal. It forms an aldehyde having molecular formula C_2H_4O on oxidation with pyridinium chlorochromate Name the compounds and give equations of these reactions.

Solution : The given molecular formula C_2H_4O of aldehyde is written as CH_3 -CHO. Hence the formula of alcohol from which this is obtained by oxidation must be CH_3-CH_2-OH. The two reactions can, therefore, be represented as follows.

$$2CH_3\text{-}CH_2\text{-}OH \xrightarrow{2Na} 2CH_3\text{-}CH_2O^{\ominus}Na^{\oplus} + H_2\uparrow$$

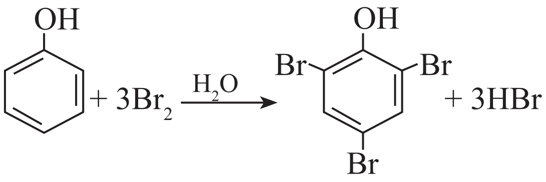
(Ethyl alcohol) (Sodium ethoxide)

$$CH_3\text{-}CH_2\text{-}OH \xrightarrow[PCC]{[O]} CH_3\text{-}CHO + H_2O$$

(Ethyl alcohol) (Acetaldehyde)

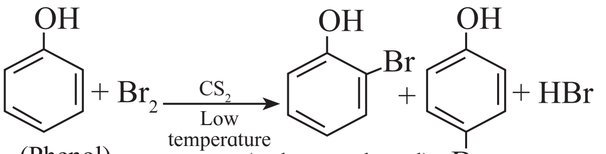
d. Reactions of phenols : Phenol undergoes electrophilic substitution reactions more readily as compared to benzene. The -OH group in phenol is ring activating and an ortho-/para-directing group.

i. Halogentaion of phenol: Phenol reacts with aqueous solution of bromine to give 2,4,6 -tribromophenol (chlorine reacts in the same way.)



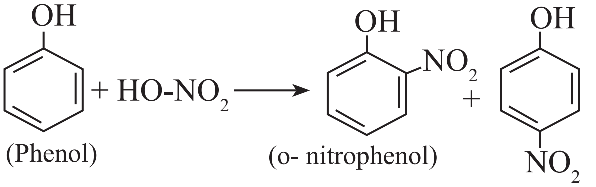
(Phenol) (2,4,6-tribromophenol)

If the reaction is carried out in a solvent of lower polarity than water, such as $CHCl_3$, CCl_4 or CS_2, a mixture of ortho- and para-bromophenol is formed.



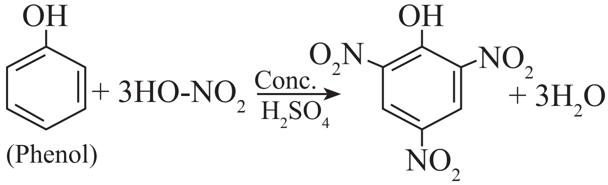
(Phenol) (o- bromophenol) (p- bromophenol)
Major product

ii. Nitration of phenol : Phenol reacts with dilute nitric acid at low temperature to give mixture of ortho- and para-nitrophenol.



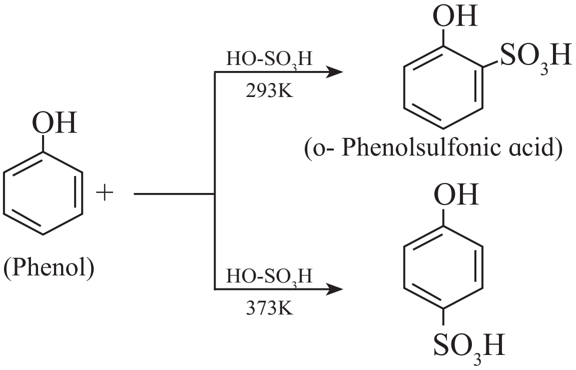
(Phenol) (o- nitrophenol) (p- nitrophenol)

Phenol reacts with concerntrated nitric acid to form 2, 4, 6-trinitrophenol (picric acid)



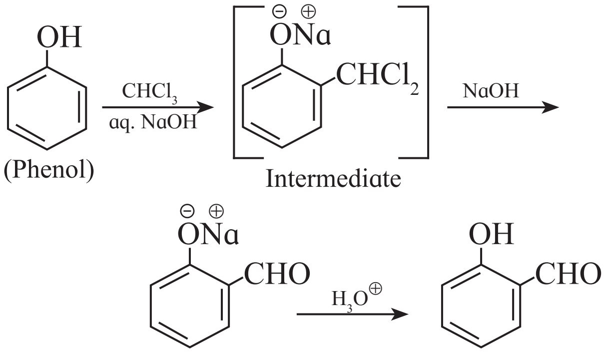
(Phenol) (picric acid)

iii. Sulfonation of phenol : Phenol reacts with concerntrated sulfuric acid at room temperature to give o-phenolsulfonic acid and at 373K, p-phenol sulfonic acid



(Phenol) (o- Phenolsulfonic acid) (p- Phenolsulfonic acid)

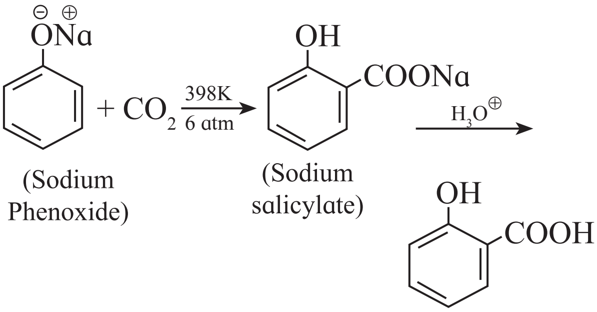
iv. Reimer-Tiemann Reaction : When phenol is treated with chloroform in aqueous sodium hydroxide solution followed by hydrolysis with acid, salicylaldehyde is formed. This reaction is known as Reimer-Tiemann reaction.



(Phenol) Intermediate (Salicyaldehyde)

If carbon tetrachloride is used in place of chloroform, salcylic acid is formed.

v. Kolbe reaction : The treatment of sodium phenoxide with carbondioxide at 398 K under pressure of 6 atm followed by acid- hydrolysis, salicylic acid (o-hydroxybenzoic acid) is formed. This reaction is known as Kolbe's reaction

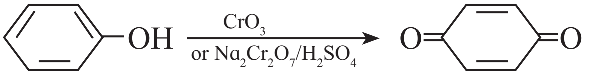


(Sodium Phenoxide) (Sodium salicylate) (Salicylic acid)

Do you know ?

Sodium phenoxide is more reactive than phenol towards electrophilic substitution. Hence it is able to react with a weak electrophile like CO_2 at high temperature and pressure in Kolbe reaction.

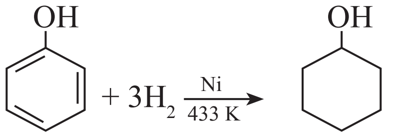
vi. Oxidation of phenol : Phenol on oxidation with chromic anhydride or sodium dichromate in presence of H_2SO_4 gives p-benzoquinone.



(Phenol) (p-Benzoquinone)

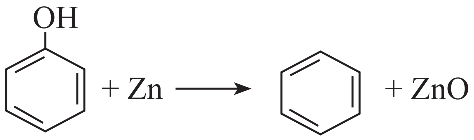
Phenol oxidizes slowly giving a dark coloured mixture in presence of air.

vii. Catalytic hydrogenation of phenol: Phenol on catalytic hydrogenation gives cyclohexanol. In this reaction a mixture of vapours of phenol and hydrogen is passed over nickel catalyst at 433 K.



(Phenol) (Cyclohexanol)

viii. Reduction of phenol : Phenol is reduced to benezene on heating with zinc dust.



(Phenol) (Benzene)

11.5 Ethers

11.5.1 Preaparation of ethers

a. Dehydration of alcohols : When alcohol is heated with dehydrating agent like concentrated H_2SO_4 or H_3PO_4 two products, either an ether or an alkene, can form depending upon the temperature. For example : dehydration of ethanol by H_2SO_4 gives ethoxyethane at 413 K, while ethene is formed at 443 K.

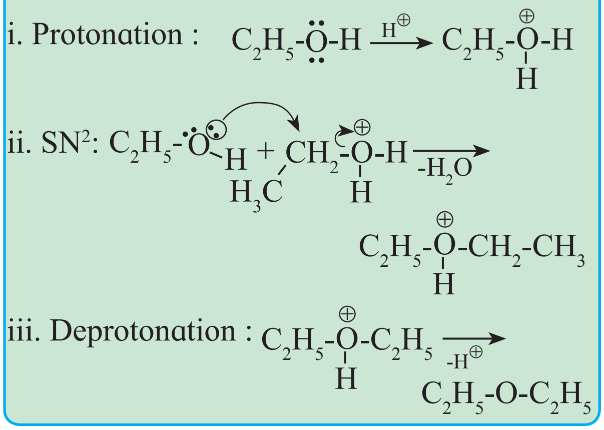
$$\underset{\text{(ethanol)}}{2C_2H_5OH} \xrightarrow[-H_2O]{H_2SO_4/413K} \underset{\text{(Ethoxyethane)}}{C_2H_5\text{-}O\text{-}C_2H_5}$$

$$\underset{\text{(ethanol)}}{C_2H_5OH} \xrightarrow[-H_2O]{H_2SO_4/443K} \underset{\text{(ethene)}}{CH_2{=}\,CH_2}$$

Symmetrical ethers can be obtained from primary alcohols by this method. Use of higher temperature or 2°/3° alcohols gives alkene as the major product.

Do you know ?

Dehydration of alcohols to form ether is a SN^2 reaction. Protonated alcohol species undergoes a backside attack by second molecule of alcohol in a slow step. Subsequent fast deprotonation results in formation of ether.



i. Protonation : $C_2H_5\text{-}\underset{\cdot\cdot}{\ddot{O}}\text{-}H \xrightarrow{H^{\oplus}} C_2H_5\text{-}\overset{\oplus}{\underset{H}{O}}\text{-}H$

ii. SN^2: $C_2H_5\text{-}\ddot{O}\text{-}H + \underset{H_3C}{CH_2}\text{-}\overset{\oplus}{\underset{H}{O}}\text{-}H \xrightarrow[-H_2O]{} C_2H_5\text{-}\overset{\oplus}{\underset{H}{O}}\text{-}CH_2\text{-}CH_3$

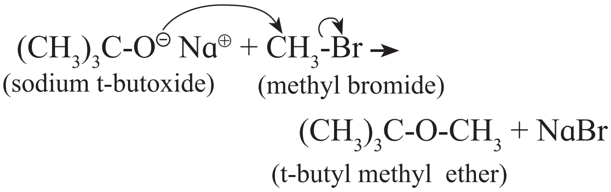
iii. Deprotonation : $C_2H_5\text{-}\overset{\oplus}{\underset{H}{O}}\text{-}C_2H_5 \xrightarrow[-H^{\oplus}]{} C_2H_5\text{-}O\text{-}C_2H_5$

b. Williamson Synthesis : Simple as well as mixed ethers can be prepared in laboratory by Williamson Synthesis. In this method alkyl halide is treated with sodium alkoxide or sodium phenoxide to give dialkyl ethers or alkyl aryl ethers.

$R\text{-}X + Na^{\oplus}\ O^{\ominus}\text{-}R \longrightarrow R\text{-}O\text{-}R + NaX$

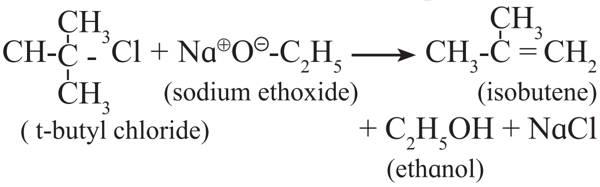
$R\text{-}X + Na^{\oplus}\ O^{\ominus}\text{-}Ar \longrightarrow R\text{-}O\text{-}Ar + NaX$

This reaction follows S_N2 mechanism. Ether is formed as a result of backside attack by alkoxide/ phenoxide ion (a nucleophile) on alkyl halide. The alkyl halide used in this reaction must be primary. For example : t-butyl methyl ether can be synthesised by reaction of methyl bromide with sodium t-butoxide.



$$\underset{\text{(sodium t-butoxide)}}{(CH_3)_3C\text{-}O^{\ominus}\ Na^{\oplus}} + \underset{\text{(methyl bromide)}}{CH_3\text{-}Br} \rightarrow \underset{\text{(t-butyl methyl ether)}}{(CH_3)_3C\text{-}O\text{-}CH_3} + NaBr$$

If secondary or tertiary alkyl halides are used, the reaction leads mainly to alkene formation (elimination reaction). For example :



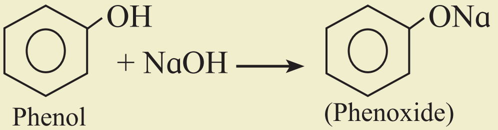
$$CH-\underset{CH_3}{\overset{CH_3}{C}}-Cl + Na^{\oplus}O^{\ominus}-C_2H_5 \longrightarrow CH_3-\overset{CH_3}{C}=CH_2 + C_2H_5OH + NaCl$$

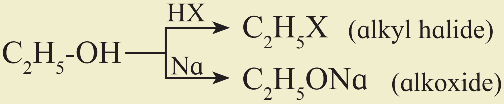
(t-butyl chloride) (sodium ethoxide) (isobutene) (ethanol)

Aryl halides do not give Williamson's synthesis.

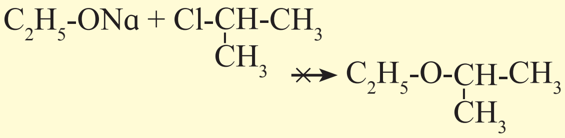
Can you think ?

Williamson synthesis is effectively a method of preparation of ethers from two hydroxy compounds. The two substrates of Williamson synthesis, namely the nucleophile and alkyl hadlides are obtained from hydroxy compounds as shown below.





Problem 11.9 : Ethyl isopropyl ether does not form on reaction of sodium ethoxide and isopropyl chloride.

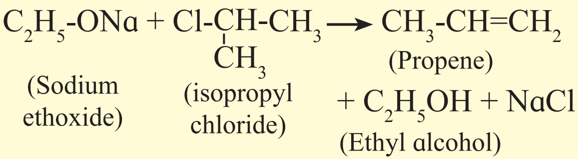


$$C_2H_5\text{-}ONa + Cl\text{-}\underset{CH_3}{CH}\text{-}CH_3 \not\longrightarrow C_2H_5\text{-}O\text{-}\underset{CH_3}{CH}\text{-}CH_3$$

i. What would be the main product of this reaction ?

ii. Write another reaction suitable for the preparation of ethyl isopropyl ether.

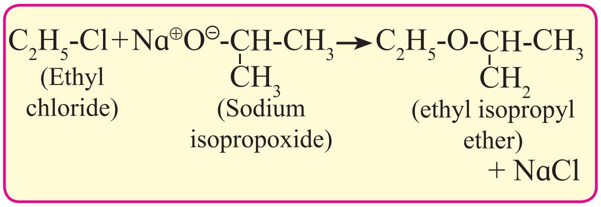
Solution : i. Isopropyl chloride is a secondary chloride. On treating with sodium ethoxide it gives elimination reaction to form propene as the main product .



$$C_2H_5\text{-}ONa + Cl\text{-}\underset{CH_3}{CH}\text{-}CH_3 \longrightarrow CH_3\text{-}CH{=}CH_2 + C_2H_5OH + NaCl$$

(Sodium ethoxide) (isopropyl chloride) (Propene) (Ethyl alcohol)

ii. Ethyl isopropyl ether can be prepared as follows using ethyl chloride (1^{0}chloride) as as substrate.



$$C_2H_5\text{-}Cl + Na^{\oplus}O^{\ominus}\text{-}\underset{CH_3}{CH}\text{-}CH_3 \longrightarrow C_2H_5\text{-}O\text{-}\underset{CH_2}{CH}\text{-}CH_3 + NaCl$$

(Ethyl chloride) (Sodium isopropoxide) (ethyl isopropyl ether)

11.5.2 Physical properties :

a. Physical states and boiling points

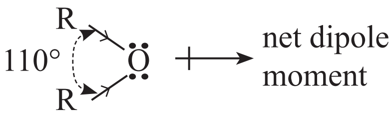
i. Dimethyl ether and ethyl methyl ether are gases. Other ethers are colourless liquids with pleasant odour.

ii. Lower ethers are highly volatile and highly inflammable substances.

iii. Boiling points of ethers show gradual increase with the increase in molecular mass.

Ether	B.P. / K
CH_3-O-CH_3	248
C_2H_5-O-CH_3	284
C_2H_5-O-C_2H_5	308

b. Polarity and solubility : Since $-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}-$ bond angle is 110° and not 180°, the bond dipole moments of the two C-O bonds donot cancel each other; therefore ethers posses a small net dipole moment (For example, dipole moment of diethyl ether is 1.18 D)

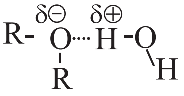


Weak polarity of ethers does not affect their boiling points, which are about the same as those of alkanes having comparable molecular mass. (see table 11.6).

Table 11.6 Comparative boiling points of alkane, ether and alcohol

Name	n-Heptane	Methyl n-pentyl ether	n-Hexyl alcohol
Molecular mass	100	102	102
Boiling point / K	371	373	430

The intermolecular hydrogen bonding that holds alcohol molecules together strongly, is not present in ethers and alkanes. However, solubility/miscibility of ethers in water is similar to that of alcohols of comparable molecular mass. This is because ethers can form hydrogen bonds with water through the ethereal oxygen.

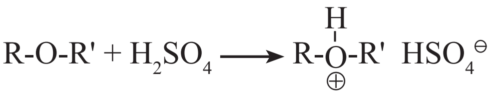


$$R\text{-}\underset{\displaystyle R}{\overset{\delta\ominus}{O}}\cdots\overset{\delta\oplus}{H}\text{-}O\text{-}H$$

For example diethyl ether and n-butyl alcohol have respective miscibilities of 7.5 and 9g per 100 g of water.

11.5.3 Chemical properties of ethers :

a. Laboratory test for ethers : Ethers are neutral compounds in aqueous medium. Ethers do not react with bases, cold dilute acids, reducing agents, oxidizing agents and active metals. However, ethers dissolve in cold concerntrated H_2SO_4 due to formation of oxonium salts.

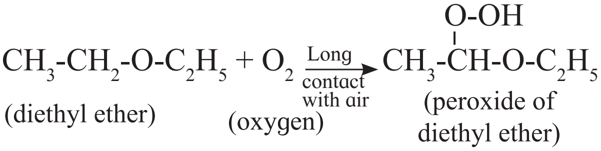


$$R\text{-}O\text{-}R' + H_2SO_4 \longrightarrow R\text{-}\underset{\oplus}{\overset{H}{O}}\text{-}R'\ \ HSO_4^{\ominus}$$

This property distinguishes ethers from hydrocarbons.

b. Reaction involving alkyl group of ether :

i. Formation of peroxide : Ethers combine with atmospheric oxygen to form peroxide.



$$CH_3\text{-}CH_2\text{-}O\text{-}C_2H_5 + O_2 \xrightarrow[\text{with air}]{\text{Long contact}} CH_3\text{-}\overset{O\text{-}OH}{CH}\text{-}O\text{-}C_2H_5$$

(diethyl ether) (oxygen) (peroxide of diethyl ether)

All ethers which have been exposed to the atmosphere contain peroxide. This is very undesirable reaction. Peroxides are hazardous because they decompose violently at high temperature.

c. Reaction involving C-O bond

i. Reaction with hot dilute sulphuric acid (Hydrolysis) : Ethers when heated with dilute sulfuric acid undergo hydrolysis to give alcohols/phenols.

$$R\text{-}O\text{-}R + H\text{-}O\text{-}H \xrightarrow[\Delta]{H_3O^{\oplus}} 2R\text{-}OH$$

$$R\text{-}O\text{-}R' + H\text{-}O\text{-}H \xrightarrow[\Delta]{H^{\oplus}} R\text{-}OH + R'\text{-}OH$$

$$Ar\text{-}O\text{-}R + H\text{-}O\text{-}H \xrightarrow[\Delta]{H^{\oplus}} Ar\text{-}OH + R\text{-}OH$$

ii. Reaction with PCl_5 : Ethers react with PCl_5 to give alkyl chlorides

$$R\text{-}O\text{-}R' + PCl_5 \xrightarrow{\Delta} R\text{-}Cl + R'\text{-}Cl + POCl_3$$

iii. Reaction with hot concentrated acid : Alkyl ethers react with hot and concentrated HI and HBr to give an alcohol and an alkyl halide.

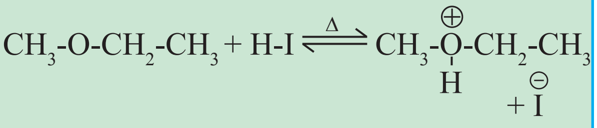
$$R\text{-}O\text{-}R + HX \longrightarrow R\text{-}X + R\text{-}OH \xrightarrow{HX} R\text{-}X$$

$$R\text{-}OH \xrightarrow{HX} R\text{-}X + H_2O$$

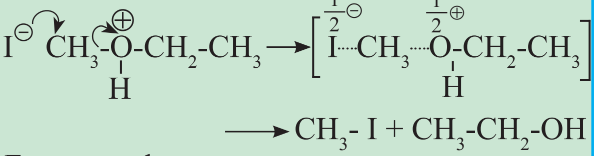
The order of reactivity of HX is HI>HBr>HCl

Do you know ?

Mechanism of first stage : Reaction of ether with hot concentrated HI involves formation of oxonium ion by protonation in the first step and subsequent nucleophilic substitution reaction brought about by the powerful nucleophile $I^{\ominus}$. The least substituted carbon in oxoinium ion is attacked by $I^{\ominus}$ following SN^2 mechanism.



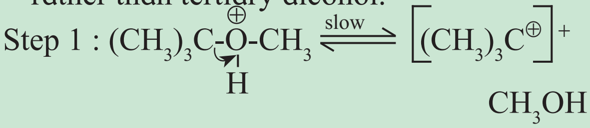
$$CH_3\text{-}O\text{-}CH_2\text{-}CH_3 + H\text{-}I \overset{\Delta}{\rightleftharpoons} CH_3\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}CH_2\text{-}CH_3 + I^{\ominus}$$



$$I^{\ominus}\ CH_3\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}CH_2\text{-}CH_3 \longrightarrow \left[\overset{\frac{1}{2}\ominus}{I}\cdots CH_3\cdots\underset{H}{\overset{\frac{1}{2}\oplus}{O}}\text{-}CH_2\text{-}CH_3\right] \longrightarrow CH_3\text{-}I + CH_3\text{-}CH_2\text{-}OH$$

For example :

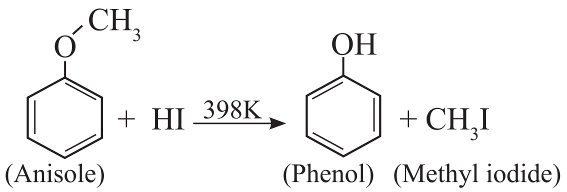
- Use of excess HI converts the alcohol into alkyl iodide.
- In case of ether having one tertiary alkyl group the reaction with hot HI follows SN^1 mechanism, and tertiary iodide is formed rather than tertiary alcohol.



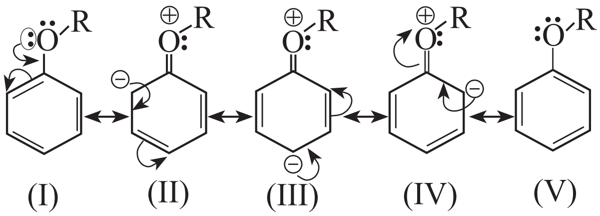
$$\text{Step 1 : } (CH_3)_3C\text{-}\underset{H}{\overset{\oplus}{O}}\text{-}CH_3 \overset{\text{slow}}{\rightleftharpoons} \left[(CH_3)_3C^{\oplus}\right]^{+} \ CH_3OH$$

$$\text{Step 2 : } (CH_3)_3C^{\oplus} + I^{\ominus} \xrightarrow[\text{fast}]{} (CH_3)_3C\text{-}I$$

Aryl alkyl ethers have stronger and shorter bond between oxygen and the aromatic ring. Hence an aryl alkyl ether undergoes cleavage of oxygen - alkyl bond and yields a phenol and an alkyl halide on reaction with HI.

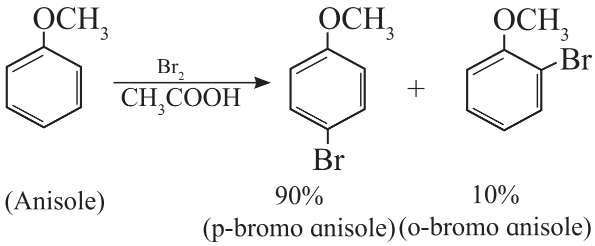


d. Electrophilic substitution in aromatic ethers : The alkoxy group in aromatic ether is a ring activating and ortho-, para-directing group toward electrophilic aromatic substitution. This is evident from the resonance structures:

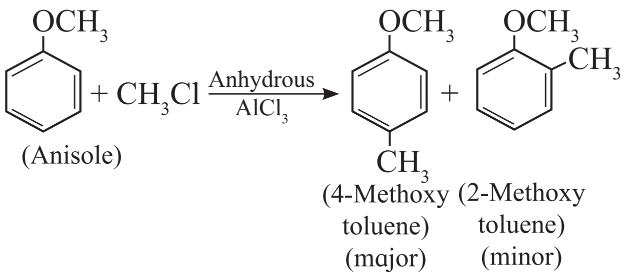


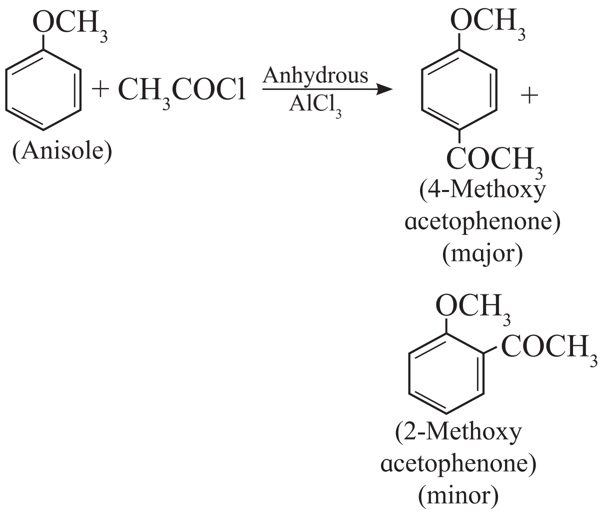
+R Effect of $-\ddot{O}R$ group results in increased electron density at the para- and two ortho-positions (see resonance structures II, III and IV).

i. Halogenation : Anisole undergoes bromination with bromine in acetic acid even in the absence of ferric bromide catalyst. It is due to activation of benzene ring by the methoxy group.

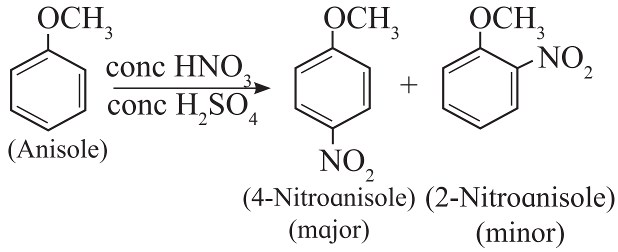


ii. Friedel Crafts reaction : Anisole reacts with alkyl halide and acyl chloride in presence of anhydrous $AlCl_3$ (Lewis acid) as catalyst.





iii. Nitration : Anisole reacts with concentrated nitric acid in presence of concentrated sulfuric acid (Nitrating mixture) to give a mixture of o-nitro anisole and p-nitro anisole.



11.6 Uses of alcohols, phenols and ethers

Alcohols :

1. Methyl alcohol is used as a solvent for paints and varnishes.
2. Ethyl alcohol is used as antifreeze agent in automobile radiators. It is also used as solvent.

Ethers :

1. Earlier diethyl ether was used as a general anaesthetic in surgical operations.
2. Diethyl ether is used as a solvent for Grignard reagents, fats, waxes, oil, etc.

Phenols :

1. Phenol is used in preparation of phenol formaldehyde resin For example : bakelite.
2. Phenols are used as antiseptic in common products like air freshners, deodarants, mouthwash, calamine lotions, floor cleaners, etc.

Exercises

1. Choose the correct option.

i. Which of the following represents the increasing order of boiling points of (1), (2) and (3)?

(1) CH_3-CH_2-CH_2-CH_2-OH

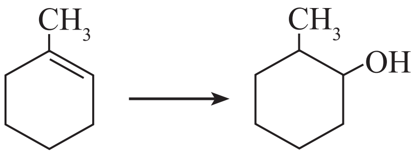
(2) $(CH_3)_2CHOCH_3$

(3) $(CH_3)_3COH$

A. (1) < (2) < (3) B. (2) < (1) < (3)

C. (3) < (2) < (1) D. (2) < (3) < (1)

ii. Which is the best reagent for carrying out following conversion ?



A. $LiAlH_4$ B. Conc. H_2SO_4, H_2O

C. H_2/Pd D. B_2H_6, H_2O_2-NaOH

iii. Which of the following substrate will give ionic organic product on reaction ?

A. CH_3-CH_2-OH + Na

B. CH_3-CH_2-OH + $SOCl_2$

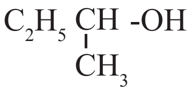
C. CH_3-CH_2-OH + PCl_5

D. CH_3-CH_2-OH + H_2SO_4

iv. Which is the most resistant alcohol towards oxidation reaction among the follwoing ?

A. CH_3-CH_2-OH B. $(CH_3)_2$CH-OH

C. $(CH_3)_3$C-OH D.


$C_2H_5\underset{CH_3}{\underset{|}{CH}}$-OH

v. Resorcinol on distillation with zinc dust gives

A. Cyclohexane B. Benzene

C. Toluene D. Benzene-1, 3-diol

vi. Anisole on heating with concerntrated HI gives

A. Iodobenzene

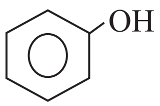
B. Phenol + Methanol

C. Phenol + Iodomethane

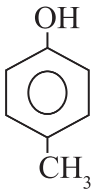
D. Iodobenzene + methanol

vii. Which of the following is the least acidic compound ?

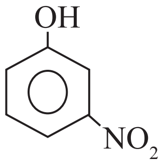
A.



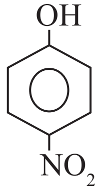
B.



C.



D.

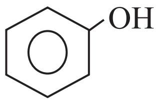


viii. The compound incapable of hydrogen bonding with water is ......

A. CH_3-CH_2-O-CH_3

B. CH_3-CH_2-CH_2-CH_3

C.



D. CH_3-CH_2-CH_2-OH

ix. Ethers are kept in air tight brown bottles because

A. Ethers absorb moisture

B. Ethers evaporate readily

C. Ethers oxidise to explosive peroxide

D. Ethers are inert

x. Ethers reacts with cold and concentrated H_2SO_4 to form

A. oxonium salt   B. alkene

C. alkoxides   D. alcohols

2. Answer in one sentence/ word.

i. Hydroboration-oxidation of propene gives.....

ii. Write the IUPAC name of alcohol having molecular formula $C_4H_{10}O$ which is resistant towards oxidation.

iii. Write structure of optically active alcohol having molecular formula $C_4H_{10}O$

iv. Write name of the electrophile used in Kolbe's Reaction.

3. Answer in brief.

i. Explain why phenol is more acidic than ethyl alcohol.

ii. Explain why p-nitrophenol is a stronger acid than phenol.

iii. Write two points of difference between properties of phenol and ethyl alcohol.

iv. Give the reagents and conditions necessary to prepare phenol from

a. Chlorobenzene

b. Benzene sulfonic acid.

v. Give the equations of the reactions for the preparation of phenol from isopropyl benezene.

vi. Give a simple chemcial test to distinguish between ethanol and ethyl bromide.

4. An ether (A), $C_5H_{12}O$, when heated with excess of hot HI produce two alkyl halides which on hydrolysis form compound (B)and (C), oxidation of (B) gave and acid (D), whereas oxidation of (C) gave a ketone (E). Deduce the structural formula of (A), (B), (C), (D) and (E).

5. Write structural formulae for

a. 3-Methoxyhexane

b. Methyl vinyl ether

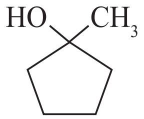
c. 1-Ethylcyclohexanol

d. Pentane-1,4-diol

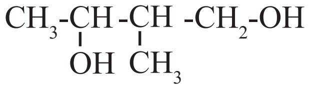
e. Cyclohex-2-en-1-ol

6. Write IUPAC names of the following

i.

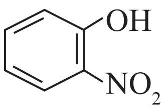


ii.

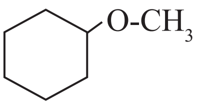


$CH_3\text{-}\underset{OH}{CH}\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}OH$

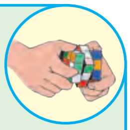
iii.



iv.



Activity :



- **Collect information about production of ethanol as byproduct in sugar industry and its importance in fuel economy.**
- **Collect information about phenols used as antiseptics and polyphenols having antioxidant activity.**

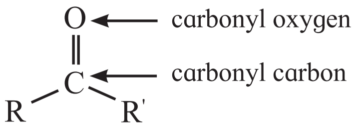
12. ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Can you recall ?

- Draw the structures of the following compounds and classify them on the basis of C-O single bond and C = O double bond present in them, Ethyl alcohol, acetaldehyde, o-nitrophenol, Diethyl ether, isopropyl alcohol, acetone.
- What are carbonyl compounds?

12.1 Introduction :

In the previous chapter, you learnt about the organic compounds which contain carbon –oxygen single bond. In this chapter, we are going to study the organic compounds containing carbon - oxygen double bond (>C=O) called **carbonyl group**, which is one of the most important functional group in organic chemistry.



Both aldehydes and ketones contain a carbon –oxygen double bond $(\underset{\overset{\|}{O}}{-C-})$ as their functional group. Therefore they are called carbonyl compounds. In aldehydes , carbonyl carbon is bonded to at least one hydrogen apart from an alkyl or aryl group. The functional group of aldehydes, therefore, is - CHO which is called **formyl group** or **aldehydic carbonyl group**. On the other hand in ketones, carbonyl carbon is bonded to two alkyl or aryl groups either identical (R = R) or different (R ≠ R'). It is called **ketonic carbonyl group**. The functional group of carboxylic acids is -COOH called **carboxyl group**. Due to the -OH group bonded to (>C=O) group, carboxylic acids are distinct from aldehydes and ketones.

12.2 Classification of aldehydes, ketones and carboxylic acids :

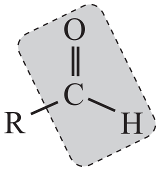
Aldehydes, ketones and carboxylic acids are classified as per the nature of carbon skeleton bonded to (>C=O).

12.2.1 Classification of aldehydes :

(Aldehydes are classified as aliphatic and aromatic aldehydes)

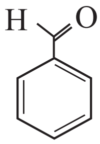
a. Aliphatic aldehydes : The compounds in which the –CHO group (formyl group) is attached directly to sp^3 hybridized carbon atom that is saturated carbon atom are called aliphatic aldehydes. (Exception : Formaldehyde, H-CHO is also classified as aliphatic aldehyde though –CHO group is not attached to any carbon). For example :

CH_3 - CHO	CH_3 - CH_2 - CHO
(Acetaldehyde)	(Propionaldehyde)

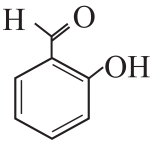


General formula
(R= H or alkyl group)

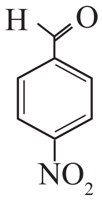
b. Aromatic aldehydes : The compounds in which –CHO group is attached directly to an aromatic ring are called aromatic aldehydes. For example :



(Benzaldehyde)



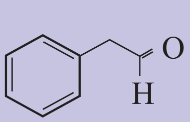
(Salicylaldehyde)

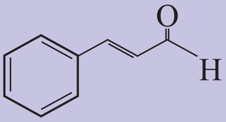


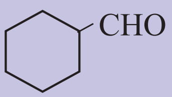
(p-Nitrobenzaldehyde)

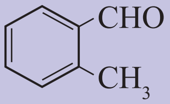
Use your brain power

Classify the following as aliphatic and aromatic aldehydes.





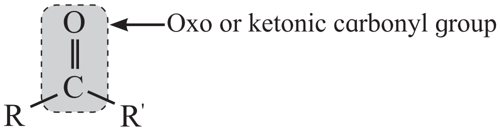




12.2.2 Classification of ketones :

Ketones are classified as aliphatic and aromatic ketones:

a. Aliphatic ketones : The compounds in which >C=O group is attached to two alkyl groups are called aliphatic ketones.



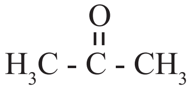
Oxo or ketonic carbonyl group

General formula

(Where R , R' = alkyl group, identical or different)

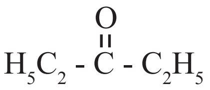
On the basis of types of alkyl groups bonded to carbonyl carbon, aliphatic ketones are further classified as simple and mixed ketones.

i. Simple or symmetrical ketones : The ketones in which both the alkyl groups bonded to carbonyl carbon are identical, are called simple ketones or symmetrical ketones. For example :



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

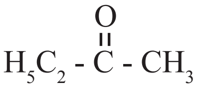
(Dimethyl ketone) (Acetone)



$H_5C_2-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5$

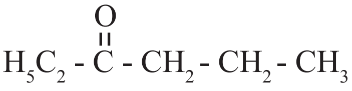
(Diethyl ketone)

ii. Mixed or unsymmetrical ketones : The ketones in which two alkyl groups bonded to carbonyl carbon are different, are called mixed ketones or unsymmetrical ketones. For example :



$H_5C_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

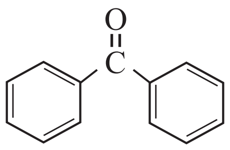
(Ethyl methyl ketone)



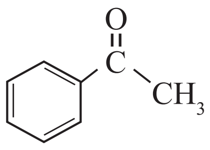
$H_5C_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_3$

(Ethyl n-propyl ketone)

b. Aromatic ketones : The compounds in which a >C=O group is attached to either two aryl groups or one aryl and one alkyl group are called aromatic ketones. For example :



Benzophenone
(Diphenyl ketone)



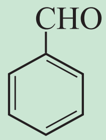
Acetophenone
(Methyl phenyl ketone)

Use your brain power

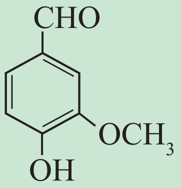
- Classify the followings as simple and mixed ketones.
- Benzophenone, acetone, butanone, acetophenone.

Do you know ?

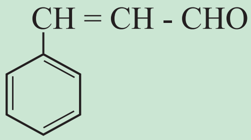
- Aldehydes and ketones are responsible for many flavours and odours that you will readily recognize :



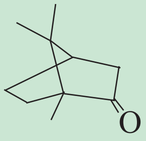
Benzaldehyde
(Bitter almond flavour)



Vanillin
(Vanilla flavour)



Cinnamaldehyde
(Cinnamon flavour)



Camphor
(Camphor fragance)

- Structures of many important biological compounds contain carbonyl moiety. For example progesterone and testosterone, the female and male sex hormones respectively.

Do you know ?

- Butyraldehyde is used in margarine and food for its buttery odour.
- Acetophenone has smell of pistachio and is used in ice-cream. Muscone has musky aroma and is used in perfumes. Popcorn has butter flavour which contains butane-2,3-dione.

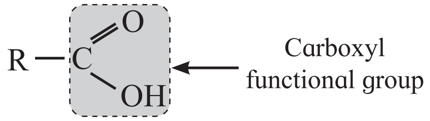
12.2.3 Classification of carboxylic acids :

Carboxylic acids are classified as aliphatic and aromatic carboxylic acids :

a. Aliphatic carboxylic acids : The organic compounds in which carboxyl (-COOH) group is bonded to an alkyl group are called aliphatic carboxylic acids or fatty acids. (Exception : Formic acid, H-COOH is also classified as aliphatic carboxylic acid though –COOH group is not attached to any carbon). For example :

$H_3C - COOH$ (Acetic acid)

$H_3C - CH_2 - COOH$ (Propionic acid)



General formula
(R= H or alkyl group)

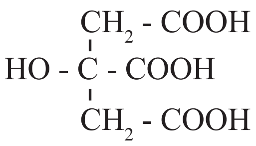
Depending on the number of –COOH groups present carboxylic acids are classified as mono, di, tri carboxylic acids and so on. For example :

$H_3C - CH_2 - COOH$

Propionic acid
(a monocarboxylic acid)

$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

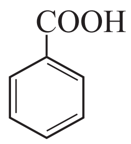
Oxalic acid
(a dicarboxylic acid)



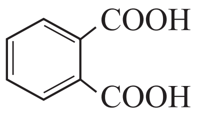
$$\begin{array}{l} \quad\quad\;\; CH_2 - COOH \\ \quad\quad\;\; | \\ HO - C - COOH \\ \quad\quad\;\; | \\ \quad\quad\;\; CH_2 - COOH \end{array}$$

Citric acid
(a tricarboxylic acid)

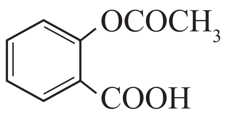
b. Aromatic carboxylic acids : These are the compounds in which one or more carboxyl groups (-COOH) are attached directly to the aromatic ring. For example :



(Benzoic acid)



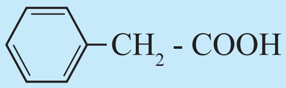
(Phthalic acid)



(Acetyl salicylic acid) (Aspirin)

Remember...

The aromatic compounds in which the –COOH group is not attached directly to the ring are called side-chain aromatic acids. For example :



(Phenyl acetic acid)

Carboxylic acids are widely distributed in nature; they are found in both the plants and animals. L-lactic acid is present in curd , citric acid is found in citrus fruit (Lemons). Acetic acid is the key ingredient of vinegar.

12.3 Nomenclature of aldehydes, ketones and carboxylic acids :

12.3.1 Nomenclature of aldehydes and carboxylic acid :

The names of aldehydes and carboxylic acids are related to each other. There are two systems of naming aldehydes and carboxylic acids : trivial and IUPAC.

a. Trivial names of aldehydes and carboxylic acids : Trivial names of aliphatic aldehydes are derived from the corresponding trivial names of carboxylic acids. Here the ending 'ic acid' of carboxylic acid is replaced by the ending 'aldehyde'. In case of substituted aliphatic carboxylic acids and aldehydes the position of substituent is indicated by labeling the carbon serially as α, β, γ and so on. The carbon atom adjacent to carbonyl carbon is labeled as α and next one is β and so on. (See Table 12.1).

Do you know ?

A series of straight chain dicarboxylic acids are commercially known by the following common names:

COOH COOH (oxalic acid)	COOH CH_2 COOH (malonic acid)	COOH $(CH_2)_2$ COOH (succinic acid)	COOH $(CH_2)_3$ COOH (glutaric acid)	COOH $(CH_2)_4$ COOH (adipic acid)

A series of lower fatty acids are commercially known by the following common names.

CH_3 COOH (Acetic acid)	CH_3 CH_2 COOH (propionic acid)	CH_3 $(CH_2)_2$ COOH (butyric acid)	CH_3 $(CH_2)_3$ COOH (valeric acid)	CH_3 $(CH_2)_4$ COOH (caproic acid)

b. IUPAC names of aldehydes and carboxylic acids :

Can you recall ?

Which suffix do appear in the IUPAC names of aldehydes and carboxylic acids ?

According to IUPAC system, the name of an aliphatic aldehyde is derived from the name of the corresponding alkane by replacing ending 'e' of alkane with ' al '. Aldehyde is named as **alkanal** (Table 12.1). The IUPAC name of **aliphatic carboxylic acid** is derived from the name of the corresponding alkane by replacing ending ' e' of alkane with ' oic acid '. (Refer to Std. XI Chemistry Textbook sec. 14.4.7).

Alkane → Alkanal

Alkane → Alkanoic acid

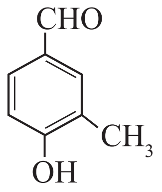
The longest chain including –CHO or –COOH group is identified as the parent chain. Numbering of the chain is done by giving number 1 to the –CHO or –COOH carbon. The name of substituent is included along with its locant.

$^{4}CH_3\text{-}^{3}CH_2\text{-}^{2}CH_2\text{-}^{1}CHO$; $^{4}CH_3\text{-}^{3}CH_2\text{-}^{2}CH_2\text{-}^{1}COOH$

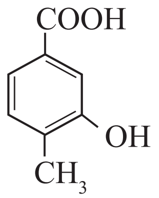
Aldehyde (-CHO) group and carboxyl (-COOH) group are always present at the end of the parent straight chain.

When two –CHO groups are present at the two ends of the chain the ending 'e'of alkane is retained and the suffix –'**dial**' is added to the name of parent aldehyde. In case of dicarboxylic acids, '**dioic acid**' is added to the name of the parent alkane. In IUPAC nomenclature an **alicyclic compound** in which –CHO group is attached directly to the ring is named as a **carbaldehyde**. The suffix 'carbaldehyde' is added after the full name of parent cycloalkane structure. Similarly an alicyclic compound having a carboxyl group directly attached to alicyclic ring is named as **cycloalkane carboxylic acid**.

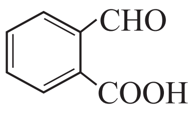
Substituted aromatic aldehydes and carboxylic acids : When two or more different functional groups are attached to a ring , the higher priority group (std. XI Chemistry Textbook, Chapter 14, sec.14.4.7) is given lower number. When –CHO group, appears as substituent prefix 'formyl' is used in the IUPAC name.



(4-Hydroxy-3-methylbenzaldehyde)



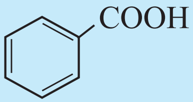
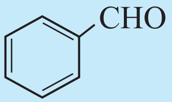
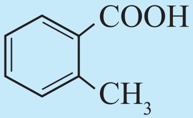
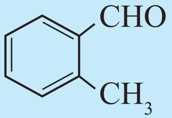
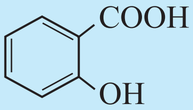
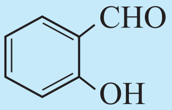
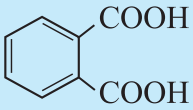
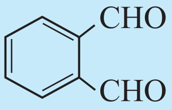
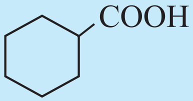
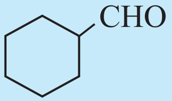
(3-Hydroxy-4-methylbenzoic acid)



(2-Formylbenzoic acid)

Trivial and IUPAC names of some aldehydes and carboxylic acids are given in Table 12.1.

Table 12.1 Trivial and IUPAC names of carboxylic acids and aldehydes

Carboxylic acids			Aldehydes		
Structure	**Trivial name**	**IUPAC name**	**Structure**	**Trivial name**	**IUPAC name**
H - COOH	Formic acid	Methanoic acid	H-CHO	Formaldehyde	Methanal
CH_3 - COOH	Acetic acid	Ethanoic acid	CH_3-CHO	Acetaldehyde	Ethanal
CH_3 - CH_2 - COOH	Propionic acid	Propanoic acid	CH_3-CH_2-CHO	Propionaldehyde	Propanal
CH_3 - CH_2 - CH_2 - COOH	n-Butyric acid	Butanoic acid	CH_3-CH_2-CH_2-CHO	Butyraldehyde	Butanal
$(CH_3)_2$CH - COOH	Isobutyric acid (α - methylpropionic acid)	2-Methylpropanoic acid	$(CH_3)_2$CH-CHO	Isobutyrlaldehyde (α - methylpropionaldehyde)	2 - Methylpropanal
CH_2 = CH - COOH	Acrylic acid	Prop-2-enoic acid	CH_2=CH-CHO	Acrolein	Prop-2-enal
HOOC - COOH	Oxalic acid	Ethanedioic acid	CHO-CHO	Oxaldehyde (Glyoxal)	Ethanedial
	Benzoic acid (Benzenecarboxylic acid)	Benzoic acid		Benzaldehyde	Benzaldehyde (Benzenecarbaldehyde)
	o-Toluic acid	2-Methylbenzoic acid		o-Tolualdehyde	2-Methylbenzaldehyde
	Salicyclic acid	2-Hydroxybenzoic acid		Salicylaldehyde	2-Hydroxybenzaldehyde
	Phthalic acid	Benzene-1,2-dicarboxylic acid		Phthalaldehyde	Benzene-1,2-dicarboaldehyde
	Cyclohexylcarboxylic acid	Cyclohexanecarboxylic acid		Cyclohexane aldehyde	Cyclohexanecarbaldehyde

Do you know ?

The trivial names of carboxylic acids are often derived from Latin names of their original natural source.

For example, Formic acid is obtained from red ants (Formica means ant), acetic acid is obtained from acetum (acetum means vinegar), propionic acid is from basic fat (propion means first fat), butyric acid is from butter (butyrum means butter).

12.3.2 Trivial and IUPAC names of ketones:

a. The trivial names of aliphatic ketones are based on the names of alkyl groups or aryl groups attached to carbonyl carbon .Names of alkyl or aryl groups are written in alphabetical order followed by the word ketone.

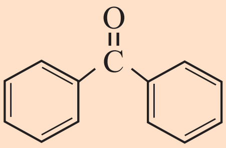
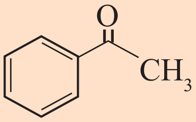
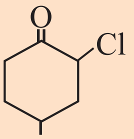
In case of substituted aliphatic ketones the position of substituent is indicated by labelling the carbon serially as α, β, γ and so on. The carbon atom adjacent to carbonyl carbon is labelled as α and next one is β and so on. Names of aromatic ketones are based on a phenone. (see Table 12.2)

b. The IUPAC names of aliphatic ketones are derived from the name of the corresponding alkanes by replacing ending 'e' of alkane with 'one'. They are named as **alkanone**. The longest chain of carbon atoms containing the ketonic carbonyl group is numbered from the end closer to the carbonyl carbon.

$$\textbf{Alkane} \longrightarrow \textbf{Alkanone}$$

When two >C=O groups are present, then ending 'e'of alkane is retained and the suffix –'dione' is added to the name of parent ketone indicating the locants of ketonic

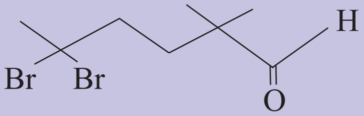
Table 12.2 Trivial and IUPAC names of some ketones

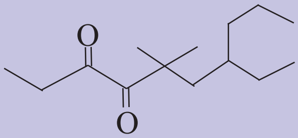
Sr.No.	Compound	Trivial name	IUPAC name
1	CH_3-CO-CH_3	Dimethyl ketone (Acetone)	Propanone
2	CH_3-CO-CH_2-CH_3	Ethyl methyl ketone	Butanone
3	CH_3-CO-CH_2-CH_2-CH_3	Methyl n-propyl ketone	Pentan-2-one
4	CH_3-CH_2-CO-CH_2-CH_3	Diethyl ketone	Pentan-3-one
5	CH_3-CHBr-CO-CH_2-CH_2-CH_3	α-Bromoethyln-propyl ketone	2-Bromohexan-3-one
6	$(CH_3)_2$C=CH-CO-CH_3	Mesityl oxide	4-Methylpent-3-en-2-one
7	CH_3-CO-CH_2-CO-CH_2-CH_3	---------------------	Hexane-2,4-dione
8	CH_3-CO-CH_2-CHO	---------------------	3-Oxobutanal
9		Diphenyl ketone (Benzophenone)	Benzophenone
10		Methyl phenyl ketone (Acetophenone)	Acetophenone
11		-----------------------	2-Chloro-4-methylcyclohexanone

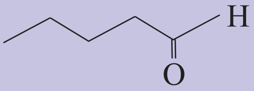
carbonyl groups. In case of polyfunctional ketones, higher priority group is given lower number. When ketonic carbonyl is a lower priority group it is named as 'oxo', preceded by the locant. In alicyclic ketones, carbonyl carbon is numbered as 1. (Refer Table 12.2).

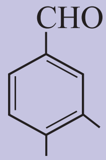
Use your brain power

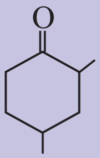
Write IUPAC names for the following compounds.

i.


ii.


iii.


iv.


v.


Try this...

Draw structures for the following

a. 2-Methylpentanal

b. Hexan-2-one

12.4 Preparation of aldehydes and ketones :

12.4.1 General methods of preparation of aldehydes and ketones :

a. By oxidation of alcohols : i. Aldehydes and ketones are prepared by the oxidation of primary and secondary alcohols respectively. (See Chapter 11)

Can you tell ?

What is the reagent which oxidizes primary alcohols to only aldehydes and does not oxidize aldehydes further into carboxylic acid ?

ii. By dehydrogenation of alcohols : This method has industrial application. Aldehydes and ketones are prepared by passing the vapours of primary and secondary alcohols respectively over hot copper powder. (See Chapter 11)

b. From hydrocarbons :

Can you recall ?

- What is ozonolysis ?
- What is the role of zinc dust in ozonolysis process?

i. By ozonolysis : Alkene reacts with ozone to give ozonide which on decomposition with zinc dust and water gives aldehyde and/or ketones. (See Std. XI Chemistry Textbook, Chapter 15)

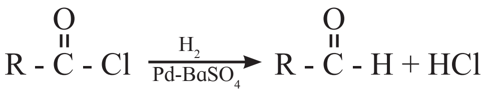
ii. By hydration of alkynes : Alkynes react with water in presence of 40% sulfuric acid and 1% mercuric sulfate to give aldehydes or ketones. (See Std. XI Chemistry Textbook, Chapter 15)

12.4.2 Other methods of preparation of aldehydes and ketones : Some methods of preparation of aldehydes and ketones involve common starting functional groups but different types.

a. From acyl chlorides (Acid chlorides) : Aldehydes and ketones both can be obtained from acyl chloride, but the reactions involved are different.

- **Preparation of aldehyde from acyl chloride**

Acyl chloride is reduced to corresponding aldehyde by hydrogen using a palladium catalyst poisoned with barium sulfate. This reaction is known as **Rosenmund reduction**.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow[\text{Pd-BaSO}_4]{H_2} R-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCl$$

(Acyl chloride) (Aldehyde)

Use your brain power

Write the structure of the product formed on Rosenmund reduction of ethanoyl chloride and benzoyl chloride.

Can you think ?

What is the alcohol formed when benzoyl chloride is reduced with pure palladium as the catalyst ?

b. Preparation of ketone (aliphatic and aromatic) from acyl chloride :

i. Preparation of aliphatic ketones from acyl chloride: ketones are obtained from acyl chloride by reaction with dialkyl cadmium which is prepared by the treatment of cadmium chloride with Grignard reagent.

$$2R\text{ - }MgX + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

$$2R'\text{ - }COCl + R_2Cd \longrightarrow 2\ R'\text{ - }CO\text{ - }R + CdCl_2$$

(Acyl chloride) (Ketone)

For example,

$$2CH_3\text{ - }COCl + (CH_3)_2Cd \longrightarrow 2CH_3\text{-}CO\text{-}CH_3 + CdCl_2$$

(Ethanoyl chloride) (Dimethyl cadmium) Propanone (Acetone)

$$2C_6H_5\text{ - }COCl + (CH_3)_2Cd \longrightarrow C_6H_5\text{ - }CO\text{ - }CH_3 + CdCl_2$$

(Benzoyl chloride) (Dimethyl cadmium) (Acetophenone)

ii. Preparation of aromatic ketones from acyl chloride : Aromatic ketones are prepared by Friedel Craft's acylation reaction (Std. XI Chemistry Textbook, Chapter 15, sec. 15.4.6)

b. From nitriles : Aldehydes and ketones both can be obtained from nitriles but by different reaction.

- **Preparation of aldehydes from nitriles :**

Nitriles are reduced to imine hydrochloride by stannous chloride in presence of hydrochloric acid which on acid hydrolysis give corresponding aldehydes. This reaction is called **Stephen reaction**.

$$R\text{ - }C \equiv N + 2[H] \xrightarrow{SnCl_2,\ HCl} R\text{ - }HC = NH.HCl \xrightarrow{H_3O^{\oplus}} R\text{ - }CHO + NH_4Cl$$

(Alkane nitrile) (imine hydrochloride) (Aldehyde)

For example,

$$H_3C\text{ - }C \equiv N + 2[H] \xrightarrow[\text{(reduction)}]{SnCl_2,\ HCl}$$

(Ethanenitrile)

$$CH_3\text{ - }HC = NH.HCl \xrightarrow{H_3O^{\oplus}} CH_3\text{-}CHO + NH_4Cl$$

(ethanimine hydrochloride) (Ethanal)

$$C_6H_5\text{ - }C \equiv N + 2[H] \xrightarrow{SnCl_2,\ HCl}$$

(Benzonitrile)

$$C_6H_5\text{ - }HC = NH.HCl \xrightarrow{H_3O^{\oplus}} C_6H_5\text{-}CHO + NH_4Cl$$

(Benzanimine hydrochloride) (Benzaldehyde)

Alternatively, nitriles are also reduced by diisobutylaluminium hydride (DIBAl-H) or AlH $(i\text{-}Bu)_2$ to imines followed by acid hydrolysis to aldehydes. An advantage of this method is that double or triple bond present in the same molecule is not reduced..

$$H_3C\text{ - }CH = CH\text{ - }CH_2\text{ - }C \equiv N \xrightarrow[H_3O^{\oplus}]{AlH\ (i\text{-}Bu)_2} H_3C\text{ - }CH = CH\text{ - }CH_2\text{ - }CHO$$

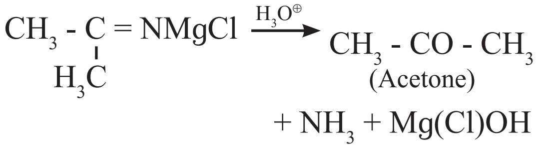
(Pent-3-enenitrile) (Pent-3-enal)

- **Preparation of ketones from nitriles :**

Ketones are prepared by reacting nitriles with Grignard reagent in dry ether as solvent followed by acid hydrolysis.

$$H_3C\text{ - }C \equiv N + H_3CMgCl \xrightarrow{\text{dry ether}}$$

(Ethanenitrile)

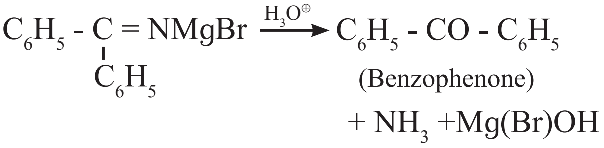


$$\underset{\displaystyle H_3C}{CH_3\text{ - }C} = NMgCl \xrightarrow{H_3O^{\oplus}} CH_3\text{ - }CO\text{ - }CH_3 + NH_3 + Mg(Cl)OH$$

(Acetone)

$$C_6H_5\text{ - }C \equiv N + C_6H_5\text{ - }MgBr \xrightarrow{\text{dry ether}}$$

(Benzonitrile)



$$\underset{\displaystyle C_6H_5}{C_6H_5\text{ - }C} = NMgBr \xrightarrow{H_3O^{\oplus}} C_6H_5\text{ - }CO\text{ - }C_6H_5 + NH_3 + Mg(Br)OH$$

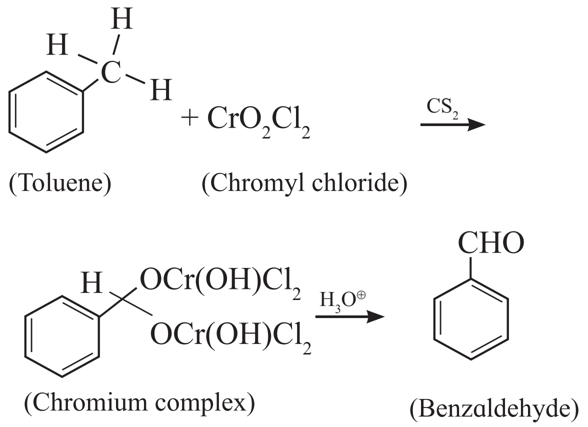
(Benzophenone)

c. From aromatic hydrocarbons : Aromatic aldehydes and ketones are both prepared from aromatic hydrocarbons but by different methods.

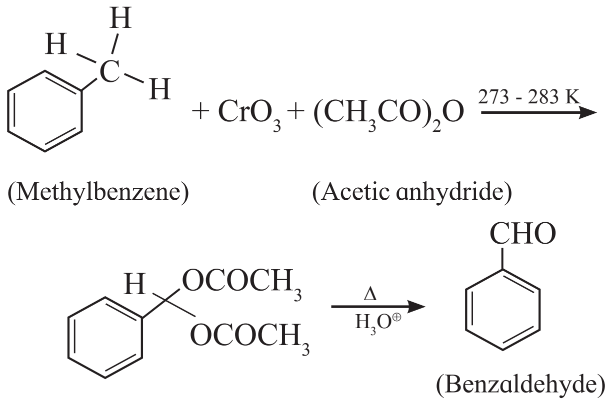
- **Preparation of aromatic aldehydes from hydrocarbon**

Strong oxidizing agents transform -CH_3 group bonded to aromatic ring into carboxyl group (-COOH). For obtaining aromatic aldehyde from methyl arene the following special methods are used.

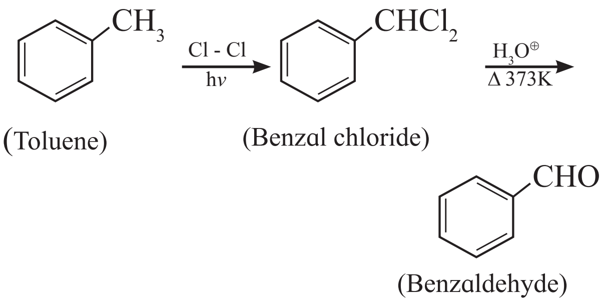
i. Etard reaction : Methyl group in methyl benzene (or methyl arene) is oxidized by oxidizing agent chromyl chloride in carbon disulfide as solvent, to form a chromium complex, from which the corresponding benzaldehyde is obtained on acid hydrolysis. This reaction is known as **Etard reaction**.



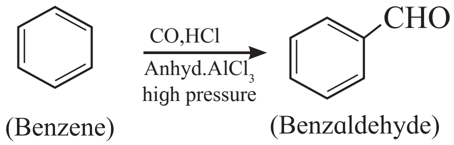
ii. By oxidation of methyl arene using CrO_3 : Methylarene is converted into a benzyllidene diacetate on treatment with chromium oxide in acetic anhydride at 273-278 K. The diacetate derivative on acid hydrolysis gives corresponding aldehyde.



iii. By side chain chlorination of toluene: Side chain chlorination of toluene gives benzal chloride which on acid hydrolysis at 373K gives benzaldehyde. **Benzaldehyde**, is manufactured commercially by this method.



iv. Gatterman –Koch formylation of arene: Benzene or substituted benzene is treated under high pressure with carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride or cuprous chloride to give benzaldehyde or substituted benzaldehyde.



- **Preparation of Aromatic ketones from hydrocarbons :**

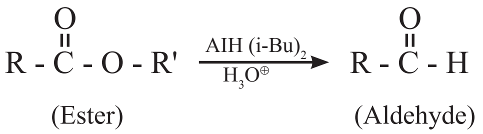
By Friedel-crafts acylation of arene : (Refer to sec. 12.4.2 (a) ii and Std. XI Chemistry Textbook, Chapter 15, sec. 15.4.6).

Use your brain power

Name the compounds which are used for the preparation of benzophenone by Friedel-Crafts acylation reaction. Draw their structures.

12.4.3 Preparation of aldehydes only from esters :

Aliphatic or aromatic esters are reduced to aldehydes by using diisobutylaluminium hydride DIBAl-H or AlH $(i\text{-}Bu)_2$. The reaction is usually carried out at 195 K to prevent further reduction of the aldehyde produced.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' \xrightarrow[H_3O^{\oplus}]{AlH\,(i\text{-}Bu)_2} R-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

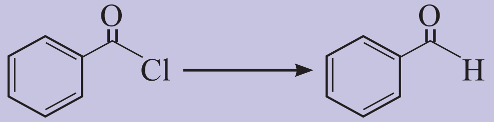
(Ester) (Aldehyde)

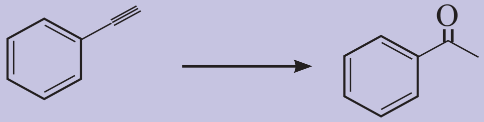
Try this...

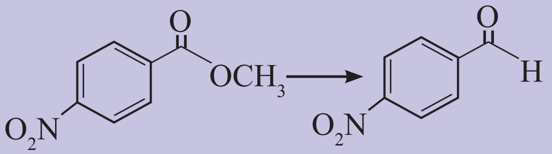
Draw the structure of the product formed by the combination of carbon monoxide and HCl.

Use your brain power

Identify the reagents necessary to achieve each of the following transformation





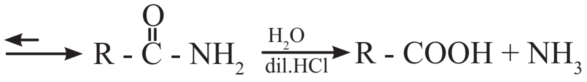


12.5 Preparation of carboxylic acids :

12.5.1 From nitriles and amides : Alkyl nitriles or aryl nitriles on acid hydrolysis give amides . Amides on further acid hydrolysis give corresponding carboxylic acids. Hydrolysis is carried out by using dilute mineral acids like dilute sulfuric acid or dilute hydrochloric acid.

$$R-C\equiv N + H_2O \longrightarrow [R-\overset{OH}{\overset{|}{C}}=NH]$$

(Nitrile)



$$\rightleftarrows R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{dil.HCl}]{H_2O} R-COOH + NH_3$$

(Amide) (carboxylic acid)

$$R-C\equiv N + 2H_2O + \text{dil.HCl} \xrightarrow{\Delta} R-COOH + NH_4Cl$$

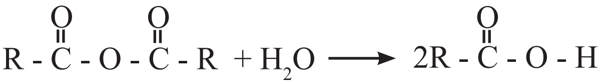
12.5.2 From acyl chloride and anhydrides :

a. Acyl chlorides on hydrolysis with water give carboxylic acids. This method is useful for preparation of aliphatic as well as aromatic acid.

$$R-COCl + H_2O \longrightarrow R-COOH + H-Cl$$

(Acyl chloride) (Carboxylic acid)

b. Anhydrides on hydrolysis with water give carboxylic acids.

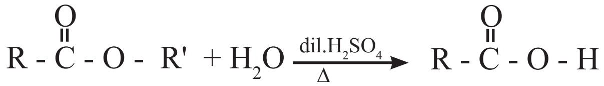


$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + H_2O \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-O-H$$

(Anhydride) (Carboxylic acid)

12.5.3 From esters : Carboxylic acids can be obtained from esters either by acid hydrolysis or alkaline hydrolysis.

a. Acid hydrolysis of ester : Esters on hydrolysis with dilute mineral acid like dilute HCl or dilute H_2SO_4 give the corresponding carboxylic acid .



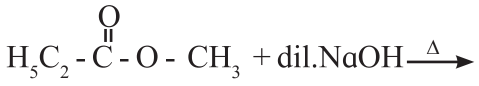
$$R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O \xrightarrow[\Delta]{\text{dil.}H_2SO_4} R-\overset{O}{\overset{\|}{C}}-O-H$$

(Ester) (Carboxylic acid)

$+ R'-OH$

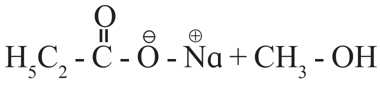
(Alcohol)

b. Alkaline hydrolysis of ester using dilute alkali like dilute NaOH or dilute KOH form solution of water soluble sodium or potassium salt of the acid (carboxylate). On acidification with concentrated HCl, free acid is formed.



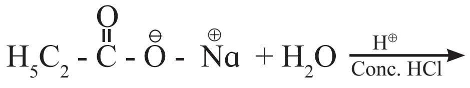
$$H_5C_2-\overset{O}{\overset{\|}{C}}-O-CH_3 + \text{dil.NaOH} \xrightarrow{\Delta}$$

(Methyl propanoate)



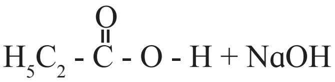
$$H_5C_2-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}-\overset{\oplus}{Na} + CH_3-OH$$

(Sodium propanoate)



$$H_5C_2-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}-\overset{\oplus}{Na} + H_2O \xrightarrow[\text{Conc. HCl}]{H^{\oplus}}$$

(Sodium propanoate)



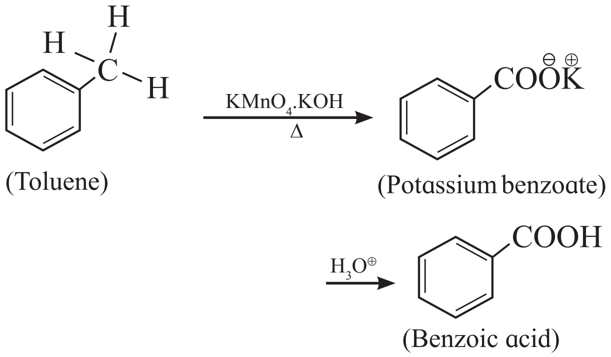
$$H_5C_2-\overset{O}{\overset{\|}{C}}-O-H + NaOH$$

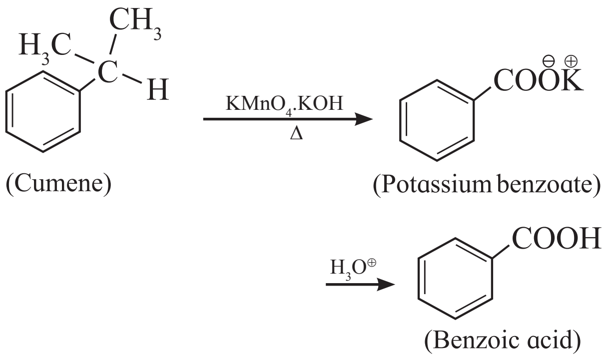
(Propanoic acid)

The sodium or potassium salts of higher fatty acids are known as soaps. Hence alkaline hydrolysis of esters is called **saponification** (Std XI Chemistry Textbook, Chapter 16).

12.5.4 From alkyl benzene : Aromatic carboxylic acids can be prepared by oxidation of alkyl benzene with dilute HNO_3 or alkaline /acidic $KMnO_4$ or chromic acid. The entire alkyl chain, regardless of its length, is oxidized to a carboxyl group. (Tertiary alkyl substituent on benzene, however, is not oxidized).

For example,

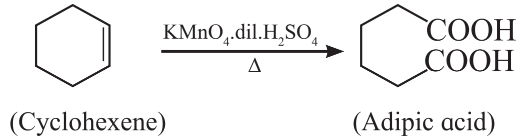




12.5.5 From alkenes : Carboxylic acids can also be prepared by the oxidation of alkenes by $KMnO_4$ in dilute H_2SO_4.

$$H_5C_6-CH=CH_2 \xrightarrow[\Delta]{KMnO_4.dil.H_2SO_4} H_5C_6-COOH$$

(Phenyl ethene) (Benzoic acid)



12.5.6 From Grignard reagent : Grignard reagent in dry ether solvent is added to solid carbon dioxide (dry ice) to give a complex which on acid hydrolysis gives corresponding carboxylic acid.

$$R-Mg-X + O=C=O \xrightarrow{\text{dry ether}} R-COOMgX$$

(Alkyl magnesium halide) (dry ice) (complex)

$$\xrightarrow[\text{dil.HCl}]{\text{HOH}} R-COOH + Mg(X)OH$$

(carboxylic acid)

Internet my friend

Collect information of dry ice and ice from internet. Draw chemical structures of dry ice and regular ice. Prepare a chart of uses of dry ice.

Use your brain power

Predict the products (name and structure) in the following reactions.

$CH_3CH_2CN \xrightarrow[\text{dil. HCl}]{\Delta} ?$

$CH_3\text{-}CONH_2 \xrightarrow[\text{dil. HCl}]{\Delta} ?$

$C_6H_5\text{-}CH_2\text{-}CH_3 \xrightarrow[\Delta]{\text{alk.}KMnO_4} ?$

$C_6H_5\text{-}COO\text{-}C_2H_5 \xrightarrow[\text{dil. }H_2SO_4]{\Delta} ?$

$CH_3MgBr \xrightarrow[\text{(ii) dil. HCl}]{\text{(i) dry ice/dry ether}} ?$

12.6 Physical properties :

12.6.1 Nature of intermolecular forces :

The carbonyl bond ($>$C=O) in aldehydes and ketones is a polar covalent bond. As a result, these compounds contain dipole-dipole forces of attraction. (Fig. 12.1) The molecules orient in such a way as to have oppositely polarized atoms facing each other.

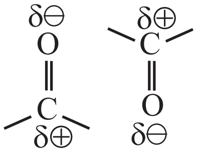


Fig. 12.1 Dipole-dipole attraction in carbonyl compounds

Carboxyl group of carboxylic acid contains O-H bond which is responsible for formation of hydrogen bonding. Thus, carboxylic acids have the strongest intermolecular forces of attraction. (Fig.12.3 in section 12.6.4).

Table 12.4 Boiling points of aldehydes and ketones

Number of carbon atoms	Aldehyde	Boiling point	Ketone	Boiling point
1	Methanal	252 K	-----	--------
2	Ethanal	294 K	-------	---------
3	Propanal	319 K	Propanone	329 K
4	Butanal	348 K	Butan -2-one	353 K
5	Pentanal	376 K	Pentan-2-one	375 K
6	Hexanal	392 K	Hexan-2-one	400 K

12.6.2 Physical state and boiling points of aldehydes and ketones :

Formaldehyde is a gas at room temperature and has irritating odour. **Acetaldehdye** is extremely volatile, colourless liquid. Higher aldehydes have pleasant odour. **Acetone** is a liquid at room temperature and has pleasant odour but most of the higher ketones have bland odours.

Increasing boiling points in the homologous series of aldehydes and ketones are listed in Table 12.4.

12.6.3 Solubility of aldehydes and ketones :

The oxygen atom of ($>$C=O) can involve in hydrogen bonding with water molecule (Fig 12.2). As a result of this, the lower aldehydes and ketones are water soluble (For example : acetaldehyde, acetone). As the molecular mass increases, the proportion of hydrocarbon part of the molecule increases which cannot form hydrogen bond; and the water solubility decreases.

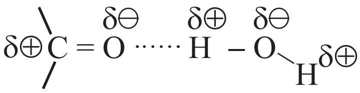


Fig. 12.2 : Hydrogen bonding in carbonyl compound and water

12.6.4 Physical state, boiling points and solubilities of carboxylic acids :

Lower **aliphatic carboxylic acids** upto nine carbon atoms are colourless liquids with irritating odours. The higher homologues are colourless, odourless wax like solids, have low volatility. Boiling points of lower carboxylic acids are listed in Table 12.5.

Carboxylic acids have higher boiling points than those of alkanes, ethers, alcohols aldehydes and ketones of comparable mass (Table 12.6). The reason is that , in liquid phase, carboxylic acids form dimer in which two molecules are held by two hydrogen bonds. Acidic hydrogen of one molecule form hydrogen bond with carbonyl oxygen of the other molecule (Fig.12.3). This doubles the size of the molecule resulting in increase in intermolecular van der Waals forces, which in turn results in high boiling point. In the case of acetic acid dimers exist even in the gas phase (Fig.12.3).

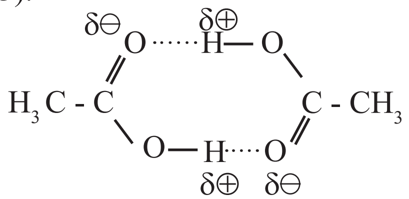


Fig. 12.3 : Dimer of acetic acid (Two molecules held by two hydrogen bonds)

Table 12.5 Increasing boiling points of carboxylic acids

Name	Formula	Boiling point in K
Formic acid	$HCOOH$	373 K
Acetic acid	CH_3COOH	391 K
Propionic acid	CH_3CH_2COOH	414 K
Butyric acid	$CH_3CH_2CH_2COOH$	437 K
Valeric acid	$CH_3CH_2CH_2CH_2COOH$	460 K

Table 12.6 : Variation of boiling point with functional group

Compound	Family	Molecular mass	Boiling point	Strength of intermolecular forces
CH_3-CH_2-CH_2-CH_3	Alkane	58	272 K	increases ↓
CH_3-O-CH_2-CH_3	Ether	60	281 K	
CH_3-CH_2-CHO	Aldehyde	58	322 K	
CH_3-CO-CH_3	Ketone	58	329 K	
CH_3-CH_2-CH_2-OH	Alcohol	60	370 K	
CH_3-COOH	Carboxylic acid	60	391 K	

Remember...

Relative strength of intermolecular force : H-Bond > dipole-dipole attraction > van der Waals force. **Hence, Boiling points :** Carboxylic acids > Alcohols > Ketones > Aldehydes > ether > Alkanes

Do you know ?

Commercially available forms of formaldehyde and acetaldehyde:

i. Formaldehyde is available commercially as solid polymer called paraformaldehyde $HO\left[CH_2-O\right]_n H$ and trioxane $(CH_2O)_3$ (Trioxane has cyclic structure). These are convenient for use in chemical reactions as source of formaldehyde.

ii. Aqueous solution of formaldehyde gas is called formalin, which is used for preservation of biological and anatomical specimens.

iii. When dry formaldehyde is required, it is obtained by heating paraformaldehyde or trioxane.

iv. Acetaldehyde is also conveniently used as solid trimer (paraldehyde) and tetramer (metaldehyde).

Lower aliphatic carboxylic acids containing upto four carbons are miscible with water due to formation of intermolecular hydrogen bonds between carboxylic acid molecules and solvent water molecules. The solubility of carboxylic acids in water decreases with increase in molecular mass. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic (water hating) interaction of hydrocarbon part with water. Aromatic acids like benzoic acid are also practically insoluble in water at room temperature. Water insoluble carboxylic acids are soluble in less polar organic solvents like ether, alcohol, benzene, and so on.

12.7 Polarity of carbonyl group : The polarity of a carbonyl group originates from higher electronegativity of oxygen relative to carbon as well as resonance effects as shown in Fig. 12.4.

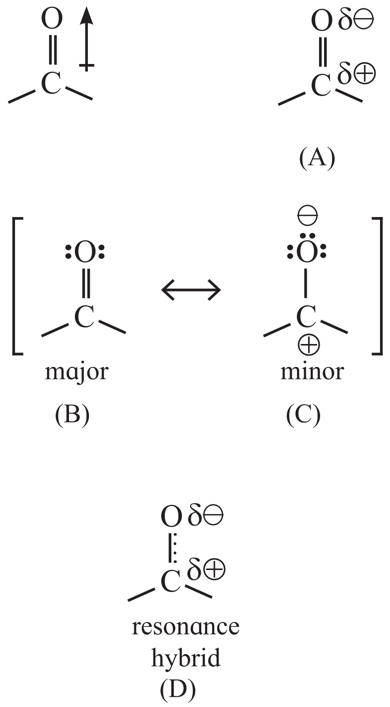


Fig. 12.4 : Polarity of carbonyl group

The carbonyl carbon has positive polarity (see structures (A) and (D)). Therefore, it is electron deficient. As a result, this carbon atom is electrophilic (electron loving) and is susceptible to attack by a nucleophile ($Nu:^{\ominus}$).

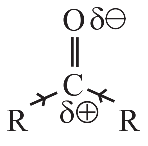
12.7.1 Reactivity of aldehydes and ketones :

Reactivity of aldehydes and ketones is due to the polarity of carbonyl group which results in electrophilicity of carbon. In general, aldehydes are more reactive than ketones toward nucleophilic attack. This can be well explained in terms of both the electronic effects and steric effect.

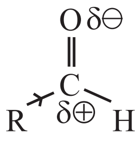
1. Influence of electronic effects : Alkyl groups have electron donating inductive effect (+I). A ketone has two electron donating alkyl groups bonded to carbonyl carbon which are responsible for decreasing its positive polarity and electrophilicity. In contrast, aldehydes have only one electron donating group bonded to carbonyl carbon. This makes aldehydes more electrophilic than ketones.

2. Steric effects : Two bulky alkyl groups in ketone come in the way of incoming nucleophile. This is called steric hindrance to nucleophilic attack.

On the other hand, nucleophile can easily attack the carbonyl carbon in aldehyde because it has one alkyl group and is less crowded or sterically less hindered . Hence aldehyde are more easily attacked by nucleophiles.



(Ketone)



(Aldehyde)

Remember...

Aromatic aldehydes are less reactive than aliphatic aldehydes in nucleophilic addition reactions. This is due to electron-donating resonance effect of aromatic ring which makes carbonyl carbon less electrophilic.

Try this...

Draw structure of propanone and indicate its polarity.

12.8 Chemical properties of aldehydes and ketones :

12.8.1 Laboratory tests for aldehydes and ketones :

Aldehydes are easily oxidized to carboxylic acids and therefore, act as reducing agents toward mild oxidizing agents. Ketones, do not have hydrogen atom directly attached to carbonyl carbon. Hence, they are not oxidized by mild oxidizing agents. On the basis of this difference in the reactivity, aldehydes and ketones are distinguished by the following tests:

a. Tests given by only aldehydes :

1. Schiff test : When alcoholic solution of aldehyde is treated with few drops of Schiff 's reagent, pink or red or magenta colour appears. This confirms the presence of aldehydic (-CHO) group.

2. Tollens' test or silver mirror test : When an aldehyde is boiled with Tollens' reagent (ammonical silver nitrate), silver mirror is formed. The aldehyde is oxidized to carboxylate ion by Tollens' reagent and $Ag^{\oplus}$ ion is reduced to Ag.

$$\underset{\text{(aldehyde)}}{R\text{ - }CHO} + \underbrace{2\,Ag\,(NH_3)_2^{\oplus} + 3OH^{\ominus}}_{\text{Tollens reagent}} \xrightarrow{\Delta}$$

$$\underset{\text{(carboxylate)}}{R\text{ - }COO^{\ominus}} + \underset{\text{(Silver mirror)}}{2\,Ag\downarrow} + 4NH_3\uparrow + 2H_2O$$

3. Fehling test : When a mixture of an aldehyde and Fehling solution is boiled in hot water, a red precipitate of cuprous oxide is formed.

An aldehyde is oxidized to carboxylate ion by Fehling solution and $Cu^{2\oplus}$ ion is reduced to $Cu^{\oplus}$ ion. It may be noted that α-hydroxy ketone also gives this test positive.

$$\underset{\text{(Aldehyde)}}{R - CHO} + \underbrace{2Cu^{2\oplus} + 5OH^{\ominus}}_{\text{(Fehling solution)}} \xrightarrow{\text{boil}}$$

$$\underset{\text{(carboxylate ion)}}{R - COO^{\ominus}} + \underset{\text{red ppt}}{Cu_2O\downarrow} + 3H_2O$$

Can you tell ?

Simple hydrocarbons, ethers, ketones and alcohols do not get oxidized by Tollens' reagent. Explain, Why ?

Use your brain power

Why is benzaldehyde NOT oxidized by Fehling solution ?

b. Laboratory test for ketonic group : Sodium nitroprusside test :

When a freshly prepared sodium nitroprusside solution is added to a ketone, mixture is shaken well and basified by adding sodium hydroxide solution drop by drop, red colour appears in the solution, which indicates the presence of ketonic (>C=O) group.

$$\underset{\text{(Acetone)}}{CH_3 - CO - CH_3} + OH^{\ominus} \longrightarrow CH_3 - CO - CH_2^{\ominus} + H_2O$$

$$\underset{\text{(Nitroprusside ion)}}{[Fe(CN)_5NO]^{2\ominus}} + CH_3 - CO - CH_2^{\ominus} \longrightarrow$$

$$\underset{\text{Red colouration}}{[Fe(CN)_5NO(CH_3 - CO - CH_2)]^{3\ominus}}$$

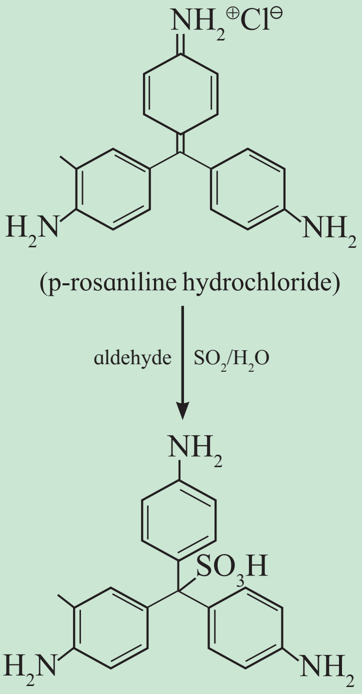
The anion of ketone formed by alkali reacts with nitroprusside ion to form a red coloured complex which indicates the presence of ketonic group.

12.8.2 Chemical reactions of aldehydes and ketones with nucleophile : In all these reactions the nucleophilic reagent brings about reactions by attacking on positively polarized electrophilic carbonyl carbon in aldehydes and ketones.

a. Addition of hydrogen cyanide (H-CN) : Hydrogen cyanide (weak acid) adds across the carbon-oxygen double bond in aldehydes and ketones to produce compounds called

Do you know ?

1. **Schiff 's reagent** is a colourless solution obtained by passing sulfur dioxide gas (oxidant) through magenta coloured solution of p-rosaniline hydrochloride .



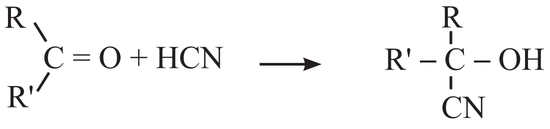
(p-rosaniline hydrochloride)

(Schiff 's reagent)

2. **Tollens' reagent** is prepared by mixing a few drops of $AgNO_3$ solution and a few mL of dilute sodium hydroxide solution. A brown precipitate is formed which is then dissolved by adding dilute ammonium hydroxide.

3. **Fehling solution** is a mixture of two solutions Fehling A and Fehling B. **Fehling A** is prepared by dissolving crystals of copper sulfate in concentrated sulfuric acid. **Fehling B** is prepared by dissolving sodium potassium tartarate in sodium hydroxide solution.

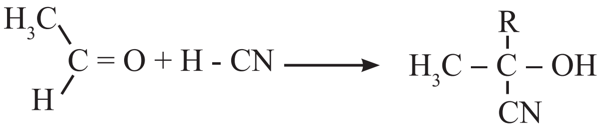
cyanohydrins. The negative part of the reagent ($^{\ominus}CN$) attacks the electrophilic carbon of carbonyl group. The reaction requires either acid or base as catalyst.



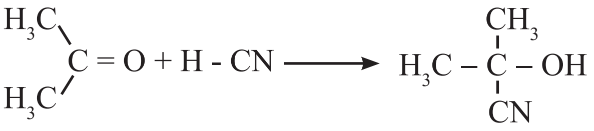
(Aldehyde when R' = H
Ketone : R' = alkyl/aryl group)

(cyanohydrin)

For example ,



(Acetaldehyde) (acetaldehyde cyanohydrin)



(Acetone) (Acetone cynohydrin)

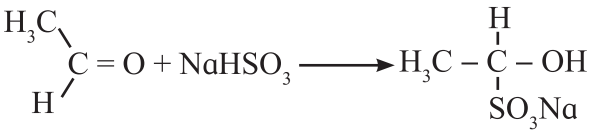
Remember...

i. Cyanohydrin formation is a 'step-up' reaction as a new carbon - carbon single bond is formed.

ii. The - C ≡ N group can be converted to –COOH, - CH_2 - NH_2 and so on.

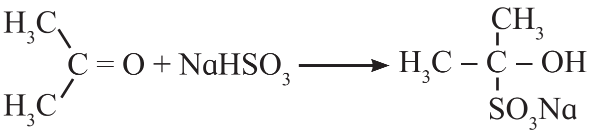
iii. Therefore, cyanohydrins are used as intermediate in step up synthesis.

b. Addition of $NaHSO_3$ (Sodium bisulphite) : Aldehydes and ketones react with saturated aqueous solution of sodium bisulfite to give crystalline precipitate of sodium bisulfite adduct (addition compound). For example ,



(Acetaldehyde)

(Acetaldehyde sodium bisulfite adduct)



(Acetone)

(Acetonesodium bisulfite adduct)

Use your brain power

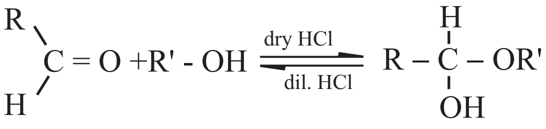
Sodium bisulfite is sodium salt of sulfurous acid, write down its detailed bond structure .

Do you know ?

Sodium bisulfite addition product so formed can be split easily to regenerate aldehydes and ketones on treatment with dilute acid or base. Thus, this reaction is used to separate and purify the aldehydes and ketones from other organic compounds.

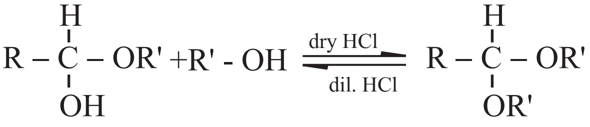
c. Addition of alcohols : Aldehyde reacts with one molecule of anhydrous monohydric alcohol in presence of dry hydrogen chloride to give alkoxyalcohol known as **hemiacetal**, which further reacts with one more molecule of anhydrous monohydric alcohol to give a geminaldialkoxy compound known as **acetal** as shown in the reaction.

Step 1 :



(Aldehyde) (Hemiacetal) unstable

Step 2 :

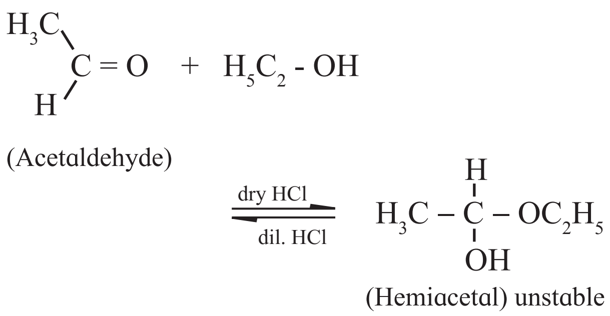


(Hemiacetal) (Acetal) stable

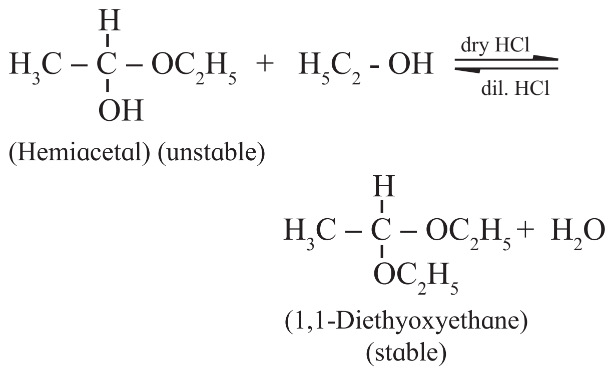
+ H_2O

For example ,

Step 1 :

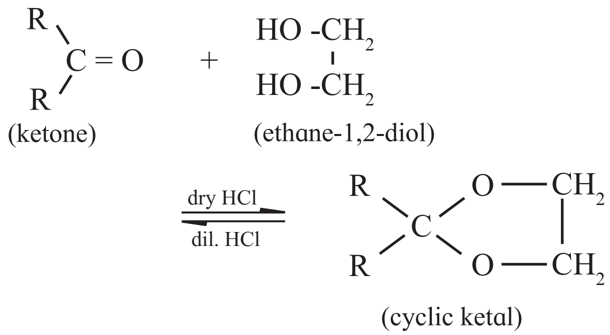


Step 2 :



Similarly, **Ketones** react with alcohol in presence of acid catalyst to form hemiketal and ketal.

Ketones react with 1,2- or 1,3- diols in presence of dry hydrogen chloride to give five- or six -membered cyclic ketals .



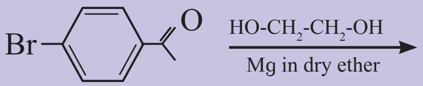
The reaction can be reversed by treating the cyclic ketal with aqueous HCl to regenerate the ketone.

Do you know ?

Cyclic ketal is used as protecting group for ketone in reactions of multifunctional compound to which ketone is sensitive.

Use your brain power

Predict the product of the following reaction :



Acetals and ketals are hydrolysed with aqueous mineral acids to give corresponding aldehydes and ketones respectively.

Remember...

Organic molecule containing an alcohol and carbonyl group can undergo intramolecular reaction with dry HCl to form cyclic hemiacetals/hemiketals.

d. Addition of Grignard reagent : Aldehydes and ketones on reaction with alkyl magnesium halide followed by acid hydrolysis give alcohols.(Refer to Chapter 11, sec. 11.4.1 d.)

e. Nucleophilic addition –elimination of aldehydes and ketones with ammonia derivatives : Aldehydes and ketones undergo addition elimination with some ammonia derivatives (NH_2-Z) to give product containing C = N bonds (imines). The reaction is reversible and takes place in weakly acidic medium. The substituted imine is called a **Schiff 's base**.

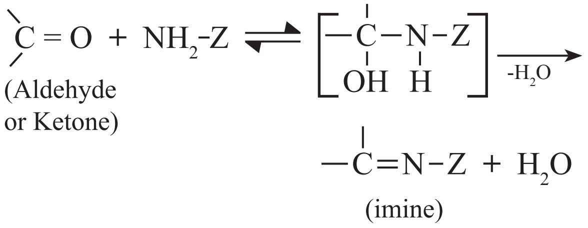
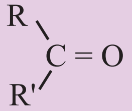
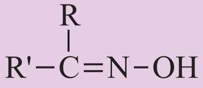
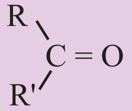
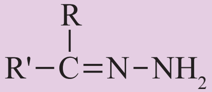
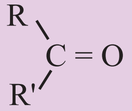
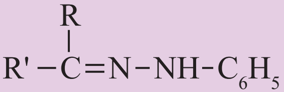
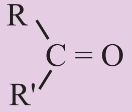
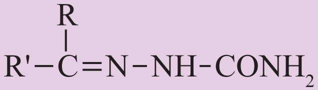
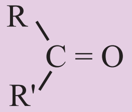
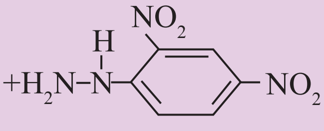
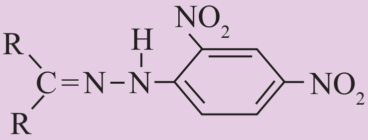
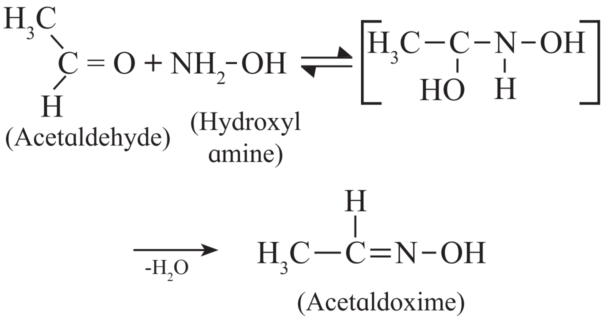


Table 12.7 Nucleophilic addition – elimination reactions of aldehydes and ketones with ammonia derivatives

Sr. No.	Aldehyde(R'=H)/ Ketone(R'≠H)	+ NH_2 - Z	$\xrightarrow[-H_2O]{}$	imine (a crystalline derivative)
1.		+ NH_2-OH Hydroxyl amine	$\xrightarrow[-H_2O]{}$	 $R'-\overset{R}{\overset{\vert}{C}}=N-OH$ oxime
2.		+ NH_2-NH_2 Hydrazine	$\xrightarrow[-H_2O]{}$	 $R'-\overset{R}{\overset{\vert}{C}}=N-NH_2$ hydrazone
3.		+ $NH_2-NH-C_6H_5$ Phenyl hydrazine	$\xrightarrow[-H_2O]{}$	 $R'-\overset{R}{\overset{\vert}{C}}=N-NH-C_6H_5$ phenylhydrazone
4.		+ $NH_2-NH-CONH_2$ Semicarbazide	$\xrightarrow[-H_2O]{}$	 $R'-\overset{R}{\overset{\vert}{C}}=N-NH-CONH_2$ semicarbazone
5.		 2, 4 - Dinitrophenyl hydrazine	$\xrightarrow[-H_2O]{}$	 2, 4 - Dinitrophenylhydrazone

Where Z = -R, -Ar, $-NH_2$, $-NHC_6H_5$, $-NHCONH_2$, $-NHC_6H_3(NO_2)_2$

For example,



All aldehydes and ketones give similar reactions .Some important reactions are listed in Table 12.7. The resulting products have high molecular mass and are crystalline solids. These reactions are, therefore, useful for characterization of the original aldehydes and ketones.

Remember...

In strong acidic medium, nitrogen atom of ammonia derivative H_2N-Z is protonated to form (H_3N^+ – Z) ion which is no longer a nucleophile.

Use your brain power

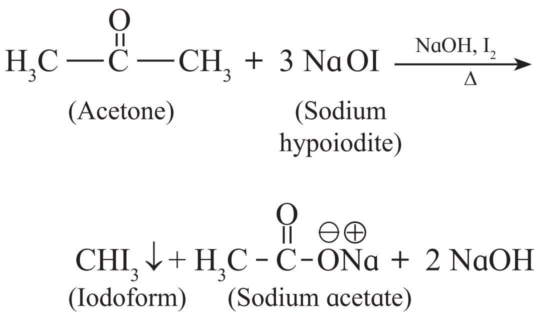
Draw the structures of

i. The semicarbazone of cyclohexanone

ii. The imine formed in the reaction between 2-methylhexanal and ethyl amine

iii. 2, 4 - dinitrophenylhydrazone of acetaldehyde.

f. Haloform reaction : This reaction is given by acetaldehyde, all methyl ketones (CH_3-CO-R) and all alcohols containing CH_3-(CHOH)- group. When an alcohol or methyl ketone is warmed with sodium hydroxide and iodine, a yellow precipitate is formed. Here the reagent sodium hypoiodite is produced in situ. During the reaction, sodium salt of carboxylic acid is formed which contains one carbon atom less than the substrate. The **methyl group** is converted in to **haloform**. For example : Acetone is oxidized by sodium hypoiodite to give sodium salt of acetic acid and yellow precipitate of iodoform.



$$\underset{\text{(Acetone)}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} + \underset{\text{(Sodium hypoiodite)}}{3\,NaOI} \xrightarrow[\Delta]{NaOH,\ I_2}$$

$$\underset{\text{(Iodoform)}}{CHI_3\downarrow} + \underset{\text{(Sodium acetate)}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O}\overset{\oplus}{Na}} + 2\,NaOH$$

Remember...

1. If C=C bond is present in a given aldehyde or ketone or methyl ketone, it is not attacked by hypohalite.
2. Non methyl ketones do not give a positive iodoform test.
3. Secondary alcohols having CH_3-CHOH- group give positive iodoform test because the reagent first oxidizes it to a CH_3-CO- group which subsequently forms iodoform.

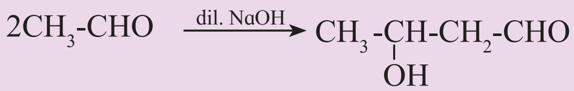
Try this...

Write chemical reactions taking place when propan-2-ol is treated with iodine and sodium hydroxide.

g. Aldol condensation :

Try this...

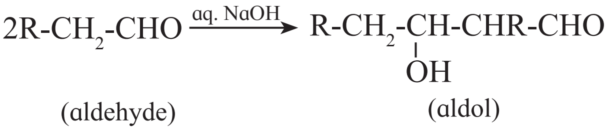
When acetaldehyde is treated with dilute NaOH, the following reaction is observed.



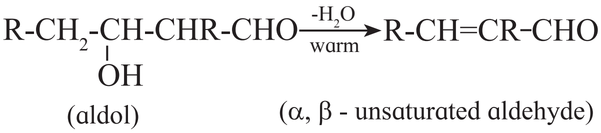
$$2CH_3\text{-}CHO \xrightarrow{\text{dil. NaOH}} CH_3\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_2\text{-}CHO$$

- What are the functional groups in the product ?
- Will there be another product formed during the same reaction ? (Deduce the answer by doing atomic audit of reactant and product)
- Is this an addition reaction or condensation reaction ?

Aldehydes containing at least one α –hydrogen atom undergo a reaction in presence of dilute alkali (dilute NaOH, KOH or Na_2CO_3) as catalyst to form β-hydroxy aldehydes (aldol). This reaction is known as **aldol reaction**. Formation of aldol is an addition reaction. Aldol formed from aldehyde having α-hydrogens undergoes subsequent elimination of water molecule on warming, giving rise to α, β - unsaturated aldehyde.



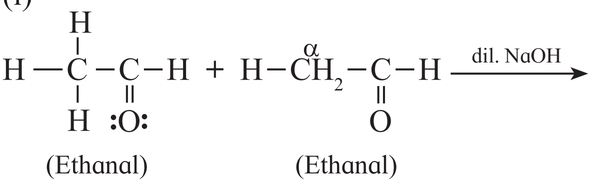
$$\underset{\text{(aldehyde)}}{2R\text{-}CH_2\text{-}CHO} \xrightarrow{\text{aq. NaOH}} \underset{\text{(aldol)}}{R\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CHR\text{-}CHO}$$



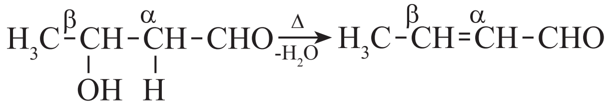
$$\underset{\text{(aldol)}}{R\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CHR\text{-}CHO} \xrightarrow[\text{warm}]{-H_2O} \underset{(\alpha,\ \beta\text{ - unsaturated aldehyde})}{R\text{-}CH=CR\text{-}CHO}$$

For example :

(i)



$$\underset{\text{(Ethanal)}}{H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle :O:}{\|}}{C}-H} + \underset{\text{(Ethanal)}}{H-\overset{\alpha}{C}H_2-\underset{\underset{\displaystyle O}{\|}}{C}-H} \xrightarrow{\text{dil. NaOH}}$$



$$H_3C\overset{\beta}{-}\underset{OH}{CH}-\underset{H}{\overset{\alpha}{CH}}-CHO \xrightarrow[-H_2O]{\Delta} H_3C-\overset{\beta}{CH}=\overset{\alpha}{CH}-CHO$$

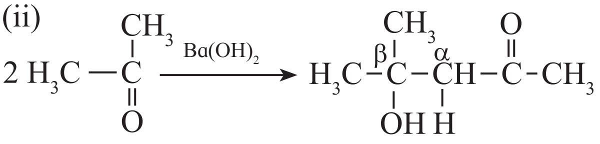
(3-Hydroxybutanal)
(an Aldol)

(But-2-enal)

The overall reaction is called **aldol condensation**. It is a **nuclephilic addition-elimination** reaction.

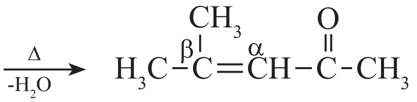
Ketones containing at least two α- hydrogen also undergo aldol condensation reaction and give an α, β - unsaturated ketone. For example:

(ii)



$$2\,H_3C-\underset{\underset{O}{\|}}{\overset{CH_3}{C}} \xrightarrow{Ba(OH)_2} H_3C\overset{\beta}{-}\underset{OH}{\overset{CH_3}{C}}-\underset{H}{\overset{\alpha}{CH}}-\overset{\overset{O}{\|}}{C}-CH_3$$

(Propanone) (4-Hydroxy-4-methylpentan-2-one)
(a Ketol)



$$\xrightarrow[-H_2O]{\Delta} H_3C\overset{\beta}{-}\overset{CH_3}{C}=\overset{\alpha}{CH}-\overset{\overset{O}{\|}}{C}-CH_3$$

(4-methylpent-3-en-2-one)

Cross aldol condensation : Cross aldol condensation refers to the aldol condensation that takes place in between two different aldehydes or ketones . If both aldehydes or ketones contain two α-hydrogen atoms each, then a mixture of four products, is formed.

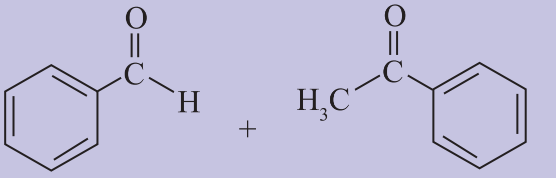
For example, a mixture of ethanal and propanal on reaction with dilute alkali followed by heating gives a mixture of four products (Fig.12.5).

Ketones can also be used as one of the components in cross aldol condensation .

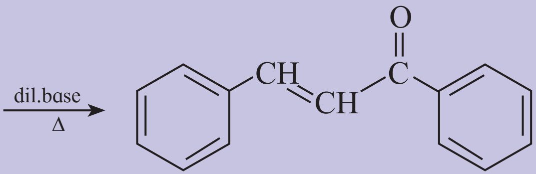
h. Cannizzaro reaction : This reaction is given only by aldehydes having no α-hydrogen atom. Aldehydes undergo self -oxidation and reduction reaction on heating with concentrated alkali. This is an example of **disproportionation reaction**. In cannizzaro reaction one molecule of an aldehyde is reduced to alcohol and at the same time second molecule is oxidized to carboxylic acid salt. For example, Formaldehyde and benzaldehyde

Use your brain power

- Observe the following reaction.



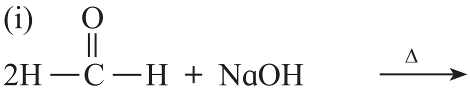
(Benzaldehyde) + (1-Phenylethanone)
(acetophenone)



(1,3-Diphenylprop-2-en-1-one)
(Benzal acetophenone)

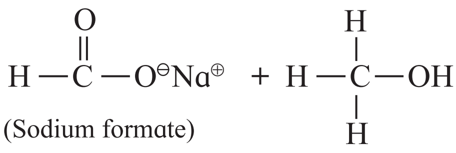
- Will this reaction give a mixture of products like a cross aldol reaction ?

(i)



$$2H-\overset{\overset{O}{\|}}{C}-H + NaOH \xrightarrow{\Delta}$$

(Formaldehyde) (sodium hydroxide)
(50%)



$$H-\overset{\overset{O}{\|}}{C}-O^{\ominus}Na^{\oplus} + H-\underset{H}{\overset{H}{C}}-OH$$

(Sodium formate) (Methanol)

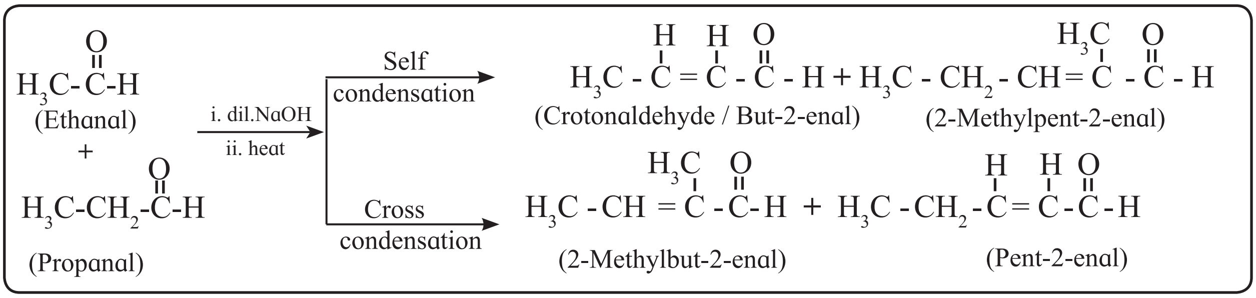
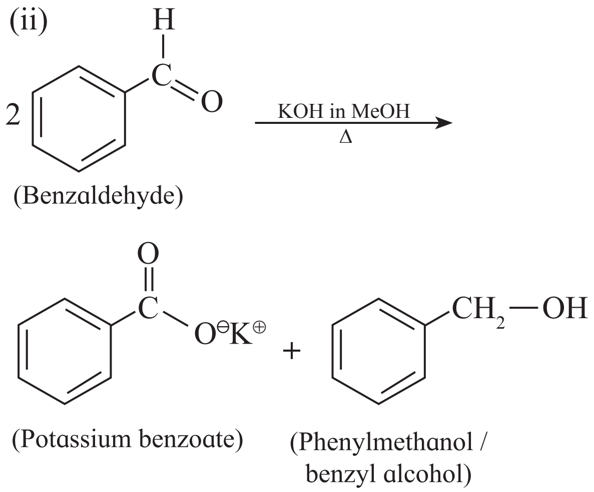


Fig. 12.5 : Cross aldol condensation

(ii)



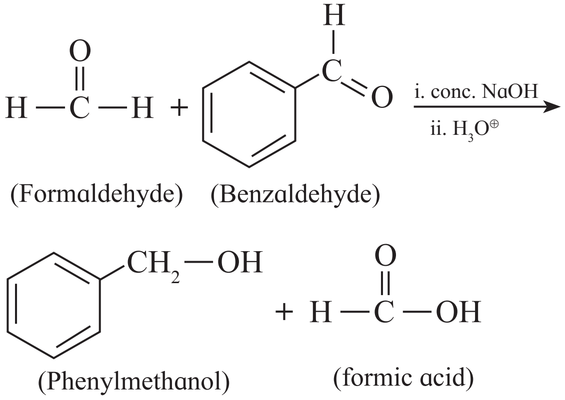
(Benzaldehyde)

(Potassium benzoate) (Phenylmethanol / benzyl alcohol)

Use your brain power

Can isobutyraldehyde undergo Cannizzaro reaction ? Explain.

Cross Cannizzaro reaction : When a mixture of formaldehyde and **non-enolisable** aldehyde (aldehyde with no α-hydrogen) is treated with a strong base, formaldehyde is oxidized to formic acid while the other non-enolisable is reduced to alcohol. Formic acid forms sodium formate with NaOH. On acidification sodium formate is converted into formic acid. For example :



(Formaldehyde) (Benzaldehyde)

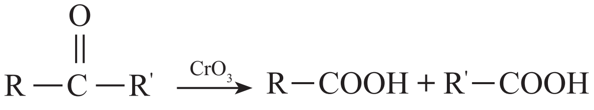
(Phenylmethanol) (formic acid)

12.8.3 Oxidation and reduction reactions of aldehydes and ketones ;

a. Oxidation of aldehydes and ketones by dilute HNO_3, $KMnO_4$ and $K_2Cr_2O_7$: **Aldehydes** are oxidized to the corresponding carboxylic acids by oxidant such as dilute nitric acid, potassium permanganate and sodium or potassium dichromate in acidic medium.

$$\underset{\text{(Aldehyde)}}{R-CHO} \xrightarrow[\text{dil. } H_2SO_4]{K_2Cr_2O_7} \underset{\text{(Carboxylic acid)}}{R-COOH}$$

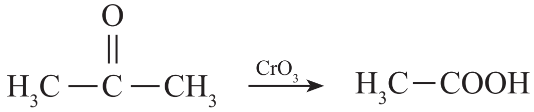
Ketones resist oxidation due to strong CO-C bond ,but they are oxidized by strong oxidizing agents such as CrO_3, alkaline $KMnO_4$ or hot concentrated HNO_3 to a mixture of carboxylic acids having less number of carbon atoms than the starting ketone. Thus, Oxidation of ketones is accompanied by breaking C - C bond.



$$\underset{\text{(Ketone)}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-R'} \xrightarrow{CrO_3} \underset{\text{(Carboxylic acids)}}{R-COOH + R'-COOH}$$

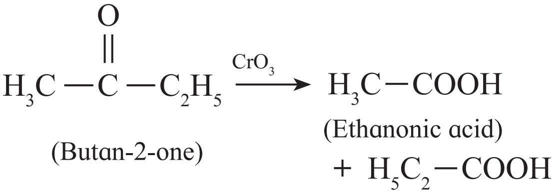
For example,

(i)



$$\underset{\text{(Acetone)}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3} \xrightarrow{CrO_3} \underset{\text{(Acetic Acid)}}{H_3C-COOH}$$

(ii)

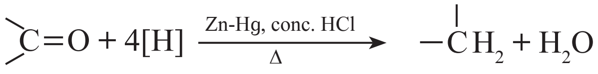


$$\underset{\text{(Butan-2-one)}}{H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5} \xrightarrow{CrO_3} \underset{\text{(Ethanonic acid)}}{H_3C-COOH} + \underset{\text{(Propanoic acid)}}{H_5C_2-COOH}$$

b. Clemmensen and Wolf-Kishner reduction: The carbonyl group of aldehydes and ketones is reduced to methylene group ($-CH_2-$) on treatment with zinc –amalgam and concentrated hydrochloric acid (**Clemmensen reduction**) or hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol (**Wolf-Kishner reduction**).

In both the reactions, oxygen is replaced by two hydrogen atoms.

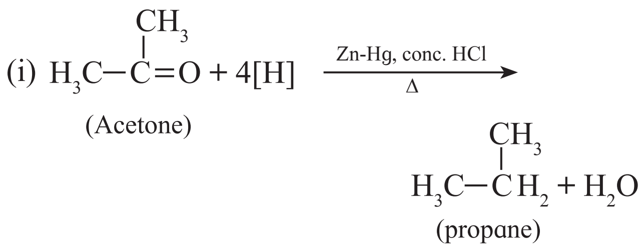
Clemmensen reduction :



$$>C=O + 4[H] \xrightarrow[\Delta]{\text{Zn-Hg, conc. HCl}} -\overset{|}{C}H_2 + H_2O$$

(Carbonyl group in aldehydes and ketones) (Methylene group)

For example :



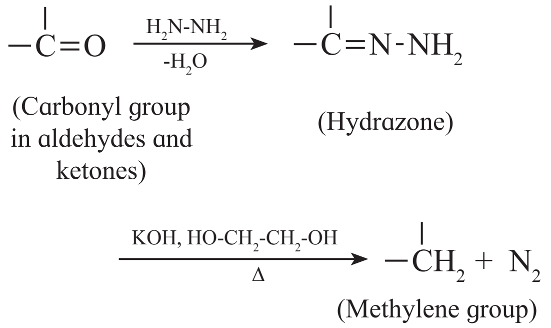
$$\text{(i) } H_3C-\overset{CH_3}{\overset{|}{C}}=O + 4[H] \xrightarrow[\Delta]{\text{Zn-Hg, conc. HCl}} H_3C-\overset{CH_3}{\overset{|}{C}}H_2 + H_2O$$

(Acetone) (propane)

$$\text{(ii) } CH_3-CH_2-CHO + 4[H] \xrightarrow[\Delta]{\text{Zn-Hg, conc. HCl}} CH_3-CH_2-CH_3 + H_2O$$

(Propanal) (Propane)

Wolf-Kishner reduction :



$$-\overset{|}{C}=O \xrightarrow[-H_2O]{H_2N\text{-}NH_2} -\overset{|}{C}=N\text{-}NH_2 \xrightarrow[\Delta]{\text{KOH, HO-}CH_2\text{-}CH_2\text{-OH}} -\overset{|}{C}H_2 + N_2$$

(Carbonyl group in aldehydes and ketones) (Hydrazone) (Methylene group)

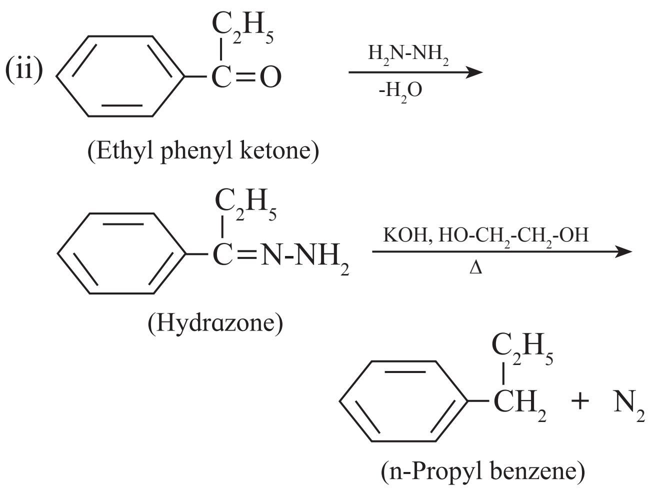
For example :

$$\text{(i) } C_2H_5-CHO \xrightarrow[-H_2O]{H_2N\text{-}NH_2} C_2H_5-CH=N\text{-}NH_2$$

(Propanal) (Hydrazone)

$$\xrightarrow[\Delta]{\text{KOH, HO-}CH_2\text{-}CH_2\text{-OH}} CH_3-CH_2-CH_3 + N_2$$

(Propane)



(Ethyl phenyl ketone)

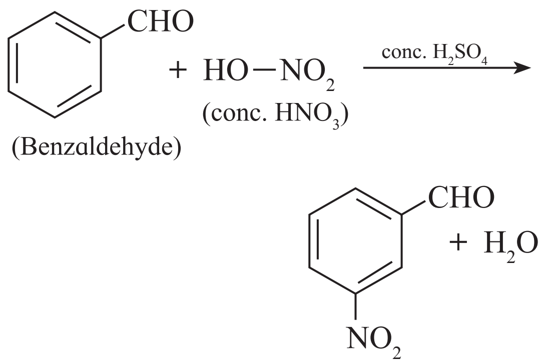
(Hydrazone)

(n-Propyl benzene)

Wolf-Kishner reduction is used to **synthesize** straight chain alkyl substituted benzenes which is not possible by Friedel-Crafts alkylation reaction.

12.8.4 Electrophilic substitution reactions:

Aromatic aldehydes and ketones undergo electrophilic substitution reactions such as nitration ,sulfonation and halogenation. The aldehydic (-CHO) and ketonic (>C=O) groups are electron-withdrawing by inductive as well as resonance effects. They deactivate the benzene ring at ***ortho-*** and ***para-*** positions. This results in the formation of ***meta***-product. For example ,



(Benzaldehyde) (conc. HNO_3)

(m-Nitrobenzaldehyde)

12.9 Chemical properties of carboxylic acids :

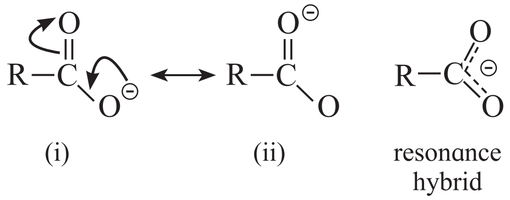
12.9.1 Acidic character of carboxylic acids:

The carboxyl group (- COOH) imparts acidic character to carboxylic acids. A carboxyl group is made of -OH group bonded to a carbonyl group. In aqueous solution the H atom in OH of carboxyl group dissociates as proton and carboxylate ion is formed as the conjugate base,

$$R\text{ - }COOH + H_2O \rightleftharpoons R\text{ - }COO^{\ominus} + H_3O^{\oplus}$$

(carboxylate ion)

Carboxylate ion is resonance stabilized by two equivalent resonance structures as shown below.



Carboxylate ion has two resonance structures (i) and (ii) and both of them are equivalent to each other (Refer to Std. XI Chemistry Textbook Chapter 14). This gives good resonance stabilization to carboxylate ion, which in turn gives acidic character to carboxylic acids.

Can you recall ?

What is the numerical parameter to express acid strength?

Remember...

Lower K_a value, higher pK_a: Weaker acid.

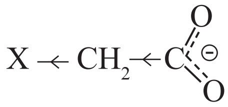
Higher K_a value, lower pKa : stronger acid.

Influence of electronic effects on acidity of carboxylic acids : All the carboxylic acids do not have the same pK_a value. The structure of 'R' in R-COOH has influence on the acid strength of carboxylic acids. Various haloacetic acids illustrate this point very well (Tables 12.8 and 12.9).

Table 12.8 : pK_a values of haloacetic acids

Acid	pK_a	Acid strength
$F-CH_2-COOH$	2.56	↓ decreases
$Cl-CH_2-COOH$	2.86	
$Br-CH_2-COOH$	2.90	
$I-CH_2-COOH$	3.18	
CH_3-COOH	4.76	

Halogens are electronegative atoms and exert electron withdrawing inductive effect (-I effect). The negatively charged carboxylate ion in the conjugate base of haloacetic acid gets stabilized by the -I effect of halogen. Which is responsible to diffuse the native charge.



$$X \leftarrow CH_2 \leftarrow \overset{O}{\underset{O}{C}}{}^{\ominus}$$

Higher the electronegativity of halogen greater is the stabilization of the conjugate base, stronger is the acid and smaller is the pK_a value.

Problem 12.1

Alcohols (R-OH), phenols (Ar-OH) and carboxylic acids (R-COOH) can undergo ionization of O-H bond to give away proton $H^{\oplus}$; yet they have different pK_a values, which are 16, 10 and 4.5 respectively. Explain

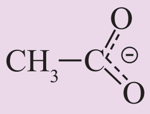
Solution : pK_a value is indicative of acid strength. Lower the pK_a value stronger the acid. Alcohols, phenols and carboxylic acids, all involve ionization of an O-H bond. But their different pK_a values indicate that their acid strength are different. This is because the resulting conjugate bases are stabilized to different extent.

Acid(HA)	Conjugate base($A^{\ominus}$)	Electronic effect	Stabilization/destabilization
R-O-H	$R \rightarrow O^{\ominus}$	+I effect of R group	destabilization of conjugate base
Ar-O-H	$Ar-O^{\ominus}$	-R effect or Ar group	stabilization of conjugate base is moderate because all the resonance structures are not equivalent to each other
$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-H$	$R-\overset{\overset{\displaystyle O}{\parallel}}{C}-\overset{\ominus}{O}$	-R effect of C = O group	stabilization is good because all the resonance structures are equivalent to each other

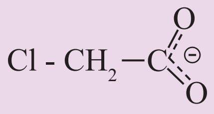
As the conjugate base of carboxylic acid is best stabilized, among the three, carboxylic acids are strongest and have the lowest pK_a value. As conjugate base of alcohols is destabilized, alcohols are weakest acids and have highest pK_a value. As conjugate base of phenols is moderately stabilized phenols are moderately acidic and have intermediate pK_a value.

Try this...

Compare the following two conjugate bases and answer.



(a)



(b)

- Indicate the inuctive effects of CH_3 - group in (a) and Cl - group in (b) by putting arrowheads in the middle of appropriate covalent bonds.
- Which species is stabilized by inductive effect, (a) or (b) ?
- Which species is destabilized by inductive effect, (a) or (b) ?

Use your brain power

- Compare the pK_a values and arrange the following in an increasing order of acid strength.

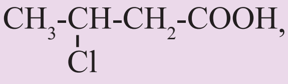
  Cl_3CCOOH, $ClCH_2COOH$, CH_3COOH, $Cl_2CHCOOH$
- Draw structures of conjugate bases of monochloroacetic acid and dichloroacetic acid. Which one is more stabilized by -I effect ?

Acidity of aromatic carboxylic acids : Benzoic acid is the simplest aromatic acid. From the pK_a value of benzoic acid (4.2) we understand that it is stronger than acetic acid (pK_a 4.76). The sp^2 hybrid carbon of aromatic ring exerts electron withdrawing inductive effect (-I effect) which stabilizes the conjugate base and increases the acid strength of aromatic acids.

Table 12.9 illustrates that more the number of electron withdrawing substituents higher is the acid strength.

Try this...

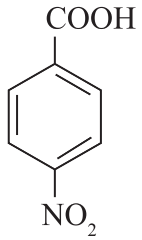
Arrange the following acids in order of their decreasing acidity.



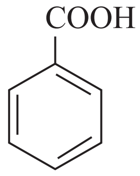
$CH_3\text{-}\underset{|\atop Cl}{CH}\text{-}CH_2\text{-}COOH$, $CCl_3\text{-}CH_2\text{-}COOH$,

CH_3COOH

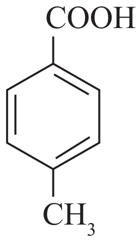
Electron–withdrawing groups like -Cl, -CN, and $-NO_2$ increase the acidity of substituted benzoic acids while electron –donating group like $–CH_3$, - OH , - OCH_3 and $-NH_2$ decrease the acidity of substituted benzoic acids .



(4-Nitrobenzoic acid) (pK_a = 3.41)



(Benzoic acid) (pK_a = 4.2)



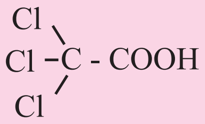
(4-Methylbenzoic acid) (pK_a = 4.4)

Try this...

Arrange the following carboxylic acids in order of increasing acidity.

m-Nitrobenzoic acid, Trichloroacetic acid, benzoic acid, α-Chlorobutyric acid.

Table 12.9 pK_a values of chloroacetic acids

Name	Structure	pK_a	Acid strength
Monochloroacetic acid	Cl - CH_2 - COOH	2.86	↓ increases
Dichloroacetic acid	 $Cl\text{ - }\underset{|\atop Cl}{CH}\text{ - }COOH$	1.26	
Trichloroacetic acid	 $Cl_3C\text{ - }COOH$	0.6	

12.9.2 Laboratory tests for carboxyl (-COOH) group

12.9.2 Laboratory tests for carboxyl (-COOH) group : The presence of -COOH group in carboxylic acids is identified by the following tests:

a. Litmus test : (valid for water soluble substances)

Aqueous solution of Organic compound containing –COOH group turns blue litmus red which indicates the presence of acidic functional group. (It may be noted that aqueous solutions of water soluble phenols also turn blue litmus red.)

b. Sodium bicarbonate test :

When sodium bicarbonate is added to an organic compound containing –COOH group, a brisk effervescence of carbon dioxide gas is evolved. Water insoluble acid goes in solution and gives precipitate on acidification with conc.HCl. This indicates the presence of –COOH group.

$$\underset{\text{(water insoluble)}}{\text{R - COOH}} + \text{NaHCO}_3\text{(aq)} \xrightarrow[-\text{H}_2\text{O}]{-\text{CO}_2}$$

$$\text{R - COONa(aq)} \xrightarrow{\text{HCl}} \text{R - COOH}\downarrow + \text{NaCl(aq)}$$

(Phenol does not evolve CO_2 gas with sodium bicarbonate. Hence, carboxylic acid and phenol are distinguished by this test.)

c. Ester test : One drop of concentrated sulfuric acid is added to a mixture of given organic compound containing –COOH group and one mL of ethanol, the reaction mixture is heated for 5 minutes in hot water bath. After this , hot solution is poured in a beaker containing water, fruity smell of ester confirms the presence of carboxylic acid.

$$\text{R - COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{warm}]{\text{H}^{\oplus}} \underset{\text{(ester)}}{\text{R - COO - C}_2\text{H}_5} + \text{H}_2\text{O}$$

12.9.3 Formation of acyl chloride

Reaction with PCl_3, PCl_5, $SOCl_2$: Carboxylic acids on heating with PCl_3, PCl_5, $SOCl_2$ give the corresponding acyl chlorides. Thionyl chloride ($SOCl_2$) is preferred because the byproducts formed are in gaseous state so they can easily escape from the reaction mixture. **In this reaction –OH group of –COOH is replaced by –Cl .**

$$\underset{\text{(Carboxylic acid)}}{\text{R-COOH}} + \text{SOCl}_2 \xrightarrow{\Delta} \underset{\text{(acyl chloride)}}{\text{R-COCl}} + \text{SO}_2\uparrow + \text{HCl}\uparrow$$

$$3\,\text{R-COOH} + \text{PCl}_3 \xrightarrow{\Delta} 3\,\text{R-COCl} + \text{P(OH)}_3$$

$$\text{R-COOH} + \text{PCl}_5 \xrightarrow{\Delta} \text{R-COCl} + \text{POCl}_3 + \text{HCl}$$

Use your brain power

Fill in the blanks and rewrite the balanced equations.

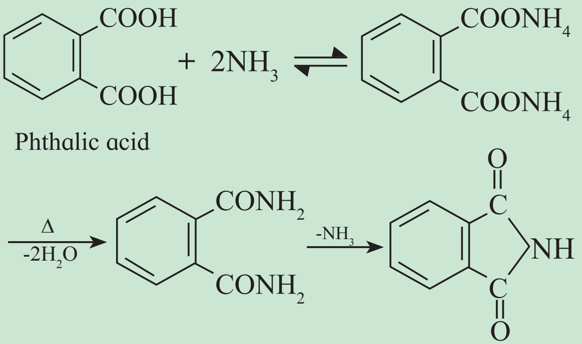
- CH_3COOH + thionyl chloride $\xrightarrow{\Delta}$ ...... + ... + ...
- CH_3-CH_2-COOH + ... $\xrightarrow{\Delta}$ ...... + ... + H_3PO_3
- C_6H_5-COOH + ... $\xrightarrow{\Delta}$ ...... + phosphorous oxylchloride + HCl
- CH_3-COOH + phosphorous trichloride $\xrightarrow{\Delta}$ ...... + ...
- CH_3-COOH $\xrightleftharpoons{\text{NH}_3}$ ...... $\xrightarrow{\Delta}$ ......
- ...... $\xrightleftharpoons{\text{NH}_3}$ ...... $\xrightarrow{\Delta}$ C_6H_5-$CONH_2$

12.9.4 Reaction with ammonia : Formation of amide

12.9.4 Reaction with ammonia : Formation of amide : Carboxylic acids react with ammonia to from ammonium carboxylate salt which on further strong heating at high temperature decomposes to give acid amide.

$$\underset{\text{(Carboxylic acid)}}{\text{R-COOH}} + \text{NH}_3 \rightleftharpoons \underset{\text{(ammonium carboxylate)}}{\text{R-CO}\overset{\ominus}{\text{O}}\overset{\oplus}{\text{NH}_4}} \xrightarrow[-\text{H}_2\text{O}]{\Delta} \underset{\text{(Acid amide)}}{\text{R-CONH}_2}$$

Do you know ?



Phthalic acid

Phthalimide

b. Acid amides can also be prepared by reacting acid chloride with ammonia.

$$R-COCl + NH_3 \longrightarrow R-CONH_2 + HCl$$

(Acyl chloride) (Acid amide)

12.9.5 Formation of acid anhydride :

Can you tell ?

What is the term used for elimination of water molecule ?

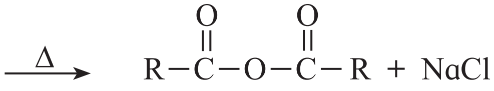
Mono carboxylic acids on heating with strong dehydrating agent like P_2O_5 concentrated H_2SO_4 give acid anhydrides. The reaction is reversible. Anhydrides are readily hydrolyzed back to acids on reaction with water.

(Carboxylic acid) (Acid anhydride)

Better yield of acid anhydride is obtained by heating sodium carboxylate with acyl chloride.

$$R-CO\overset{\ominus}{O}\overset{\oplus}{Na} + R-COCl$$

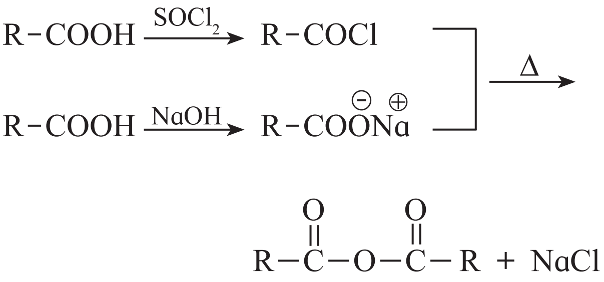
(sodium carboxylate) (acyl chloride)



$$\xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + NaCl$$

(acid anhydride)

Acyl chloride and sodium salt of acid are prepared by reacting carboxylic acid separately with thionyl chloride and sodium hydroxide respectively.



$$R-COOH \xrightarrow{SOCl_2} R-COCl$$
$$R-COOH \xrightarrow{NaOH} R-CO\overset{\ominus}{O}\overset{\oplus}{Na}$$
$$\xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + NaCl$$

(Anhydride)

Can you recall ?

Which molecule is eliminated in a decarboxylation ?

12.9.6 Decarboxylation of carboxylic acids :

Sodium salts of carboxylic acids on heating with soda lime give hydrocarbons which contain one carbon atom less than the carboxylic acid. For example,

$$R-CO\overset{\ominus}{O}\overset{\oplus}{Na} + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

$$CH_3-CO\overset{\ominus}{O}\overset{\oplus}{Na} + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

(Sodium acetate) (Methane)

12.9.7 Reduction of carboxylic acids :

Carboxylic acids are reduced to primary alcohols by powerful reducing agent like lithium aluminium hydride. **Carboxylic acid** can also be reduced by diborane (diborane does not reduce –COOR , -NO_2, -X).

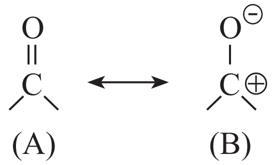
(Note : Sodium borohydride ($NaBH_4$)does not reduce-COOH group).

$$R-COOH + LiAlH_4 \underset{ether}{\overset{dry}{\rightleftharpoons}} R-CH_2OH$$

Exercises

1. Choose the most correct option.

i. In the following resonating structures A and B, the number of unshared electrons in valence shell present on oxygen respectively are



a. 2, 4　　b. 2, 6

c. 4, 6　　d. 6, 4

ii. In the Wolf -Kishner reduction, alkyl aryl ketones are reduced to alkyl benzenes. During this change, ketones are first converted into

a. acids　　b. alcohols

c. hydrazones　　d. alkenes

iii. Aldol condensation is

a. electrophilic substitution reaction

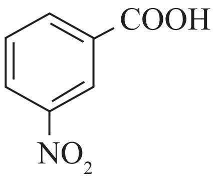
b. nucleophilic substitution reaction

c. elimination reaction

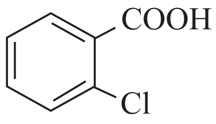
d. addition - elimination reaction

iv. Which one of the following has lowest acidity ?

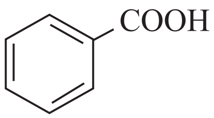
a.



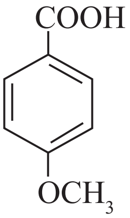
b.



c.



d.



v. Diborane reduces

a. ester group　　b. nitro group

c. halo group　　d. acid group

vi. Benzaldehyde does NOT show positive test with

a. Schiff reagent

b. Tollens' ragent

c. Sodium bisulphite solution

d. Fehling solution

2. Answer the following in one sentence

i. What are aromatic ketones?

ii. Is phenyl acetic acid an aromatic carboxylic acid ?

iii. Write reaction showing conversion of ethanenitrile into ethanol.

iv. Predict the product of the following reaction:

$$CH_3-CH_2-COOCH_3 \xrightarrow[\text{ii. } H_3O^{\oplus}]{\text{i. AlH (i-Bu)}_2} ?$$

v. Name the product obtained by reacting toluene with carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride.

vi. Write reaction showing conversion of Benzonitrile into benzoic acid.

vii. Name the product obtained by the oxidation of 1,2,3,4-tetrahydronaphthalene with acidified potassium permanganate .

viii. What is formalin ?

ix. Arrange the following compounds in the increasing order of their boiling points :

Formaldehyde, ethane, methyl alcohol.

x. Acetic acid is prepared from methyl magnesium bromide and dry ice in presence of dry ether. Name the compound which serves not only reagent but also as cooling agent in the reaction.

3. Answer in brief.

i. Observe the following equation of reaction of Tollens' reagent with aldehyde. How do we know that a redox reaction has taken place. Explain.

$$R-CHO + 2\ Ag(NH_3)_2^+ + OH^- \xrightarrow{\Delta} R-COO^- + 2\ Ag\downarrow + 4\ NH_3 + 2\ H_2O$$

ii. Formic acid is stronger than acetic acid. Explain.

iii. What is the action of hydrazine on cyclopentanone in presence of ---.

KOH in ethylene glycol ?

iv. Write reaction showing conversion of Acetaldehyde into acetaldehyde dimethyl acetal.

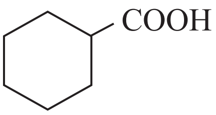
v. Aldehydes are more reactive toward nucleophilic addition reactions than ketones. Explain.

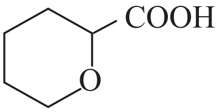
vi. Write reaction showing the action of the following reagent on propanenitrile –

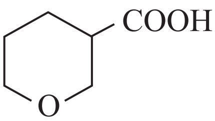
a. Dilute NaOH

b. Dilute HCl ?

vi. Arrange the following carboxylic acids with increasing order of their acidic strength and justify your answer.







4. Answer the following

i. Write a note on –

a. Cannizaro reaction

b. Stephen reaction.

ii. What is the action of the following reagents on toluene ?

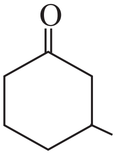
a. Alkaline $KMnO_4$, dil. HCl and heat

b. CrO_2Cl_2 in CS_2

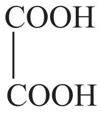
c. Acetyl chloride in presence of anhydrous $AlCl_3$.

iii. Write the IUPAC names of the following structures :

a.



b.



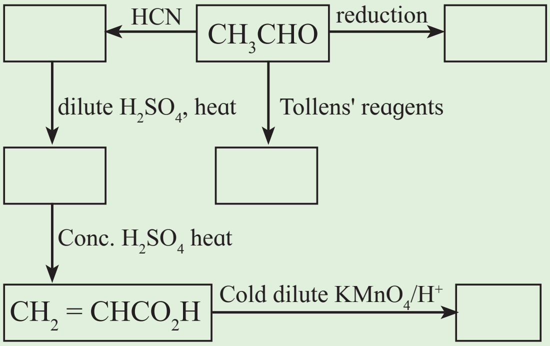
$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

iv. Write reaction showing conversion of p- bromoisopropyl benzene into p-Isopropyl benzoic acid (3 steps).

v. Write reaction showing aldol condensation of cyclohexanone.

Activity :

Draw and complete the following reaction scheme which starts with acetaldehyde. In each empty box, write the structural formula of the organic compound that would be formed.



13 AMINES

Can you recall ?

- Write some examples of nitrogen containing organic compounds.
- What are the types of amines?

Amines are nitrogen containing organic compounds having basic character. Amines are present in structure of many natural compounds like proteins, vitamins, hormones and many plant products like nicotine.

13.1 Classification of Amines : Amines are classified as primary (1°), secondary (2°) and tertiary (3°) amines. Their structures are obtained in simple way by replacing one, two or three hydrogen atoms of NH_3 molecule by alkyl/aryl groups (see Table 13.1).

Secondary and tertiary amines are further classified as simple / symmetrical amines and mixed / unsymmetrical amines. When all the alkyl or aryl groups on nitrogen are same, it is a simple amine. If these groups are different, then the amine is a mixed amine.

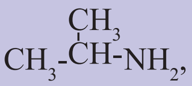
Amines are also divided into two major classes, namely, aliphatic and aromatic amines on the basis of nature of the groups attached to the nitrogen atom.

Use your brain power

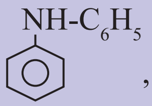
Classify the following amines as simple/mixed; 1°, 2°, 3° and aliphatic or aromatic.

$(C_2H_5)_2NH$, $(CH_3)_3N$, C_2H_5-NH-CH_3,

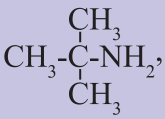
C_6H_5-NH_2,



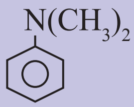
$CH_3\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}NH_2$,



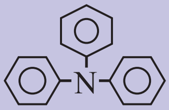
,



$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{-}NH_2$,



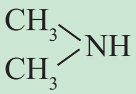
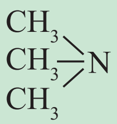
,



Remember...

Other organic compopunds like alkyl halides or alcohols are classified as 1°, 2°, 3° depending upon the nature of the carbon atom to which functional group is attached where as amines are classified depending upon the number of alkyl or aryl groups directly attached to the nitrogen atom. Thus, isopropyl amine is 1^0 amine, but isopropyl alcohol is 2^0 alcohol.

Table 13.1 Types of amines

Type	Functional group		Examples	
	Name	Formula	Formula	Common Name
Primary amine, (1^0)	Amino	$-NH_2$	C_2H_5-NH_2	Ethylamine
Secondary amine, (2^0)	Imino	$>NH$	 $\begin{matrix}CH_3\\CH_3\end{matrix}\rangle NH$	Dimethylamine
Tertiary amine, (3^0)	Tertiary nitrogen	$\geqslant N$	 $\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\rangle N$	Trimethylamine

13.2 Nomenclature of Amines :

13.2.1 Common names : Common names of aliphatic amines are given by writing the name of alkyl group followed by suffix-amine, that is, 'alkyl amine'. In the case of mixed amines, the names of alkyl groups are written in alphabetical order. If two or three identical alkyl groups are attached to nitrogen atom, the prefix 'di-' or 'tri-' is added before the name of alkyl group. The parent arylamine, $C_6H_5\text{-}NH_2$, is named as aniline. Other aromatic amines are named as derivatives of aniline (see Table 13.2).

13.2.2 IUPAC names : In IUPAC system, primary amines are named by replacing the ending 'e' of the parent alkane by suffix -amine (alkanamine). A locant indicating the position of amino group is added before the suffix amine. When two or more amino groups are present, the prefix 'di-', 'tri-' etc. are used with proper locant. In this case the ending 'e' of parent alkane is retained.

Secondary or tertiary amines are named as N-substituted derivatives of primary amines. The largest alkyl group attached to nitrogen is taken as the parent alkane and other alkyl groups as N-substituents. While naming arylamines ending 'e' of arene is replaced by 'amine'. The common name of aniline is also accepted by IUPAC (see Table 13.2).

Remember...

The name of amine (common or IUPAC) is always written as one word. For example: $C_2H_5\text{-}NH_2$ Ethylamine (Ethanamine)

Try this...

Draw possible structures of all the isomers of $C_4H_{11}N$. Write their common as well as IUPAC names.

13.3 Preparation of Amines :

13.3.1 : By ammonolysis of alkyl halides :

When alkyl halide is heated with alcoholic solution of excess ammonia it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino ($-NH_2$) group to form primary amine. This process of breaking of C-X bond by ammonia is known as ammonolysis. The reaction is also known as alkylation of ammonia. The reaction is carried out in a sealed tube at 373 K. It may be noted that the primary amine obtained in the 1st step is stronger nucleophile than ammonia. Hence, it further reacts with alkyl halide to form secondary and tertiary amines and finally quaternary ammonium salt if NH_3 is not used in large excess.

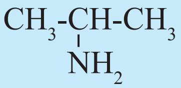
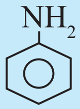
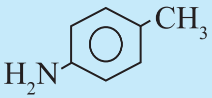
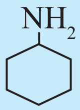
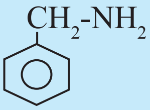
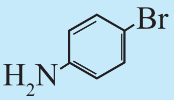
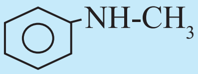
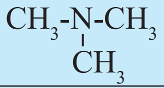
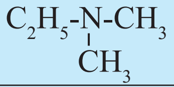
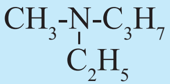
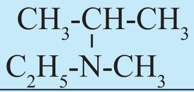
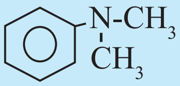
$$R\text{-}X + \underset{\text{(excess)}}{NH_3(alc).} \xrightarrow{\Delta} \underset{1^0\text{ amine}}{R\text{-}NH_2}$$

The order of reactivity of alkyl halides with ammonia is R-I > R-Br > R-Cl.

Use your brain power

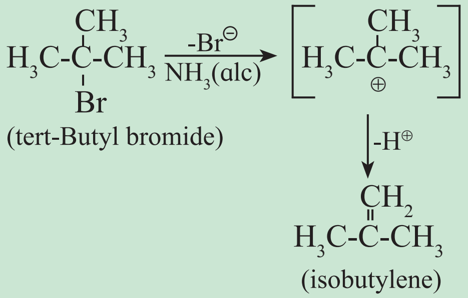
- Write chemical equations for
  1. reaction of alc. NH_3 with C_2H_5I.
  2. Ammonolysis of benzyl chloride followed by the reaction with two moles of $CH_3\text{-}I$.
- Why is ammonolysis of alkyl halide not a suitable method for the preparation of primary amine ?

Table 13.2 : Common and IUPAC names of some alkyl and arylamines

Amines	Common names	IUPAC names
a. Primary amines :		
$CH_3\text{-}NH_2$	Methylamine	Methanamine
$CH_3\text{-}CH_2\text{-}CH_2\text{-}NH_2$	n-Propylamine	Propan-1-amine
 $CH_3\text{-}\underset{\displaystyle NH_2}{\underset{\mid}{CH}}\text{-}CH_3$	Isopropylamine	Propan-2-amine
$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$	Ethylenediamine	Ethane-1, 2-diamine
$CH_2\text{=}CH\text{-}CH_2\text{-}NH_2$	Allylamine	Prop-2-en-1-amine
	Aniline/ Phenylamine	Aniline or Benzenamine
$H_2N\text{-}(CH_2)_6\text{-}NH_2$	Hexamethylenediamine	Hexane-1, 6-diamine
	p-Toluidine	4-Methylaniline
	Cyclohexylamine	Cyclohexanamine
	Benzylamine	Phenylmethanamine
	p-Bromoaniline	4-Bromoaniline or 4-Bromobenzenamine
b. Secondary Amines		
$CH_3\text{-}NH\text{-}CH_3$	Dimethylamine	N-methylmethanamine
$CH_3\text{-}CH_2\text{-}NH\text{-}CH_3$	Ethylmethylamine	N-methylethanamine
	Methylphenylamine	N-methylaniline or N-methylbenzenamine
$C_6H_5\text{-}NH\text{-}C_6H_5$	Diphenylamine	N-Phenylbenzenamine
c. Tertiary Amines		
 $CH_3\text{-}\underset{\displaystyle CH_3}{\underset{\mid}{N}}\text{-}CH_3$	Trimethylamine	N, N-Dimethylmethanamine
 $C_2H_5\text{-}\underset{\displaystyle CH_3}{\underset{\mid}{N}}\text{-}CH_3$	Ethyldimethylamine	N, N-Dimethylethanamine
 $CH_3\text{-}\underset{\displaystyle C_2H_5}{\underset{\mid}{N}}\text{-}C_3H_7$	Ethylmethyln-propylamine	N-Ethyl-N-methyl propan-1-amine
 $CH_3\text{-}\overset{\displaystyle CH_3\text{-}\overset{}{CH}\text{-}CH_3}{}$ $C_2H_5\text{-}N\text{-}CH_3$	Ethylmethylisopropylamine	N-Ethyl-N-methyl propan-2-amine
	N, N-Dimethylaniline	N, N-Dimethylbenzenamine

Do you know ?

When tert-butyl bromide is treated with alcoholic NH_3, isobutylene is formed. This is the result of elimination reaction preferred over nucleophilic substitution through the stable tertiary butyl carbocation intermediate.



13.3.2 Reduction of nitrocompounds :

Aliphatic and aromatic nitrocompounds can be reduced to primary amines by using metal-acid mixture (Sn/HCl or Fe/HCl or Zn/HCl) or catalytic hydrogenation (H_2/Ni or Pt or Pd) or $LiAlH_4$ in ether.

$$R-NO_2 + 6[H] \xrightarrow{Sn/HCl} R-NH_2 + 2H_2O$$

13.3.3 Reduction of alkyl cyanide (alkanenitriles) :

Can you recall ?

- How is alkyl halide converted into alkyl cyanide ?

Primary amines can be obtained by the reduction of alkyl cyanide with sodium and ethanol. This is known as **Mendius reduction**. The reaction can also be brought about by lithium aluminium hydride.

$$R-C\equiv N + 4[H] \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} \underset{1^\circ \text{ amine}}{R-CH_2-NH_2}$$

Problem 13.1 : Write reaction to convert methyl bromide into ethyl amine ? Also, comment on the number of carbon atoms in the starting compound and the product.

Solution : Methyl bromide can be converted into ethyl amine in two stage reaction sequence as shown below.

$$CH_3-Br + KCN \longrightarrow CH_3-CN + KBr$$

$$CH_3-CN \xrightarrow[\text{(reduction)}]{Na/C_2H_5OH} CH_3-CH_2-NH_2$$

The starting compound methyl bromide contains one carbon atom while the product ethylamine contains two carbon atoms. A reaction in which number of carbons increases involves a step up reaction. The overall conversion of methyl bromide into ethyl amine is a step up conversion.

Use your brain power

Use your brain power:

Identify 'A' and 'B' in the following conversions.

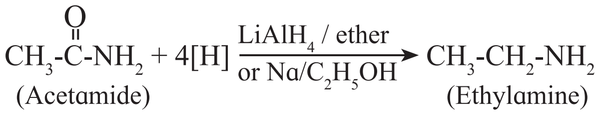
(i) $CH_3-I \xrightarrow{KCN} A \xrightarrow{Na/C_2H_5OH} B$

(ii) $CH_3-Br \xrightarrow{AgNO_2} A \xrightarrow{Sn/HCl} B$

(iii) $C_2H_5-I \xrightarrow{AgCN} A \xrightarrow{Na/C_2H_5OH} B$

13.3.4 By reduction of amides :

Primary amines having same number of carbon atoms can be obtained by the reduction of amides by $LiAlH_4$ in ether or by Na/C_2H_5OH.



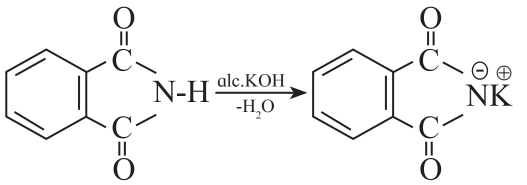
$$\underset{\text{(Acetamide)}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + 4[H] \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4\text{ / ether}} \underset{\text{(Ethylamine)}}{CH_3-CH_2-NH_2}$$

13.3.5 Gabriel phthalimide synthesis : This method is used for the synthesis of primary amine. It involves the following three stages.

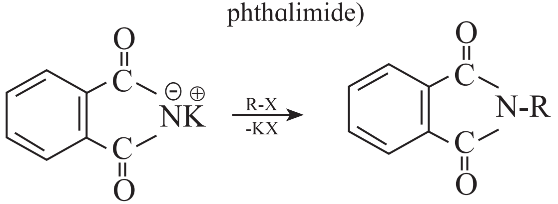
i. Formation of potassium salt of phthalimide from phthalimide on reaction with alcoholic potassium hydroxide.

ii. Formation of N-alkyl phthalimide from the potassium salt by reaction with alkyl halide.

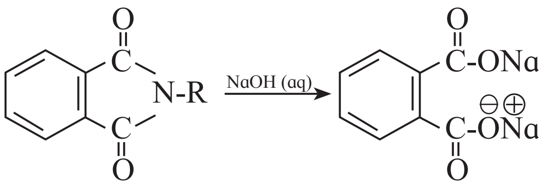
iii. Alkaline hydrolysis of N-alkyl phthalimide to form the corresponding primary amine.

i. 

(Phthalimide) (Potassium salt of phthalimide)

ii. 

(N-Alkylphthalimide)

iii. 

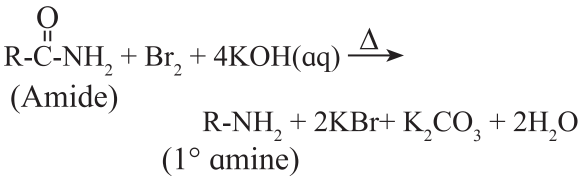
(sodium phthalate)

+ **R-NH$_2$**
(1° amine)

Aromatic amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

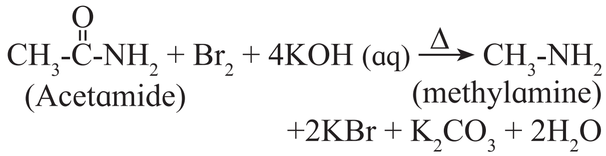
13.3.6 By Hofmann degradation (Hofmann rearrangement / Hofmann bromamide degradation / Hofmann hypobromite degradation) :

This is a good laboratory method for the conversion of an amide into primary amine containing one carbon less. The reaction is brought about by warming the amide with bromine and concentrated aqueous KOH solution.



$$\underset{\text{(Amide)}}{R-\overset{\overset{O}{\|}}{C}-NH_2} + Br_2 + 4KOH(aq) \xrightarrow{\Delta} \underset{\text{(1° amine)}}{R-NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

For example :



$$\underset{\text{(Acetamide)}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2} + Br_2 + 4KOH\ (aq) \xrightarrow{\Delta} \underset{\text{(methylamine)}}{CH_3-NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

The overall result is removal of the $-\overset{\overset{O}{\|}}{C}-$ group from the amide. As the product contains one carbon atom less than the original amide. It is a **step down** reaction.

Use your brain power

Write the chemical equations for the following conversions :

i. Methyl chloride to ethylamine.

ii. Benzamide to aniline.

iii. 1, 4 - Dichlorobutane to hexane - 1, 6 - diamine.

iv. Benzamide to benzylamine.

13.4 Physical properties of Amines :

13.4.1 Intermolecular forces, boiling points and solubility : The N-H bond in amines is polar because the electronegativities of Nitrogen (3.0) and Hydrogen (2.1) are different. Due to the polar nature of N-H bond primary and secondary amines have intermolecular hydrogen bonding. The intermolecular hydrogen bonding is to greater extent in primary amine than in secondary amines, because primary amines have two hydrogen atoms bonded to nitrogen for hydrogen bond formation (see Fig 13.1).

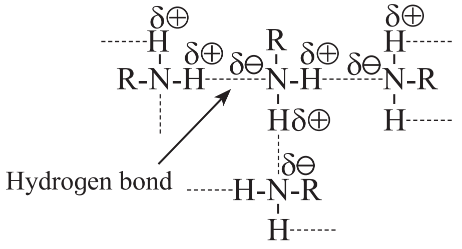


Fig. 13.1 : Intermolecular hydrogen bonding in primary amines

Tertiary amines do not have intermolecular hydrogen bonding as there is no hydrogen atom on nitrogen of tertiary amine. But due to polar N-C bonds, tertiary amines are polar molecules, and have intermolecular dipole-dipole attractive forces. Thus intermolecular forces of attraction are strongest in primary amines and weakest in tertiary amines.

The observed order of boiling points of isomeric amines is : primary amine > secondary amine > tertiary amine (see Table 13.3 serial numbers 1, 2, 3). It can be explained on the basis of the intermolecular forces in them.

The lower aliphatic amines are gases with fishy odour, middle members are liquids and higher members are solids under ordinary temperature and pressure.

Aniline and other arylamines are usually colourless liquids but get coloured as they are easily oxidised by air.

Due to their ability to form hydrogen bond with water molecule, lower aliphatic amines are soluble in water (see Fig. 13.2). Solubility of amines decreases with increase in molar mass of amines due to increase in size of hydrophobic alkyl group. Aromatic amines and higher aliphatic amines are insoluble in water.

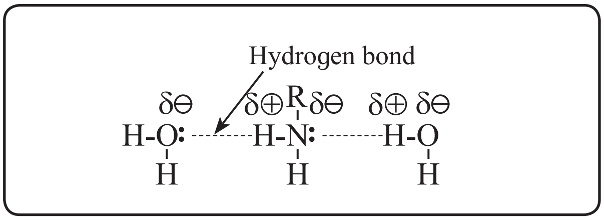


Fig. 13.2 : Hydrogen bonding between amine and water molecule

Since N-H bonds in amines are less polar than O-H bond in alcohol, water solubilities of alcohols, amines and alkanes of comparable molar mass in water are in the decreasing order: **alcohols > amines > alkanes.**

The order of boiling points of alkanes, amines, alcohols and carboxylic acid of comparable molar mass is as follows :

Alkanes < Amines < Alcohols < Carboxylic acid. (Table 13.3, serial number 4, 5, 6, 7)

Use your brain power

Arrange the following :

a. In decreasing order of the b.p.
C_2H_5-OH, C_2H_5-NH$_2$, $(CH_3)_2NH$

b. In increasing order of solubility in water:
C_2H_5-NH$_2$, C_3H_7-NH$_2$, C_6H_5-NH$_2$

Table 13.3 Boiling points of alkane, alcohol and amines of similar molar masses

Sr. No	Compound	Molar mass	B.P. (K)
1	n-$C_4H_9NH_2$	73	350.8
2	$(C_2H_5)_2NH$	73	329.3
3	$C_2H_5N(CH_3)_2$	73	310.5
4	C_2H_5COOH	74	414.4
5	n-C_4H_9OH	74	390.3
6	$(CH_3)_3C\text{-}NH_2$	73	318.15
7	$C_2H_5CH(CH_3)_2$	72	300.8

13.5 Basicity of Amines

The basic nature of amines is due to presence of a lone pair of electrons on the nitrogen atom. In terms of Lewis theory, amines are bases because they can share a lone pair of electrons on 'N' atom with an electron deficient species. For example : Trimethylamine shares its lone pair of electrons with the electron deficient boron trifluoride.

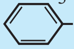
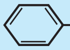
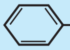
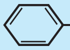
$$Me_3N\colon + BF_3 \longrightarrow Me_3\overset{\oplus}{N}\text{-}\overset{\ominus}{B}F_3$$

Basic strength of amines is expressed quantitatively as K_b or pK_b value. In terms of Lowry-Bronsted theory, the basic nature of amines is explained by writing the following equilibrium.

$$\underset{\text{(amine)}}{>N\colon} + H_2O \rightleftharpoons \underset{\text{(conjugate acid)}}{>\overset{\oplus}{N}\text{-H}} + \overset{\ominus}{O}H \text{ .... (13.1)}$$

In this equilibrium amine accepts $H^{\oplus}$, hence an amine is a Lowry-Bronsted base. For stronger base, this equilibrium shifts towards right, thereby the K_b value is larger and pK_b value is smaller and vice versa (refer to Chapter 3). Table 13.4 gives pK_b values of some amines.

Table 13.4 : pK_b Values of some amines in aqueous medium

Amine	Structural Formula	pK_b value
Primary alkanamines :		
Methanamine	CH_3-NH_2	3.38
Ethanamine	$CH_3-CH_2-NH_2$	3.29
Propan-2-amine	$(CH_3)_2-CH-NH_2$	3.40
Phenylmethanamine	$-CH_2-NH_2$	4.70
Secondary alkanamines :		
N-Methylmethanamine	$(CH_3)_2NH$	3.27
N-Ethylethanamine	$(CH_3CH_2)_2NH$	3.00
Tertiary alkanamines :		
N, N-Dimethylmethanamine	$(CH_3)_3N$	4.22
N, N-Diethylethanamine	$(CH_3CH_2)_3N$	3.25
Ammonia	NH_3	4.75
Arylamines :		
Benzenamine (aniline)	$-NH_2$	9.38
N-Methylaniline	$-NHCH_3$	9.30
N, N-Dimethylaniline	$-N(CH_3)_2$	8.92

13.5.1 : Basic strength of aliphatic amines :

The trend in the observed pK_b values (see table 13.4) and basic strength of 1°, 2°, 3° amines and NH_3 can be represented as shown below :

Order of pK_b values:

$NH_3 > R-NH_2 > R_2NH < R_3N$

Order of basic strength :

$NH_3 < R-NH_2 < R_2NH > R_3N$ .... (13.2)

Thus as per the observed pK_b values of the aliphatic amines, **secondary amines are the strongest bases**. Basic strength increases as we move from NH_3 to $R-NH_2$ and from $R-NH_2$ to R_2NH, but basic strength decreases as we move from R_2NH to R_3N (Table 13.4).

The basic strength and the corresponding pK_b value depends upon the position of the equilibrium shown in Eq. (13.1). Greater the stabilization of the conjugate acid more on right side the equilibrium will lie and stronger will be the base and smaller will be its pK_b value.

Can you recall ?

- What is meant by +I effect ?
- Which of the following species is better stabilized and by which effect ?

$CH_3-\overset{\oplus}{C}H_2$ and $CH_3-\overset{\oplus}{C}H-CH_3$

Basicity of amines is related to the structural effects which influence stabilization of various species. Greater is the stabilization of the protonated amine, that is, the conjugate acid, greater is the basicity of the amine.

Use your brain power

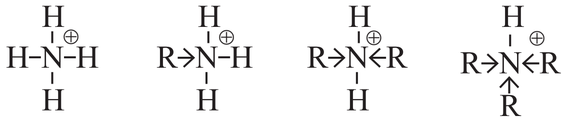
Refer to pK_b values from Table 13.4 and answer which compound from the following pairs is stronger base ?

i. CH_3-NH_2 and $(CH_3)_2NH$

ii. $(C_2H_5)_2NH$ and $(C_2H_5)_3N$

iii. NH_3 and $(CH_3)_2CH-NH_2$

a. Influence of +I effect on stabilization of conjugate acids of aliphatic amines and NH_3 can be represented as shown below :



An alkyl group exerts electron releasing inductive effect (+I) which stabilizes positive charge on atom bonded to it. As we move from conjugate acid of ammonia ($NH_4^{\oplus}$) to that of tertiary amine ($R_3NH^{\oplus}$), the number of alkyl groups (R) bonded to Nitrogen goes on increasing steadily. This results in increasing stabilization of the conjugate acids and thereby an increasing order of basic strength is expected.

Order of stabilization :

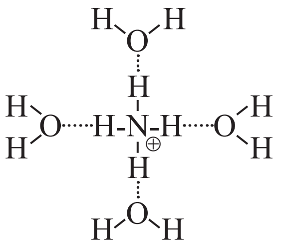
$$\overset{\oplus}{N}H_4 < R\text{-}\overset{\oplus}{N}H_3 < R_2\overset{\oplus}{N}H_2 < R_3\overset{\oplus}{N}\text{-}H$$

Expected order of basic strength :

$$NH_3 < R\text{-}NH_2 < R_2NH < R_3N$$

The expected order of basic strength on the basis of +I effect differs from the observed order (Eq.13.2). It is seen that the observed increasing basic strength from ammonia to amine and from 1° amine to 2° amine is explained on the basis of increased stabilization of conjugate acids by +I effect of increased number of alkyl (R) groups. However, decreased basic strength of 3° amine implies that the conjugate acid of 3° amine is less stabilized even though the +I effect of three alkyl groups in $R_3\overset{\oplus}{N}H$ is expected to be large. This is suggestive of existance of another influencing factor in stabilization of conjugate acids of amines.

b. Influence of solvation by water on stabilization of conjugate acids of aliphatic amines and ammonia can be represented as shown below :



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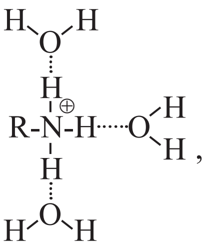

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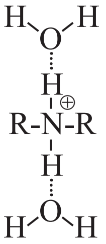

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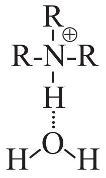
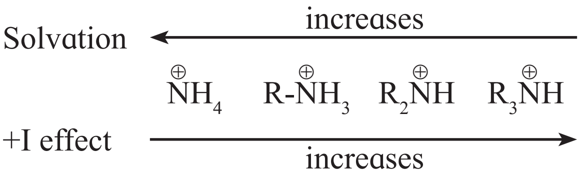


The solvent water stabilizes the conjugate acid by hydrogen bonding through the 'H' bonded to the 'N⊕'. The number of 'H' atoms bonded to the 'N⊕' decreaes from 4 in $NH_4^{\oplus}$ to 1 in $R_3NH^{\oplus}$. As a result $NH_4^{\oplus}$ is best stabilized by solvation while the stabilization by solvation is very poor in $R_3NH^{\oplus}$.

c. Combined influence of +I effect and solvation on stabilization if conjugate acids of aliphatic amines decides the observed basic strength and pK_b value. These two influencing factors operate in opposite directions.



The net results is that as we move from NH_3 to RNH_2 to R_2NH, the basic strength increases due to better stabilization of the corresponding conjugate acids. But 3° amine is weaker base than 2° amine because the stabilization of conjugate acid of 3° amine by solvation is very poor.

13.5.2 Basicity of arylamines :

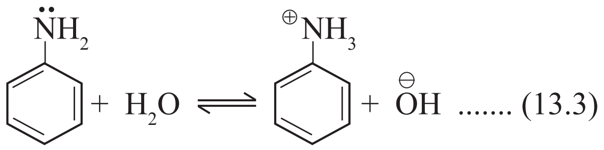
Can you recall ?

Refer to Table 13.4 and answer :

Are the pK_b values of aniline, N-methylaniline and N, N-dimethylaniline larger or smaller than those of NH_3 and CH_3NH_2 ?

Which one of the two, aniline or CH_3NH_2, is stronger base ?

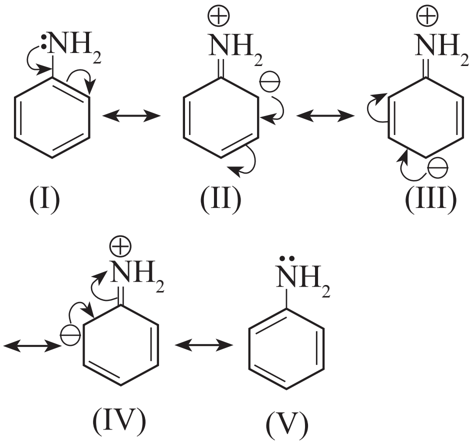
From the pK_b values we understand that arylamines in general are weaker bases than ammonia and aliphatic amines. Strength of arylamines is explained in accordance with Lowery Bronsted theory by writing the following equilibrium (Eq. 13.3) For aniline (similar to eq. 13.1).



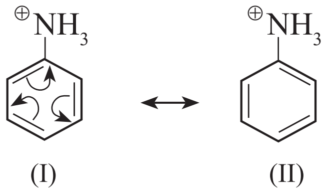
(Base) (Conjugate acid)

Here, both the species base and conjugate acid, are resonance stabilized but to different extent.

In arylamines, the $-NH_2$ group is attached directly to an aromatic ring. The lone pair of electrons on nitrogen is conjugated to the aromatic ring and is less available for protonation. Aniline is resonance stabilized by the following five resonance structures.



On the other hand anilinium ion obtained by accepting a proton does not have lone pair of electrons on nitrogen. Hence it can be stabilized by only two resonance structures and therefore less stabilized than aniline.



As a result the equilibrium (13.3) is shifted towards left side. This makes aniline (and also other arylamines) weaker bases than aliphatic amines and ammonia.

Use your brain power

Arrange the following amines in decreasing order of their basic strength -

NH_3, $CH_3\text{-}NH_2$, $(CH_3)_2NH$, $C_6H_5NH_2$.

13.6 Chemical properties of amines

13.6.1 Laboratory test for amines :

a. Test for amines as the 'base' : All amines 1°, 2° and 3° are basic compounds. Aqueous solution of water soluble amines turns red litmus blue.

The 'basic' nature of amines is detected in laboratory by reaction with aqueous solution of strong mineral acid HCl.

$$\underset{\text{(amine)}}{\geqslant N\!:} + HCl(aq) \longrightarrow \underset{\text{(a substituted ammonium chloride)}}{\geqslant \overset{\oplus}{N}\text{-}H(aq)} + Cl^{\ominus}\,(aq)$$

$$\geqslant \overset{\oplus}{N}\text{-}H(aq) + Cl^{\ominus}(aq) + \underset{\text{(excess)}}{NaOH(aq)} \longrightarrow \geqslant N\!: + NaCl(aq) + H_2O$$

Water insoluble amine dissolves in aqueous HCl due to formation of water soluble substituted ammonium chloride, which on reaction with excess aqueous NaOH regenerates the original insoluble amine.

b. Diazotization reaction/ Orange dye test: In a sample of aromatic primary amine, 1-2 mL of conc. HCl is added. The aqueous solution of $NaNO_2$ is added with cooling. This solution is transfered to a test tube containing solution of β naphthol in NaOH. Formation of orange dye indicates presence of aromatic primary amino group. (It may be noted that temperature of all the solutions and reaction mixtures is maintined near 0°C throughout the reaction).

The reaction involved in this test will be discussed in section 13.6.5.

13.6.2: Alkylation of amines : Hofmann's exhaustive alkylation : When a primary amine is heated with excess of primary alkyl halide it gives a mixture of secondary amine, tertiary amine along with tetraalkylammonium halide (also refer to sec. 13.3.1).

$$R\text{-}NH_2 \xrightarrow[\text{-HX}]{\text{R-X}} R_2NH \xrightarrow[\text{-HX}]{\text{R-X}} R_3N \xrightarrow[\text{-HX}]{\text{R-X}} R_4\overset{\oplus}{N}X^{\ominus}$$

(1° Amine) (2° Amine) (3° Amine) (Tetraalkyl ammonium halide)

If excess of alkyl halide is used tetraalkyl ammonium halide is obtained as major product. The reaction is known as exhaustive alkylation of amines.

The tetraalkylammonium halides are called quaternary ammonium salts which are crystalline solids. They are the derivatives of ammoium salts in which all the four hydrogen atoms attached to nitrogen in $\overset{\oplus}{N}H_4$ are replaced by four alkyl groups (same or different). Primary, secondary and tertiary amines consume three, two and one moles of alkyl halide respectively to get converted into quaternary ammonium salt. The reaction is carried out in presence of mild base $NaHCO_3$, to neutralize the large quantity of HX formed. If the alkyl halide is methyl iodide, the reaction is called exhaustive methylation of amines.

For example : When methylamine is heated with excess methyl iodide, it gives tetramethyl ammonium iodide.

$$CH_3\text{-}NH_2 + CH_3\text{-}I \xrightarrow{\Delta} (CH_3)_2NH + HI$$

$$(CH_3)_2NH + CH_3\text{-}I \xrightarrow{\Delta} (CH_3)_3N + HI$$

$$(CH_3)_3N + CH_3\text{-}I \xrightarrow{\Delta} (CH_3)_4\overset{\oplus}{N}I^{\ominus}$$

Use your brain power

$$C_2H_5\text{-}NH_2 + \underset{\text{excess}}{C_2H_5\text{-}I} \xrightarrow{\Delta} ?$$

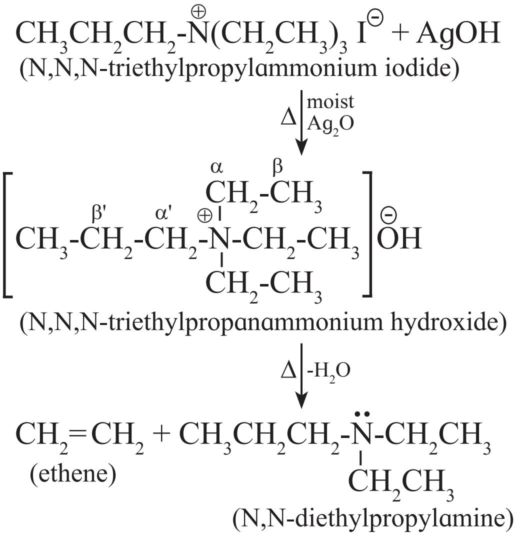
$$(C_2H_5)_2NH + \underset{\text{excess}}{CH_3\text{-}I} \xrightarrow{\Delta} ?$$

$$C_6H_5\text{-}NH_2 + \underset{\text{excess}}{CH_3\text{-}I} \xrightarrow{\Delta} ?$$

13.6.3 Hofmann Elimination :

When tetraalkylammonium halide is hetated with moist silver oxide, it gives quanternary ammonium hydroxide which is a deliquescent crystalline solid, and strongly basic like NaOH or KOH. Quaternary ammonium hydroxides on strong heating undergo β-elimination to give an alkene, the reaction is called Hofmann elimination. The least substituted alkene is obtained as major product (in contrast to Saytzeff elimination)

For example :



$$CH_3CH_2CH_2\text{-}\overset{\oplus}{N}(CH_2CH_3)_3\ I^{\ominus} + AgOH$$

(N,N,N-triethylpropylammonium iodide)

$$\Big\downarrow \Delta \quad \text{moist } Ag_2O$$

$$\left[CH_3\text{-}\overset{\beta'}{CH_2}\text{-}\overset{\alpha'}{CH_2}\text{-}\underset{\underset{CH_2\text{-}CH_3}{|}}{\overset{\overset{\overset{\alpha\quad\ \beta}{CH_2\text{-}CH_3}}{|}}{\overset{\oplus}{N}}}\text{-}CH_2\text{-}CH_3\right]\overset{\ominus}{O}H$$

(N,N,N-triethylpropanammonium hydroxide)

$$\Big\downarrow \Delta \quad \text{-}H_2O$$

$$CH_2{=}CH_2 + CH_3CH_2CH_2\text{-}\underset{\underset{CH_2CH_3}{|}}{\ddot{N}}\text{-}CH_2CH_3$$

(ethene) (N,N-diethylpropylamine)

Use your brain power

Complete the following reaction:

$$CH_3\text{-}CH_2\text{-}\overset{\oplus}{N}(CH_3)_3I^{\ominus} \xrightarrow[Ag_2O]{\text{Moist}} ? \xrightarrow{\Delta}$$

Do you know ?

- Acetylcholine is a quaternary ammonium salt which occurs in nervous system and functions as neurotransmitter

  $CH_3\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}\overset{\oplus}{N}(CH_3)_3$
- Quaternary ammonium salts are also present in cationic detergents.

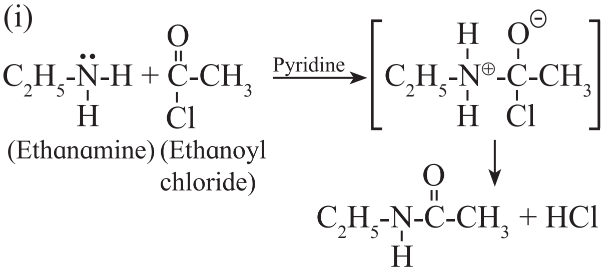
13.6.4 Acylation of amines :

Can you recall ?

- What is an acyl group ?
- How are alcohols acylated ?

Aliphatic and aromatic primary and secondary amines undergo acylation reaction. These amines contain replaceable hydrogen atoms (positively polarised H) on the nitrogen atom. These hydrogen atoms are replaced by acyl groups such as acetyl group. On reaction of amines with acetyl chloride or acetic anhydride, acetyl derivative of amine is obtained. It is also called amide. Amide is less basic than the amine. Acylation is a nucleophilic substitution reaction. The reaction is carried out in presence of strong base like pyridine, which neutralizes the acid produced during the reaction. For example :

(i)

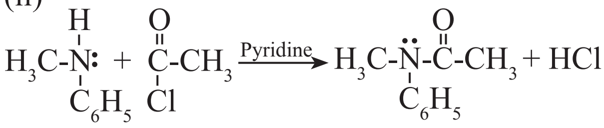


$$C_2H_5\text{-}\ddot{N}H\text{-}H + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow{\text{Pyridine}} \left[C_2H_5\text{-}\overset{H}{\overset{|}{\underset{H}{\underset{|}{N^{\oplus}}}}}\text{-}\overset{O^{\ominus}}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}\text{-}CH_3\right] \longrightarrow C_2H_5\text{-}\underset{H}{\underset{|}{N}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + HCl$$

(Ethanamine) (Ethanoyl chloride)

(N-Ethylethanamide)

(ii)



$$H_3C\text{-}\underset{C_6H_5}{\underset{|}{\ddot{N}}}\text{-}H + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl \xrightarrow{\text{Pyridine}} H_3C\text{-}\underset{C_6H_5}{\underset{|}{\ddot{N}}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + HCl$$

(N-Methylaniline) (N-methyl-N-phenylethanamide)

Benzoyl chloride also gives similar reaction with amines.

Use your brain power

- $CH_3\text{-}NH_2 + Ph\text{-}CO\text{-}Cl \longrightarrow$?
- $(CH_3)_3N + Ph\text{-}CO\text{-}Cl \longrightarrow$?

13.6.5 Carbylamine reaction :

Aliphatic or aromatic primary amines on heating with chloroform give foul (offensive) smelling products called alkyl/aryl isocyanides or carbylamines. This reaction is a test for primary amines. Secondary and tertiary amines do not give this test.

$$\underset{(1^{\circ}\ \text{amine})}{R\text{-}NH_2} + CHCl_3 + 3KOH \xrightarrow{\Delta} \underset{(\text{Alkyl isocyanide})}{R\text{-}NC} + 3KCl + 3H_2O$$

Use your brain power

Write the carbylamine reaction by using aniline as starting material.

13.6.6 Reaction with nitrous acid : Primary, secondary and tertiary amines react differently with nitrous acid. Reactions of only primary amines will be considered here.

Can you tell ?

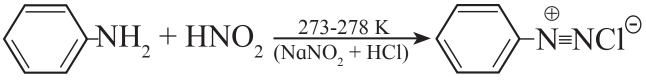
- What is the formula of nitrous acid ?
- Can nitrous acid be stored in bottle ?

Nitrous acid is an unstable compound. Hence it is prepared *in situ* by adding aqueous sodium nitrite to hydrochloric acid already mix with the substrate, that is amine.

a. Aliphatic primary amines on reaction with nitrous acid form aliphatic diazonium salts as very unstable intermidiates which decompose immediately by reaction with solvent water. Corresponding alcohol is formed as the product of the reaction and nitrogen gas is liberated .

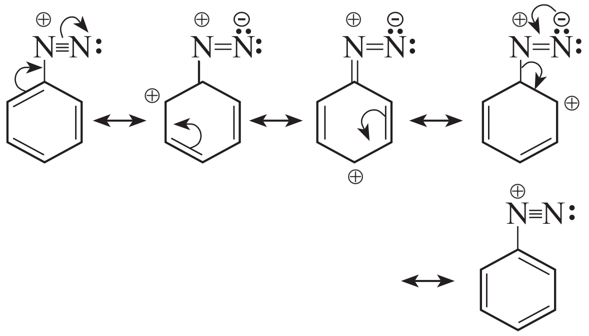
$$R\text{-}NH_2 + HNO_2 \xrightarrow[(NaNO_2 + HCl)]{273\text{-}278\ K} \underset{(\text{alkyl diazonium chloride})}{\left[R\text{-}\overset{\oplus}{N_2}\ Cl^{\ominus}\right]} \xrightarrow{H_2O} R\text{-}OH + N_2\uparrow + HCl$$

b. Aromatic primary amines react with nitrous acid to form diazonium salts which have reasonable stability at 273 K.



(benzene diazonium chloride)

Aryl diazonium salts are resonance stabilized and useful as versatile intermidiates to obtain a variety of products.



13.7 Reactions of arene diazonium salts:

Aryl diazonium salts show two types of reactions.

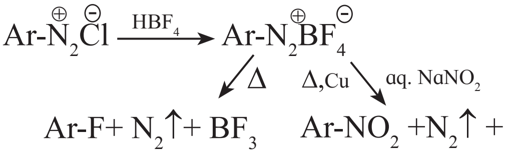
13.7.1 Reactions involving displacement of diazo group : The diazonium group ($-N_2^{\oplus}$) is a very good leaving group due to the positive charge on nitrogen atom bonded to aromatic ring. As a result, the arene diazonium salts undergo nucleophilic substitution reaction with a variety of nucleophiles. Table 13.5 shows reactions of diazonium salts involving displacement of diazo group.

Table 13.5 Reactions of arene diazonium salts

Title of reaction	Substrate	Reagent	Products
Sandmeyer reaction (good yield)	$Ar-\overset{\oplus}{N_2}\overset{\ominus}{X}$ $Ar-\overset{\oplus}{N_2}\overset{\ominus}{X}$ $Ar-\overset{\oplus}{N_2}\overset{\ominus}{X}$	$\xrightarrow{CuCl/HCl}$ $\xrightarrow{CuBr/HBr}$ $\xrightarrow{CuCN/KCN}$	$Ar-Cl+N_2$ $Ar-Br+N_2$ $Ar-CN+N_2$
Gatterman reaction	$Ar-\overset{\oplus}{N_2}\overset{\ominus}{X}$ $Ar-\overset{\oplus}{N_2}\overset{\ominus}{X}$	$\xrightarrow[HCl]{Cu\ powder}$ $\xrightarrow[HBr]{Cu\ powder}$	$Ar-Cl+N_2$ $Ar-Br+N_2$
Iodoarene formation	$Ar-\overset{\oplus}{N_2}\overset{\ominus}{Cl}$	$\xrightarrow{KI}$	$Ar-I+N_2$
Mild Reduction	$Ar-\overset{\oplus}{N_2}\overset{\ominus}{Cl}$ $Ar-\overset{\oplus}{N_2}\overset{\ominus}{Cl}$	$\xrightarrow[H_2O]{H_3PO_2}$ $\xrightarrow{CH_3-CH_2-OH}$	$Ar-H+N_2+H_3PO_3+HCl$ $Ar-H+N_2+CH_3CHO+HCl$
Phenol formation	$Ar-\overset{\oplus}{N_2}\overset{\ominus}{Cl}$	$\xrightarrow[283\ K]{H_2O}$	$Ar-OH+N_2+HCl$

Reaction with fluoroboric acid :

Arene diazonium salt on reaction with fluoroboric acid gives precipitate of diazonium fluoroborate which on heating decomposes to yield fluoroarene. On the other hand when heated with aqueous sodium nitrite in presence of copper it gives nitroarene.



$$Ar-\overset{\oplus}{N_2}\overset{\ominus}{Cl} \xrightarrow{HBF_4} Ar-\overset{\oplus}{N_2}\overset{\ominus}{BF_4}$$

$$Ar-\overset{\oplus}{N_2}\overset{\ominus}{BF_4} \xrightarrow{\Delta} Ar-F+N_2\uparrow+BF_3$$

$$Ar-\overset{\oplus}{N_2}\overset{\ominus}{BF_4} \xrightarrow[\Delta,Cu]{aq.\ NaNO_2} Ar-NO_2+N_2\uparrow+BF_3$$

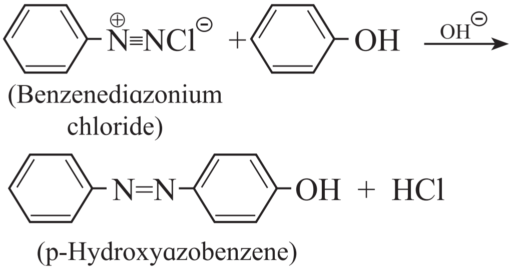
Use your brain power

Complete the following reactions :

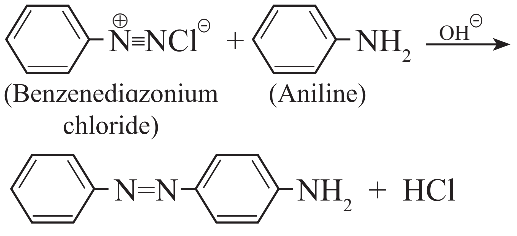
- $Ar-NH_2 \xrightarrow{?} Ar-\overset{\oplus}{N_2}\overset{\ominus}{Cl} \xrightarrow[\text{Cupprous chloride}]{HCl} ?$
- $Ar-\overset{\oplus}{N_2}\overset{\ominus}{Cl} \xrightarrow{H_3PO_2} ?$

13.7.2 Reactions involving retention of diazo group: (Coupling reactions) :

Arenediazonium salts when treated with certain reactive aromatic compounds such as phenols or aromatic amines, give azo compounds. These have extended conjugated system of double bonds in which two aromatic rings are joined through azo group -N=N-. This reaction is called **azo coupling**. Azo compounds are brightly coloured and are used as dyes. This is an example of electrophilic aromatic substitution reaction. Here the electrophiles are positively charged diazonium ions. Substitution usually occurs para to the ring activating group. For example : Benzenediazonium chloride reacts with phenol in mild alkaline medium to give p-Hydroxyazobenzene (orange dye).



Azo coupling with β-naphthol in NaOH is used as a confirmatory test for primary aromatic amines. Benzenediazonium chloride reacts with aniline in mild alkaline medium to give p-aminoazo-benzene (yellow dye.)

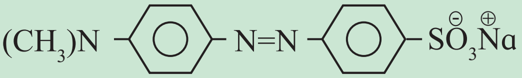


(Benzenediazonium chloride) (Aniline)

(p-Aminoazobenzene)

Do you know ?

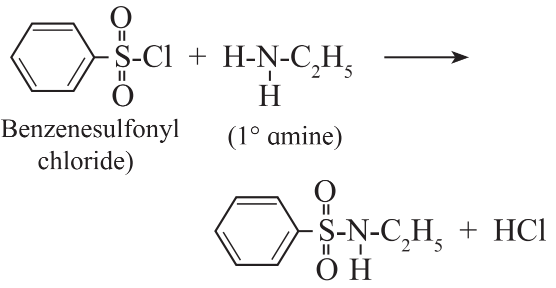
The acid-base indicator methyl orange is an azo dye.



13.8 Reaction with arenesulfonyl chloride :

(Hinsberg's test) : Benzenesulfonyl chloride ($C_6H_5SO_2Cl$) is known as **Hinsberg's reagent**.

a. Ethyl amine (primary amine) reacts with benzenesulfonyl chloride to form N-ethyl benzenesulfonyl amide.

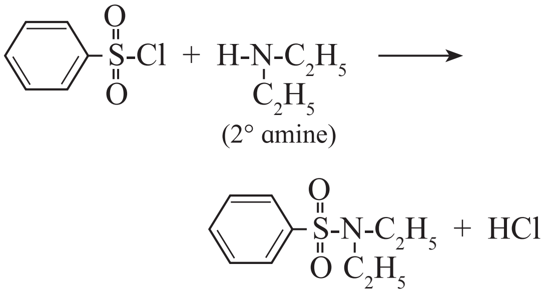


(Benzenesulfonyl chloride) (1° amine)

(N-Ethylbenzene sulfonamide)
(Soluble in alkali)

The hydrogen attached to nitrogen in sulfonamide ethanamine (a primary amine) is strongly acidic. Hence it is soluble in alkali.

b. Diethyl amine reacts with benzene-sulfonyl chloride to give N, N- diethyl benzene sulfonamide.



(2° amine)

(N, N-diethylbenzene sulfonamide)

N,N-diethylbenzenesulfonamide does not contain any H-atom attached to nitrogen atom. Hence it is not acidic and does not dissolve in alkali.

Can you tell ?

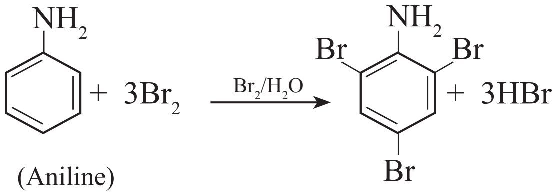
- Do tertiary amines have 'H' bonded to 'N' ?
- Why do tertiary amines not react with benzene sulfonyl chloride ?

Use your brain power

How will you distinguish between methylamine, dimethylamine and trimethylamine by Hinsberg's test ?

13.9 Electrophilic aromatic substitution in aromatic amines : Amino group is ortho and para directing and powerful ring activating group. As a result aromtic amines readily undergo electrophilic substitution reactions.

a. Bromination : Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6- tribromoaniline.

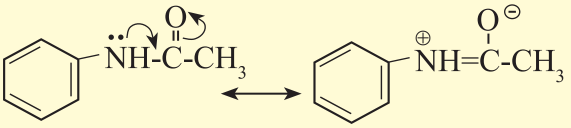


(Aniline)

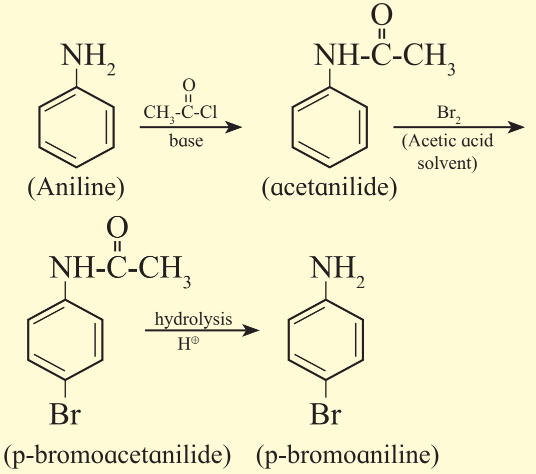
(2,4,6-tribromoaniline)

Problem 13.1 : Write the scheme for preparation of p-bromoaniline from aniline. Justify your answer.

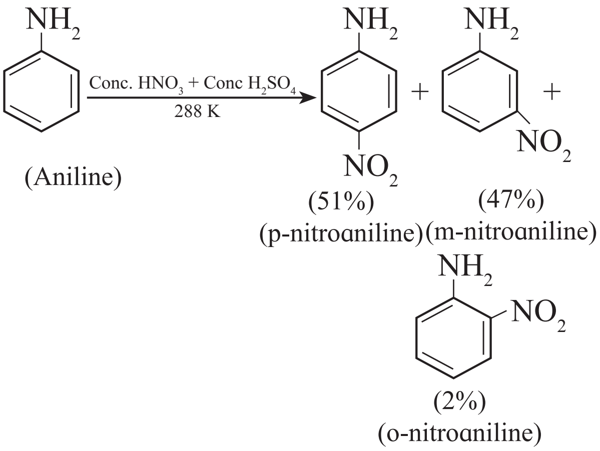
Solution : NH_2- group in aniline is highly ring activating and o-/p- directing due to involvement of the lone pair of electrons on 'N' in resonance with the ring. As a result, on reaction with Br_2 it gives 2,4,6-tribromoniline. To get a monobromo product, it is necessary to decrease the ring activating effect of $-NH_2$ group. This is done by acetylation of aniline. The lone pair of 'N' in acetanilide is also involved in resonance in the acetyl group. To that extent ring activation decreases.



Hence, acetanilide on bromination gives a monobromo product p-bromoacetanilide. After monobromination the original $-NH_2$ group is regenerated. The protection of $-NH_2$ group in the form of acetyl group is removed by acid catalyzed hydrolysis to get p-bromoaniline, as shown in the following scheme.



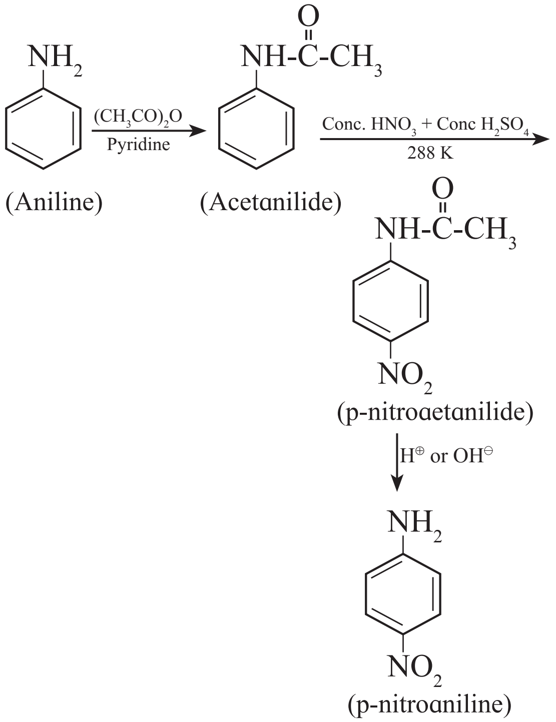
b. Nitration : Direct nitration of aniline yeilds a mixture of ortho, meta and para nitroanilines. In acidic medium $-NH_2$ group is protonated to $-\overset{\oplus}{N}H_3$ group which is meta-directing and deactivating. Hence considerable amount of m-nitroaniline is obtained.



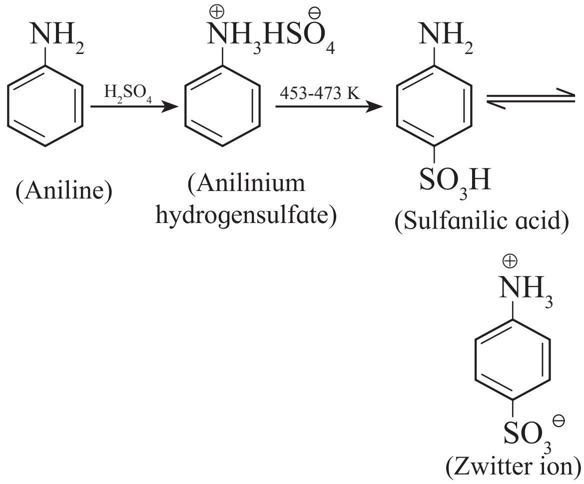
Internet my friend

Search the pK_a or pK_b values of ortho, meta and para nitroaniline on internet and arrange them in increasing order of their basic strength.

However, to get p-nitroaniline as major product, $-NH_2$ group is first protected by acetylation, nitration is carried out and then amide is hydrolysed.



c. Sulfonation : Aniline reacts with concerntrated sulfuric acid to form anilinium hydrogen sulfate which on heating with sulfuric acid at 453-473K produces p-aminobenzene sulfonic acid (sulfanilic acid) as major product.



Sulfanilic acid exists as a salt; called **dipolar ion or zwitter ion**. It is produced by the reaction between an acidic group and a basic group present in the same molecule.

Use your brain power

- Can aniline react with a Lewis acid ?
- Why aniline does not undergo Friedel Craft's reaction using aluminium chloride ?

Exercises

1. Choose the most correct option.

i. The hybridisation of nitrogen in primary amine is ....

a. sp b. sp^2 c. sp^3 d. sp^3d

ii. Isobutylamine is an example of ....

a. 2° amine b. 3° amine

c. 1° amine

d. quaternary ammonium salt.

iii. Which one of the following compounds has the highest boiling point ?

a. n-Butylamine b. sec-Butylamine

c. isobutylamine d. tert-Butylamine

iv. Which of the following has the highest basic strength ?

a. Trimethylamine b. Methylamine

c. Ammonia d. Dimethylamine

v. Which type of amine does produce N_2 when treated with HNO_2 ?

a. Primary amine b. Secondary amine

c. Tertiary amine

d. Both primary and secondary amines

vi. Carbylamine test is given by

a. Primary amine

b. Secondary amine

c. Tertiary amine

d. Both secondary and tertiary amines

vii. Which one of the following compounds does not react with acetyl chloride ?

a. $CH_3\text{-}CH_2\text{-}NH_2$ b. $(CH_3\text{-}CH_2)_2NH$

c. $(CH_3\text{-}CH_2)_3N$ d. $C_6H_5\text{-}NH_2$

viii. Which of the following compounds will dissolve in aqueous NaOH after undergoing reaction with Hinsberg reagent ?

a. Ethylamine b. Triethylamine

c. Trimethylamine d. Diethylamine

ix. Identify 'B' in the following reactions

$CH_3\text{-}C\equiv N \xrightarrow{Na/C_2H_5OH} A \xrightarrow{NaNO_2/dilHCl} B$

a. $CH_3\text{-}CH_2\text{-}NH_2$ b. $CH_3\text{-}CH_2\text{-}NO_2$

c. $CH_3\text{-}CH_2N_2^{\oplus}Cl^{\ominus}$ d. $CH_3\text{-}CH_2\text{-}OH$

x. Which of the following compounds contains azo linkage ?

a. Hydrazine

b. p-Hydroxyazobenzene

c. N-Nitrosodiethylamine

d. Ethylenediamine

2. Answer in one sentence.

i. Write reaction of p-toluenesulfonyl chloride with diethylamine.

ii. How many moles of methylbromide are required to convert ethanamine to N, N-dimethyl ethanamine ?

iii. Which amide does produce ethanamine by Hofmann bromamide degradation reaction?

iv. Write the order of basicity of aliphatic alkylamine in gaseous phase.

v. Why are primary aliphatic amines stronger bases than ammonia ?

vi. Predict the product of the following reaction.

Nitrobenzene $\xrightarrow{\text{Sn/Conc. HCl}}$?

vii. Write the IUPAC name of benzylamine.

viii. Arrange the following amines in an increasing order of boiling points.

n-propylamine, ethylmethyl amine, trimethylamine.

ix. Write the balanced chemical equations for the action of dil H_2SO_4 on diethylamine.

x. Arrange the following amines in the increasing order of their pK_b values.

Aniline, Cyclohexylamine, 4-Nitroaniline

3. Answer the following

i. Identify A and B in the following reactions.

$C_6H_5CH_2Br \xrightarrow[\text{KCN}]{\text{alco.}} A \xrightarrow{\text{Na/ethanol}} B.$

ii. Explain the basic nature of amines with suitable example.

iii. What is diazotisation ? Write diazotisation reaction of aniline.

iv. Write reaction to convert acetic acid into methylamine.

v. Write a short note on coupling reactions.

vi. Explain Gabriel phthalimide synthesis.

vii. Explain carbylamine reaction with suitable examples.

viii. Write reaction to convert (i) methanamine into ethanamine (ii) Aniline into p-bromoaniline.

ix. Complete the following reactions :

a. $C_6H_5N_2^{\oplus}Cl^{\ominus} + C_2H_5OH \longrightarrow$

b. $C_6H_5NH_2 + Br_2(aq) \longrightarrow$?

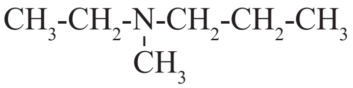
x. Explain Ammonolysis of alkyl halides.

xi. Write reaction to convert ethylamine into methylamine.

4. Answer the following.

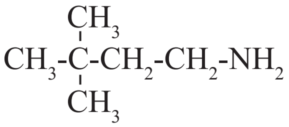
i. Write the IUPAC names of the following amines :

a.



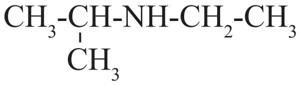
$CH_3\text{-}CH_2\text{-}\underset{\substack{|\\CH_3}}{N}\text{-}CH_2\text{-}CH_2\text{-}CH_3$

b.



$CH_3\text{-}\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}\text{-}CH_2\text{-}CH_2\text{-}NH_2$

c.



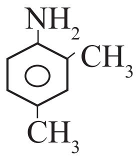
$CH_3\text{-}\underset{\substack{|\\CH_3}}{CH}\text{-}NH\text{-}CH_2\text{-}CH_3$

ii. What are amines ? How are they classified ?

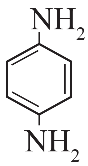
iii. Write IUPAC names of the following amines.

a. $H_2N\text{-}(CH_2)_6\text{-}NH_2$

b.



c.



iv. Write reactions to prepare ethanamine from

a. Acetonitrile b. Nitroethane

c. Propionamide

v. What is the action of acetic anhydride on ethylamine, diethylamine and triethylamine ?

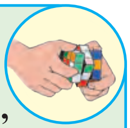
vii. Distinguish between ethylamine, diethylamine and triethylamine by using Hinsberg's reagent ?

viii. Write reactions to bring about the following conversions :

a. Aniline into p-nitroaniline

b. Aniline into sulphanilic acid ?

Activity :



- **Prepare a chart of azodyes, colours and its application.**
- **Prepare a list of names and structures of N-containing ingredients of diet.**

14. BIOMOLECULES

Can you recall ?

- What are the constituents of balanced diet ?
- What are the products of digestion of carbohydrates?
- Which constituent of diet is useful for building muscles?
- Which constituent of diet is a source of high energy?
- What is the genetic material of organisms?

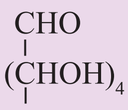
14.1 Introduction : Principal molecules of the living world : Bodies of living organisms contain large number of different molecules which constitute their structure. They are also part of various physiological processes taking place in them. Primary structural materials of organisms are proteins and cellulose. By means of the unique process of photosynthesis plants produce carbohydrates. Plants utilize the minerals absorbed by their roots to produce proteins. Lipids are the main ingredient of vegetable oils and milk fats. Nucleic acids constitute the genetic material of organisms.

In this chapter we are going to study some aspects of three principal biomolecules, namely, carbohydrates, proteins and nucleic acids.

14.2 Carbohydrates : From the simple chemical reactions of many carbohydrates it is understood that carbohydrates are polyhydroxy aldehydes or ketones or compounds which give rise to such units on hydrolysis. Some carbohydrates like glucose, fructose are sweet in taste, and are called sugars. The most commonly used sugar is sucrose which is obtained from sugarcane or sugar beet. The sugar present in milk is called lactose. Greek word for sugar is sakkharon. Hence carbohydrates are also called **saccharides**. Origin of the term carbohydrate lies in the finding that molecular formulae of many of them can be expressed as $C_x(H_2O)_y$(hydrates of carbon). For example: glucose ($C_6H_{12}O_6$ Or $C_6(H_2O)_6$, sucrose ($C_{12}H_{22}O_{11}$ or $C_{12}(H_2O)_{11}$), starch [$(C_6H_{10}O_5)_n$ or $[C_6(H_2O)_5]_n$].

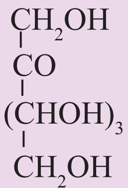
Try this...

Observe the following structural formulae carefully and answer the questions.



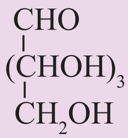
$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{(CHOH)_4}\\ |\\ \mathrm{CH_2OH}\end{array}$$

(glucose)



$$\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{CO}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\end{array}$$

(fructose)



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{(CHOH)_3}\\ |\\ \mathrm{CH_2OH}\end{array}$$

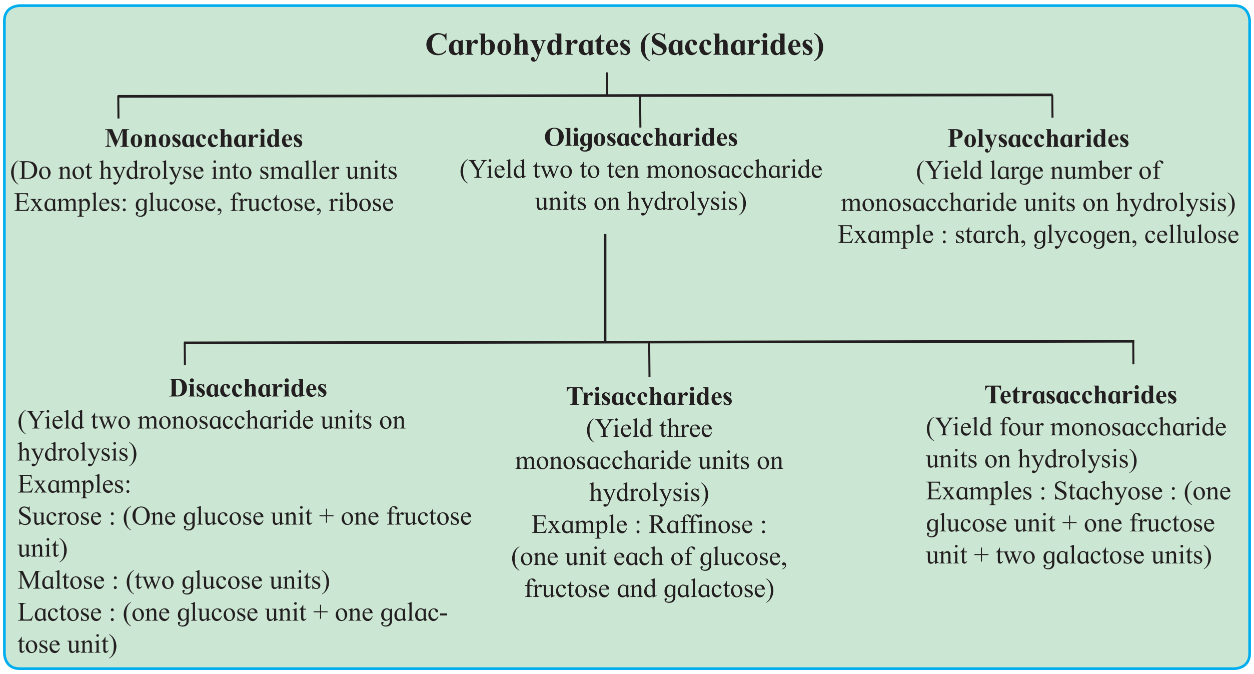
(ribose)

1. How many OH groups are present in glucose, fructose and ribose respectively?
2. Which other functional groups are present in these three compounds?

14.2.1 Classification of carbohydrates :

Carbohydrates are clssified into three broad groups in accordance with their behaviour on hydrolysis. These are monosaccharides, oligosaccharides and polysaccharides (Fig. 14.1).

Monosaccharides do not hydrolyse further into smaller units of polyhydroxy aldehydes or ketones. **Oligosaccharides** on hydrolysis yield two to ten units of monosaccharides and accordingly they are further classified as **disaccharides**, **trisaccharides** and so on. **Polysaccharides** give very large number of monosaccharide units on complete hydrolysis.



Carbohydrates (Saccharides)

Monosaccharides
(Do not hydrolyse into smaller units
Examples: glucose, fructose, ribose

Oligosaccharides
(Yield two to ten monosaccharide units on hydrolysis)

Polysaccharides
(Yield large number of monosaccharide units on hydrolysis)
Example : starch, glycogen, cellulose

Disaccharides
(Yield two monosaccharide units on hydrolysis)
Examples:
Sucrose : (One glucose unit + one fructose unit)
Maltose : (two glucose units)
Lactose : (one glucose unit + one galactose unit)

Trisaccharides
(Yield three monosaccharide units on hydrolysis)
Example : Raffinose : (one unit each of glucose, fructose and galactose)

Tetrasaccharides
(Yield four monosaccharide units on hydrolysis)
Examples : Stachyose : (one glucose unit + one fructose unit + two galactose units)

Fig. 14.1 : Classification of carbohydrates

Remember...

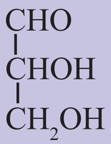
- About **twenty different monosaccharides** are found in carbohydrates.
- **Disaccharides** are the most common oilgosacchrides. The two monosaccharide units in disaccharides may be same or different.
- **Polysaccharides** : **Starch** is common ingredient of food grains. **Cellulose** is constituent of cell wall of plant cells. Animals store in their body in the form of **glycogen**.

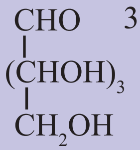
14.2.2 Nomenclature of monosaccharides :

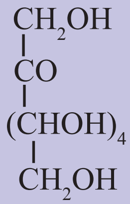
According to IUPAC system of nomenclature, general name for monosaccharide is **glycose**. Monosaccharide with one aldehydic carbonyl group is called **aldose** while that with one ketonic carbonyl group is called **ketose**. These names are further modified in accordance with the total number of carbon atoms in the monosaccharide. For example, glucose ($C_6H_{12}O_6$) is an aldose with six carbons, and is thereby, an **aldohexose**. Fructose ($C_6H_{12}O_6$) is a ketose with six carbons, and is, thereby, a **ketohexose**.

Use your brain power

Give IUPAC names to the following monosaccharides.

1.

$$\begin{array}{c} CHO \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

2.

$$\begin{array}{c} CHO \\ | \\ (CHOH)_3 \\ | \\ CH_2OH \end{array}$$

3.

$$\begin{array}{c} CH_2OH \\ | \\ CO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

14.2.3 Glucose :

Glucose occurs in nature in free as well as in combined state. Glucose can be obtained from sucrose or starch by acid catalysed hydrolysis as shown below.

a. Prepartion of glucose from sucrose :

Sucrose is hydrolysed by warming with dilute hydrochloric acid or sulfuric acid for about two hours. This hydrolysis converts sucrose into mixture of glucose and fructose. Glucose is separated from fructose by adding ethanol during cooling. Glucose being almost insoluble in alcohol crystallizes out first. The solution is filltered to obtain crystals of glucose.

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\Delta]{H^{\oplus}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

b. Prepartion of glucose from starch :

Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute sulfuric acid at 393K under 2 to 3 atm pressure.

$$(C_6H_{10}O_5)_n + n\,H_2O \xrightarrow[393K,\ 2\text{-}3\ atm]{H^{\oplus}} n\,C_6H_{12}O_6$$

(Starch) (Glucose)

14.2.4 Structure and properties of glucose

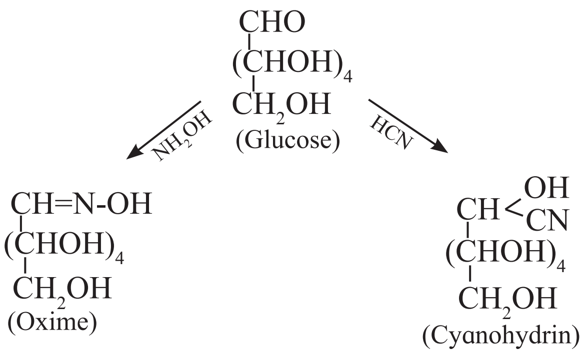
Glucose has an aldohexose structure. In other words, glucose molecule contains one aldehydic, that is, formyl group and the remaining five carbons carry one hydroxyl group (-OH) each. The six carbons in glucose form one straight chain. This aldohexose structure of glucose was established on the basis of the following **chemical properties**.

1. Molecular formula of glucose was found to be $C_6H_{12}O_6$, on the basis of its elemental compostion and colligative properties.

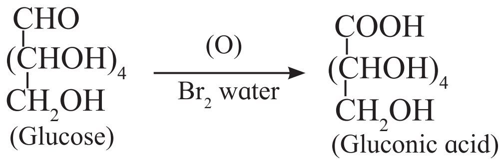
2. The six carbons in glucose molecule form a straight chain. This was inferred from the following observation : Glucose gives n-hexane on prolonged heating with HI.

$$\underset{\text{(Glucose)}}{CHO - (CHOH)_4 - CH_2OH} \xrightarrow{HI,\ \Delta} \underset{\text{(n-Hexane)}}{CH_3 - (CH_2)_4 - CH_3}$$

3. Glucose molecule contains one carbonyl group. This was inferred from the observation that glucose forms oxime by reaction with hydroxylamine and gives cyanohydrin on reaction with hydrogen cyanide.



4. The carbonyl group in glucose is in the form of aldehyde. This was inferred from the observation that glucose gets oxidised to a six carbon monocarboxylic acid called gluconic acid on reaction with bromine water which is a mild oxidizing agent.



$$\underset{\text{(Glucose)}}{\begin{array}{l}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}} \xrightarrow[Br_2\ water]{(O)} \underset{\text{(Gluconic acid)}}{\begin{array}{l}COOH\\ |\\ (CHOH)_4\\ |\\ CH_2OH\end{array}}$$

Problem 14.1 :

An alcoholic compound was found to have molcular mass of 90 u. It was acetylated. Molecular mass of the acetyl derivative was found to be 174 u. How many alcoholic (-OH) groups must be present in the original compound?

Solution : In acetylation reaction H atom of an (-OH) group is replaced by an acetyl group $(-COCH_3)$. This results in an increase in molcular mass by $[(12+16+12+3\times1)-1]$, that as, 42 u.

In the given alcohol,

increase in molecular mass = 174 u - 90 u

= 84 u

$\therefore$ Number of -OH groups = $\dfrac{84\ u}{42\ u} = 2$

Can you recall ?

What are the products of reaction of

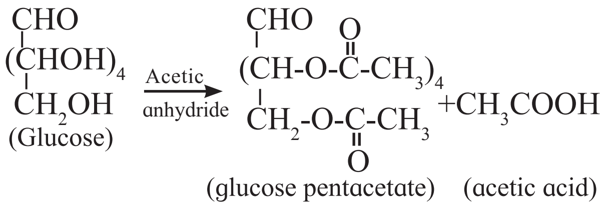
i. $CH_3 - CO - CH_3$ with $NH_2 - OH$?

ii. $CH_3 - CHO$ with HCN?

iii. $CH_3 - OH$ with $CH_3 - CO - O - CO- CH_3$?

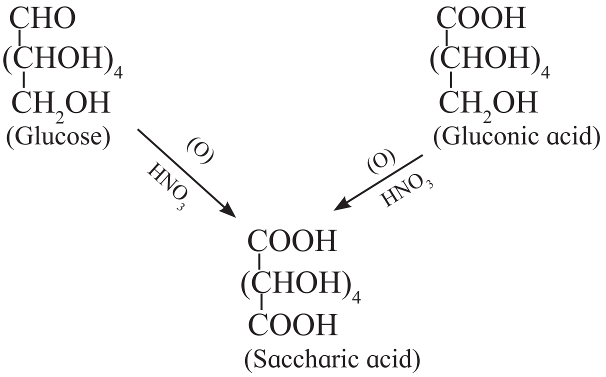
5. Glucose contains five hydoxyl groups :

This was inferred from the observation that Glucose reacts with acetic anhydride to form glucose pentaacetate. As glucose is a stable compound, it was further inferred that the five hydroxyl groups are bonded to five different carbon atoms in glucose molecule.



$$\begin{array}{c}CHO\\ |\\ (CHOH)_4\\ |\\ CH_2OH\\ \text{(Glucose)}\end{array} \xrightarrow[\text{anhydride}]{\text{Acetic}} \begin{array}{c}CHO\\ |\\ (CH\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3)_4\\ |\\ CH_2\text{-}O\text{-}\underset{O}{\underset{\|}{C}}\text{-}CH_3\\ \text{(glucose pentacetate)}\end{array} + \begin{array}{c}CH_3COOH\\ \text{(acetic acid)}\end{array}$$

6. Glucose contains one primary alcoholic (- CH_2OH) group : This was inferred from the following observation : Glucose and gluconic acid both on oxidation with dilute nitric acid give the same dicarboxylic acid called saccharic acid.



Use your brain power

- Write structural formula of glucose showing all the bonds in the molecule.
- Number all the carbons in the molecules giving number 1 to the (-CHO) carbon.
- Mark the chiral carbons in the molecule with asterisk (*).
- How many chiral carbons are present in glucose?

14.2.5 Optical isomerism in glucose :

Structural formula of glucose shows that it contains four chiral carbon atoms. You have learnt that every chiral carbon can have two distinct spatial arrangements of groups around it (section 10.5.1). In other words, two distinct configurations are possible for each of the four chiral carbons of glucose. Stereostructure of glucose is therefore one out of several possible stereostructures of an aldohexose.

Do you know ?

A structural formula containing 'n' number of chiral carbon can have maximum '2^n' numbers of stereostructures or optical isomers. An aldohexose therefore, can exist as sixteen ($2^4 = 16$) optical isomers, and glucose is one of them.

Can you recall ?

- What are the ways to represent three dimensional structure of an organic molecule?
- How is a Fischer projection formula drawn?

On the basis of very elaborate chemical evidence and measurement of optical activity of various chemicals involved, Emil Fischer, a German Nobel laureate (1902), determined the configuration of the four chiral carbons (C-2, C-3, C-4, C-5) in glucose.

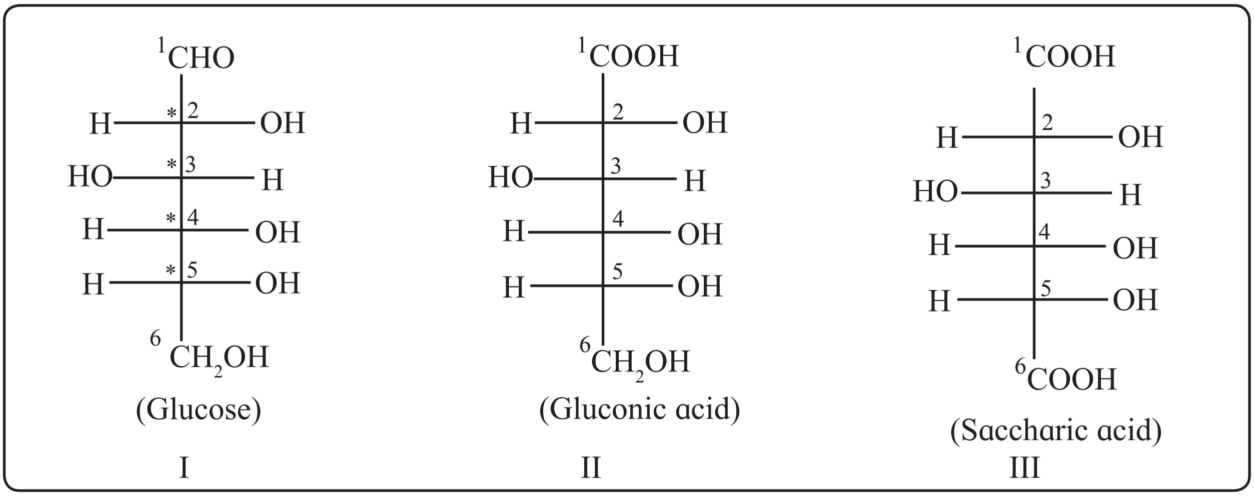
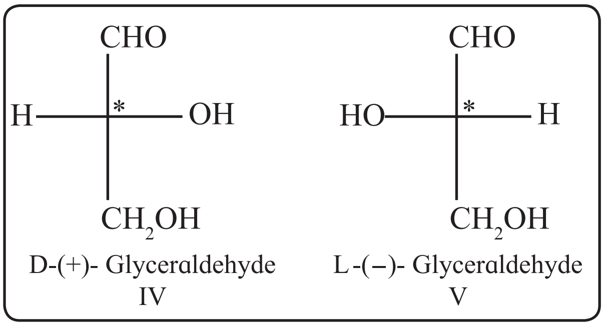


Fig 14.2 : Fischer projection formulae of glucose, gluconic acid and saccharic acid

Figure 14.2 shows the Fisher projection formulae of glucose (I), gluconic acid (II) and saccharic acid (III).

Glucose is an optically active compound and has its specific rotation, $[\propto]_D^{20}$, equal to $+52.7^0$. Due to its dextrorotation glucose is also called **dextrose**. The designations **(+)-glucose** or **d-glucose** imply the dextrorotatory nature of glucose. **D-glucose** is another designation of glucose, which is more common. This designation indicates the configuration of glucose rather than the sign of its optical rotation.

D/L configuration system : The prefix D- or L- in the name of a compound indicates relative configuration of a stereoisomer. It refers to a particular enantiomer of glyceraldehyde. **Glyceraldehyde** has one chiral carbon(C-2) and exists as two enantiomers. These are represented by two Fischer projection formulae (see Fig. 14.3).



D-(+)- Glyceraldehyde
IV

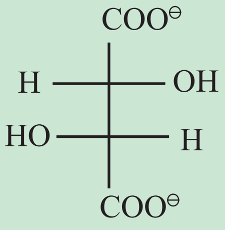
L -(–)- Glyceraldehyde
V

Fig. 14.3 : Enantiomers of glyceraldehyde

Conventionally (+)-glyceraldehyde is represented by the Fischer projection formula having OH group attached to C-2 on right side (IV) and this configuration is denoted by symbol '**D**'. Similarly, configuration of (-) glyceraldehyde (V) is denoted by symbol '**L**'. All the compounds which can be correlated by a series of chemical reactions to (+) - glyceraldehyde are said to have D-configuration. The compounds which are chemically correlated to (-) - glyceraldehyde are said to have L- configuration. This is the system of **relative configuration** of chiral compounds.

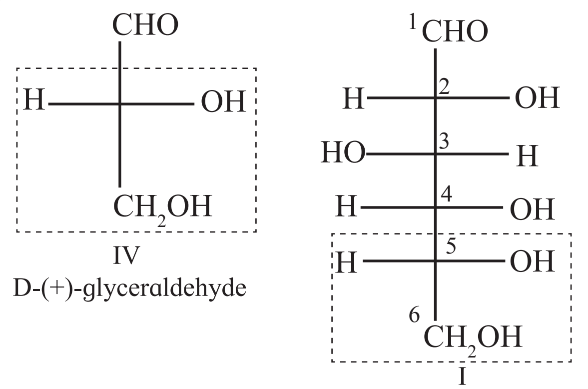
Do you know ?

Optical rotation is an experimentally measurable property of a compound. Configuration of chiral carbon, on the other hand, is difficult to observe by simple experiment. In 1951 X-ray crystallographic studies of (+) - sodium rubidium tartarate established its configuration as :



This was the first instance of determining absolute configuration.

A monosaccharide is assigned D/L configuration on the basis of the configuration of the lowest chiral carbon in its Fischer projection formula. Figure 14.4 illustrates the D-configuration of (+) - glucose.



IV
D-(+)-glyceraldehyde

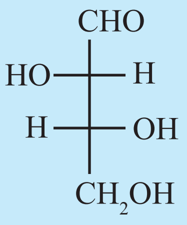
I
D-(+)-glucose

Fig. 14.4 : Relative configuration of (+) - glucose

14.2.6 Ring structure of glucose : On the basis of chemical evidence stereostructure of D-glucose was represented by the Fischer projection formula **I** (Fig. 14.2 and Fig. 14.4). Glucose, however, was found to exhibit some more chemical properties which could not be explained on the basis of the structure **I.** It was necessary to write another structure for glucose which will explain all the properties. Ring structure of glucose fulfils this requirement.

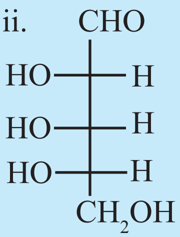
Problem 14.2 : Assign D/L configuration to the following monosaccharides.

i.



(Threose)

ii.

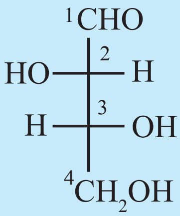


(Ribose)

Solution :

D/L configuration is assigned to Fischer projection formula of monosaccharide on the basis of the lowest chiral carbon.

i.

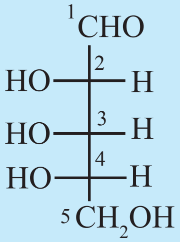


(Threose)

Threose has two chiral carbons C-2 and C-3. The given Fischer projection formula of threose has -OH groups at the lowest C-3 chiral carbon on right side.

∴ It is D-threose.

ii.



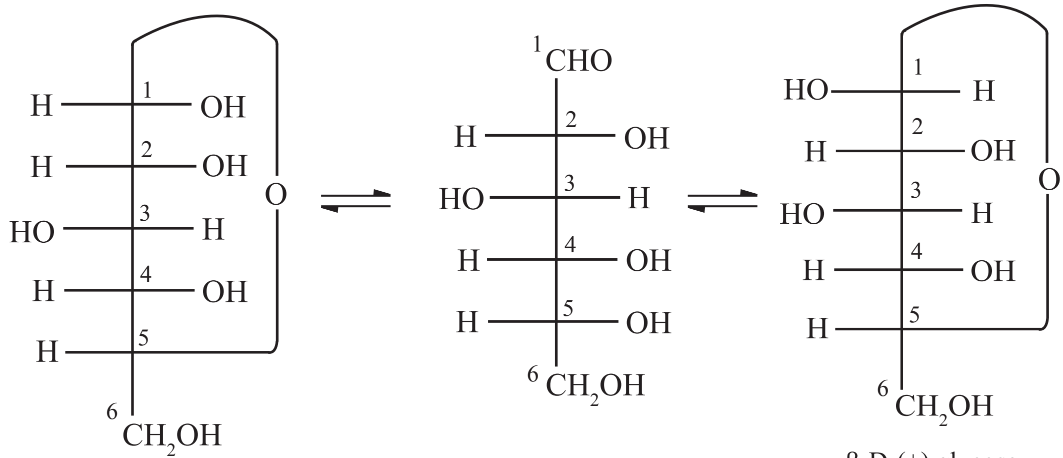
(Ribose)

Ribose has three chiral carbons C-2, C-3 and C-4. The given Fischer projection formula of ribose has -OH group at the lowest C-4 chiral carbon on left side.

∴ It is L-ribose

Glucose is found to have two cyclic structures (VI and VII) which are in equilibrium with each other through the open chain structure (I) in aqueous solution (Fig.14.5).

The ring structure of glucose is formed by reaction between the formyl (-CHO) group and the alcoholic (-OH) group at C-5. Thus, the ring structure is a **hemiacetal** structure (section 12.8.2 c). The two hemiacetal structures (VI and VII) differ only in the configuration of C-1 (Fig. 14.5), the additional chiral centre resulting from ring closure. The two ring structures are called **∝- and β- anomers** of glucose and C-1 is called the anomeric carbon. The ring of the cyclic structure of glucose contains five carbons and one oxygen. Thus, it is a six membered ring. It is called pyranose structure, in analogy with the six membered heterocyclic compound pyran (Fig. 14.6). Hence glucose is also called **glucopyranose**. Haworth formula is a better way than Fischer projection formula to represent structure of glucopyranose (Fig. 14.6). In the **Haworth formula** the pyranose ring is considered to be in a perpendicular plane with respect to the plane of paper. The carbons and oxygen in the ring are in the places as they appear in Fig. 14.6. The lower side of the ring is called **∝-side** and the upper side is the **β-side**. The ∝-anomer has its anomeric hydroxyl (-OH) group (at C-1) on the ∝-side, whereas the β-anomer has

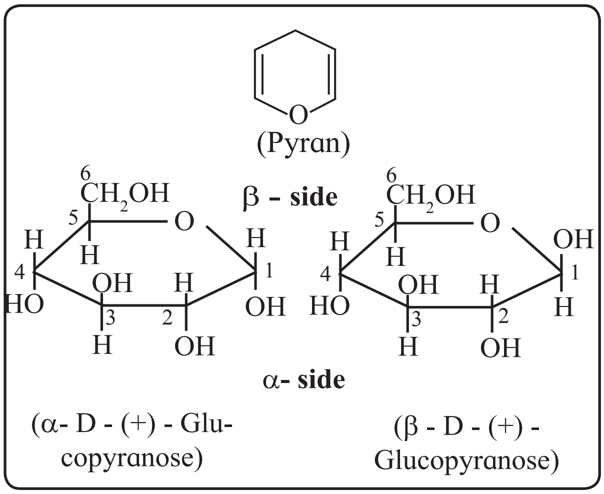


(∝-D-(+) Glucose)
VI

I

β-D-(+) glucose
VII

Fig. 14.5 Ring structures of glucose: Fischer projection formulae



(α- D - (+) - Glucopyranose) (β - D - (+) - Glucopyranose)

Fig. 14.6 : Haworth formula of anomers of glucopyranose

its anomeric hydroxyl (-OH) group (at C-1) on the β-side. The groups which appear on right side in the Fischer projection formula appear on α-side in the Haworth formula, and viceversa.

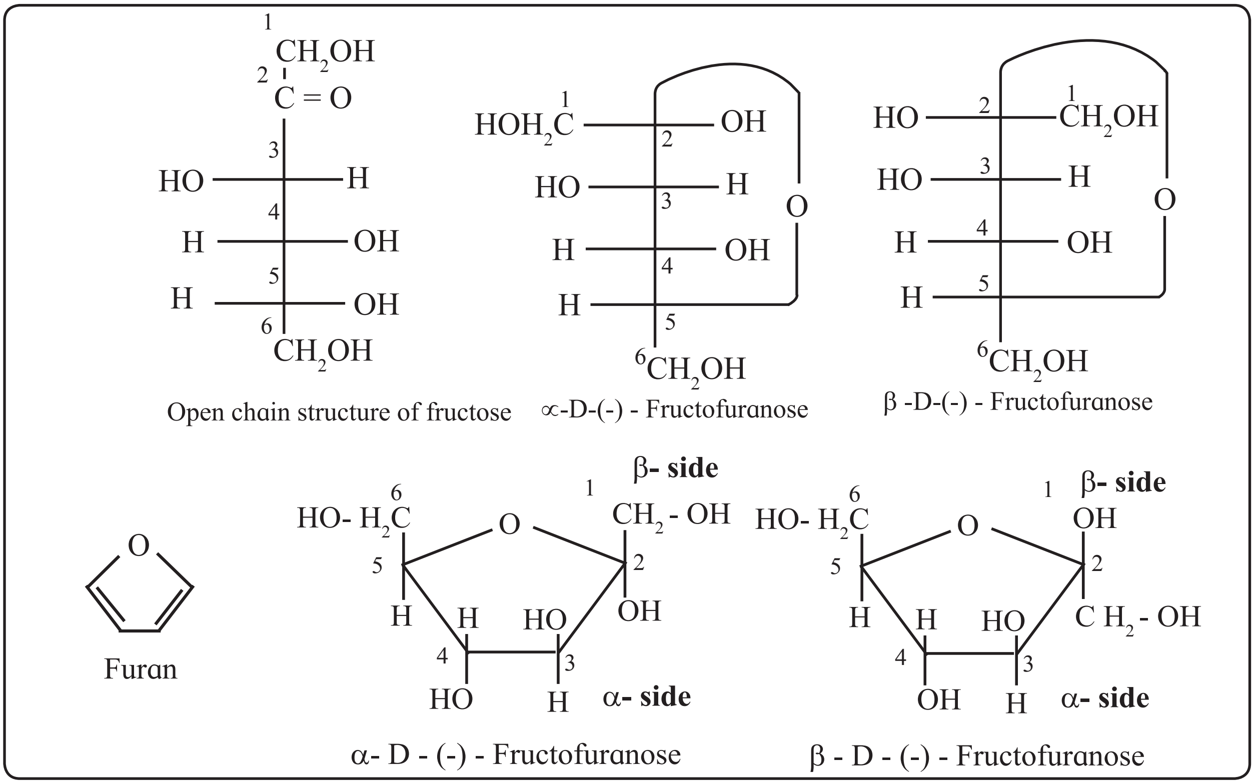
14.2.7 Reducing nature of glucose :

Hemiacetal group of glucopyranose structure is a **potential aldehyde group**. It imparts reducing properties to glucose. Thus, glucose gives **positive Tollens test and positive Fehling test** (Section 12.8.1 a).

14.2.8 Representation of Fructose structure

Fructose ($C_6H_{12}O_6$) is a laevorotatory ketohexose. Fructose is also called laevulose due to its laevorotation $[\propto]_D^{20} = -92.4^0$. Being an ∝-hydroxy keto compound fructose is a **reducing sugar**. In free state it exists as mixture of fructopyranose (major) and fructofuranose. In combined state fructose is found in the form of **fructofuranose** ring structre (as in sucrose, see section 14.2.9). The name furanose is given by analogy with furan, a five membered heterocyclic compound. Figure 14.7 shows representations of open chain structure of fructose and ring structures of ∝- and β- anomers of fructofuranose. Ring structure of fructose is a hemiketal (section 12.8.2 c).

14.2.9 Disaccharides : Disaccharides give rise to two units of same or different monosaccharides on hydrolysis with dilute acids or specific enzymes. The two monosaccharide units are linked together by an ether oxide linkage (-O-), which is termed as **glycosidic linkage** in carbohydrate chemistry. Glycosidic linkage is formed by removal of a water molecule by reaction of two hydroxyl



Open chain structure of fructose ∝-D-(-) - Fructofuranose β -D-(-) - Fructofuranose

α- D - (-) - Fructofuranose β - D - (-) - Fructofuranose

Fig. 14.7 : Representations of fructose structure

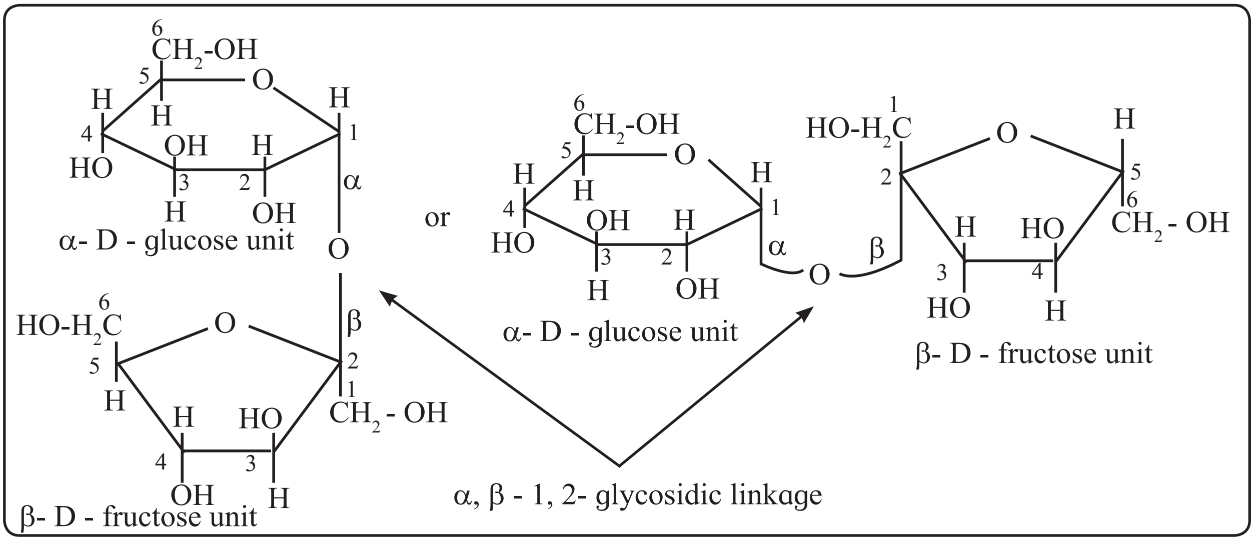


Fig. 14.8 : Haworth formula of sucrose

(-OH) groups from two monosaccharide units. At least one of the two monosaccharide units must use its anomeric hydroxyl group in formation of the glycosidic linkage. Three most common disaccharides are sucrose, maltose and lactose.

a. Sucrose : Sucrose ($C_{12}H_{22}O_{11}$) is dextrorotatory $(+66.5^0)$. On hydrolysis with dilute acid or an enzyme called invertase sucrose gives equimolar mixture of D-(+) glucose and D-(-) fructose.

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{or invertase}]{H^{\oplus}} \underset{\text{(D-(+) glucose)}}{C_6H_{12}O_6} + \underset{\text{(D-(-)fructose)}}{C_6H_{12}O_6}$$

Since the laevoratotion of fructose (-92.4^0) is larger than the dextrorotation of glucose $(+52.7^0)$, the hydrolysis product has net laevorotation. Hence hydrolysis of sucrose is also called **inversion of sucrose**, and the product is called **invert sugar**. Structure of sucrose contains glycosidic linkage between C-1 of ∝-glucose and C-2 of β-fructose (Fig. 14.8).

Try this...

Make models corresponding to the two Haworth formulae of sucrose in Fig. 14.8. Check that both are identical.

Since the potential aldehyde and ketone groups of both the monosaccharide units are involved in formation of the glycosidic bond, sucrose is a **non reducing sugar**.

b. Maltose : Maltose ($C_{12}H_{22}O_{11}$) is a disaccharide made of two units of D-glucose. The glycosidic bond in maltose is formed between C-1 of one glucose ring and C-4 of the other. The glucose ring which uses its hydroxyl group at C-1 is ∝-glucopyranose. Hence the linkage is called ∝-1,4-glycosidic linkage. The hemiacetal group at C-1 of the second ring is not involved in glycosidic linkage. Hence maltose is a **reducing sugar**. Maltose gives glucose on hydrolysis with dilute acids or the enzyme maltase. Figure 14.9 shows Haworth formula of maltose.

Do you know ?

Invert sugar is commerically available as invert syrup. It is used as sweetene in bakery and confectionary products and also in fruit **preserves** and beverages. It is sweeter than sucrose and glucose. It is resistant to crystallization and promotes retention of moisture, enhances flavour and texture and also prolongs shelf life.

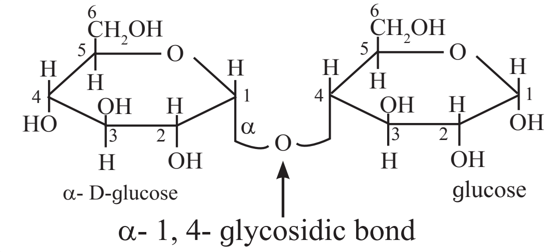


Fig. 14.9 : Haworth formula of maltose

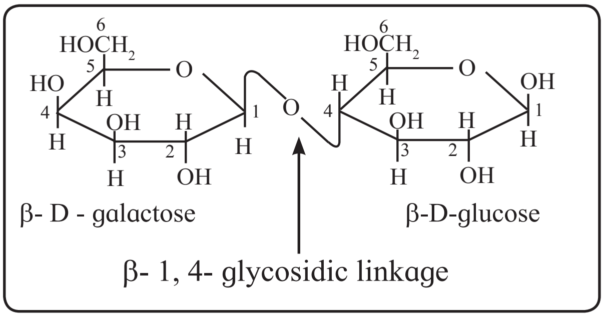


Fig. 14.10 : Haworth formula of lactose

c. Lactose : Lactose ($C_{12}H_{22}O_{11}$) is a disaccharide present in milk. It is formed from two monosaccharide units, namely D-galactose and D-glucose. The glycosidic linkage is formed between C-1 of β-D-galactose and C-4 of glucose. Therefore the linkage in lactose is called β-1,4-glycosidic linkage. The hemiacetal group at C-1 of the glucose unit is not involved in glycosidic linkage but is free. Hence lactose is a **reducing sugar**. Figure 14.10 shows Haworth formula of lactose.

14.2.10 Polysaccharides :

Polysaccharides are formed by linking large number of monosaccharide units by glycosidic linkages.

Use your brain power

- Is galactose an aldohexose or a ketohexose?
- Which carbon in galactose has different configuration compared to glucose?
- Draw Haworth formulae of ∝-D-galactose and β-D-galactose.
- Which disaccharides among sucrose, maltose and lactose is/are expected to give positive Fehling test?
- What are the expected products of hydrolysis of lactose?

Starch, cellulose and glycogen are the most common natural polysaccharides. Starch is storage carbohydrate of plants and important nutrient for humans and other animals. Cellulose is the main constituent of cell wall of plant and bacterial cells. It is also main constituent of wood and cotton. Glycogen constitutes storage carbohydrate of animals and is present in liver, muscles and brain. It is also found in yeast and fungi.

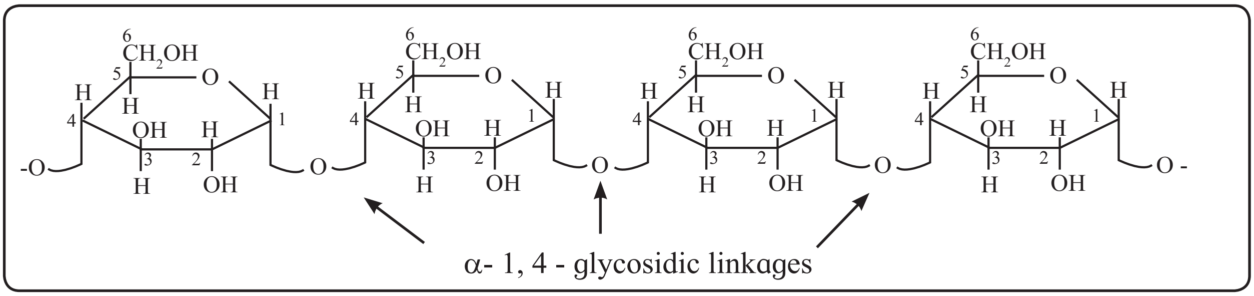


Fig. 14.11 : Amylose

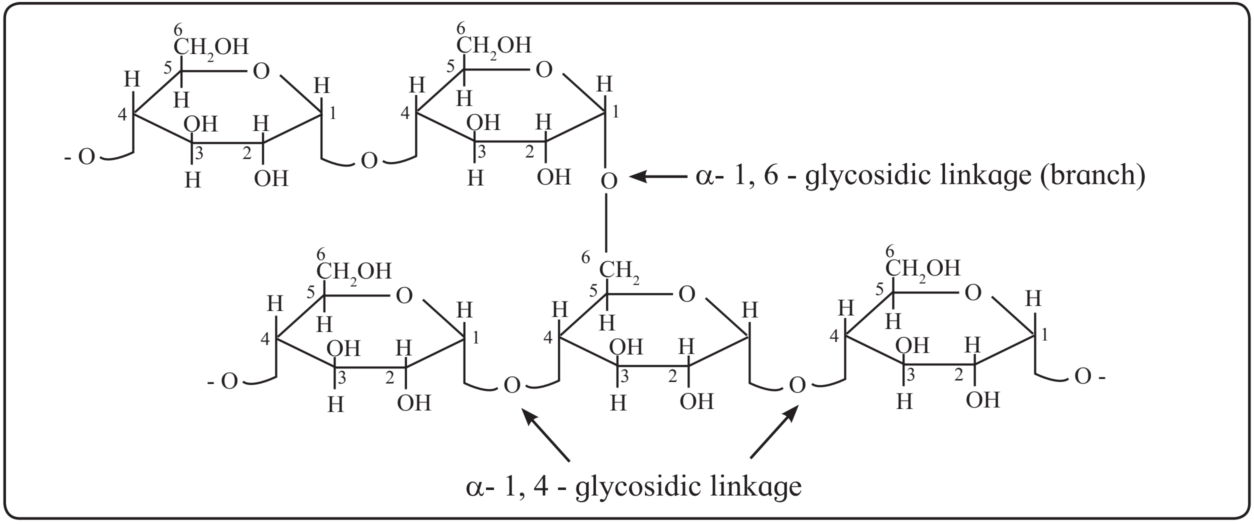


Fig. 14.12 : Amylopectin

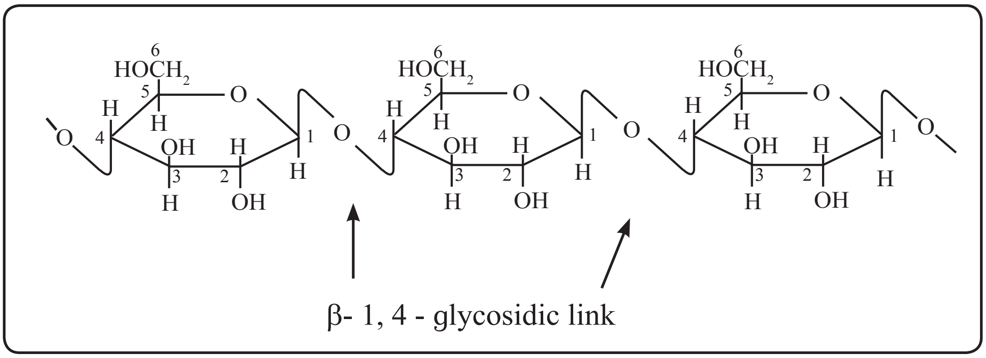


Fig. 14.13 : Cellulose

Can you think ?

When you chew plain bread, *chapati* or *bhaakari* for long time, it tastes sweet. What could be the resason ?

a. Starch : Starch is a polymer of ∝-D-glucose.Starch has two components, namely, **amylose** (15-20%) and **amylopectin** (80-85%). Amylose is soluble in water and forms blue coloured complex with iodine. It contains 200-1000 ∝-glucose units linked by ∝-1,4- glycosidic linkages giving rise to unbranched chain of variable length (Fig. 14.11). Amylopectin is water insoluble component of starch which forms blue-violet coloured complex with iodine. It is a branched chain polysaccharide. In amylopectin, chains are formed by ∝-1,4- glycosidic linkages between ∝-glucose units, where as branches are formed by ∝-1,6- glycosidic linkages (Fig. 14.12).

b. Cellulose : Cellulose is a straight chain polysaccharide of β-glucose units linked by β-1,4- glycosidic bonds. Chemical hydrolysis of cellulose requires use of concerntrated strong acids at high temperature and pressure. This implies that the β-1,4- glycosidic bond is very strong and difficult to hydrolyse. Humans do not have enzymes which can hydrolyse this linkage. Hence cellulose cannot be digested by human beings; it serves as the fibrous content of food useful for bowel movement. Figure 14.13 shows the Haworth formula of cellulose.

c. Glycogen : Glycogen has its structure similar to that of amylopectin, but it is more highly branched.

Do you know ?

The symbiotic bacteria in guts of insects called termites have enzymes that can hydrolyse β-1,4- glycosidic linkage in cellulose.

14.3 Proteins

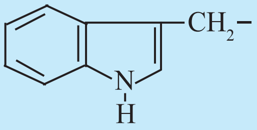
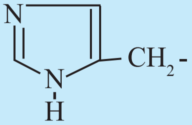
Can you recall ?

- What is the product of reaction of acetic acid with ammonia ?
- Write the structural formula of N-methyl acetamide. What is the name of the functional group in this compound?
- What are the nitrogenous nutrients in human diet?

Proteins are the fundamental structural materials of animal bodies. Proteins in the form of enzymes play prime role in all the physiological reactions. The name protein is derived form the Greek word, 'proteios' which means 'primary' or 'of prime importance'. Nutritional sources of proteins are milk, pulses, nuts, fish, meat, etc. Chemically proteins are polyamides which are high molecular weight polymers of the monomer units called ∝-amino acids.

14.3.1 ∝-Amino acids : Proteins on complete hydrolysis give rise to a mixture of ∝-amino acids. ∝-Amino acids are carboxylic acids having an amino ($-NH_2$) group bonded to

Table 14.1 Natural α - amino acids : L - RCH (NH_2) COOH (* Essential α - amino acids)

Type	Name	R	Three letter symbol	One letter symbol
Neutral ∝-amino acids	1. Glycine	H-	Gly	G
	2. Alanine	CH_3-	Ala	A
	3. Valine*	Me_2CH-	Val	V
	4. Leucine*	Me_2CH-CH_2 -	Leu	L
	5. Isoleucine*	CH_3-CH_2-CH(Me)-	Ile	I
	6. Asparagine	H_2N-CO-CH_2 -	Asn	N
	7. Glutamine	H_2N-CO-CH_2-CH_2-	Gin	Q
	8. Serine	HO-CH_2-	Ser	S
	9. Threonine*	CH_3-CHOH-	Thr	T
	10. Cysteine	HS-CH_2 -	Cys	C
	11. Methionine*	Me-S-CH_2-CH_2	Met	M
	12. Phenylalanine*	Ph-CH_2-	Phe	F
	13. Tyrosine	p-HO-C_6H_4-CH_2-	Tyr	Y
	14. Tryptophan*		Trp	W
	15. Proline	 (entire structure)	Pro	P
Acidic	16. Aspartic acid	HOOC-CH_2 -	Asp	D
	17. Glutamic acid	HOOC-CH_2-CH_2-	Glu	G
Basic	18. Lysine*	H_2N-$(CH_2)_4$-	Lys	K
	19. Arginine*	HN = C(NH_2) - NH - (CH_2)-	Arg	R
	20. Histidine*		His	H

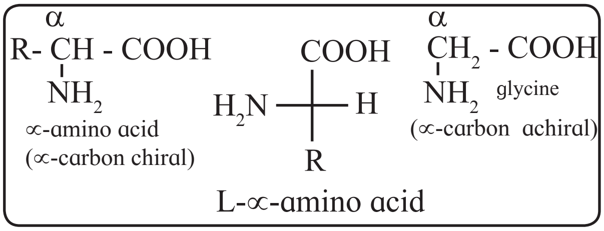


Fig. 14.14 : Natural ∝-amino acids

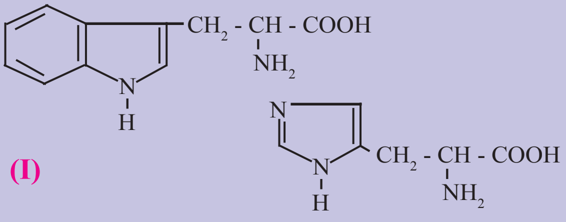
the ∝-Carbon, that is, the carbon next to the carboxyl (- COOH) group (Fig. 14.14). ∝-carbon in all the ∝-amino acids (except glycine) is chiral. It is found that the ∝- carbon in ∝-amino acids obtained by hydrolysis of proteins has 'L' configuration. The L-∝-amino acids are represented by the Fischer projection formula as shown in Fig. 14.14.

The symbol 'R' in the structure of ∝-amino acids respresents side chain and may contain additional functional groups. If 'R' contains a carboxyl (-COOH) group the amino acid is **acidic amino acid**. If 'R' contains an amino (1^0,2^0 or 3^0) group, it is called **basic amino acid**. The other amino acids having neutral or no functional group in 'R' are called **neutral amino acids**.

∝-Amino acids have trivial names and are generally represented by three letter symbols or sometimes by one letter symbol. Table 14.1 lists the twenty ∝-amino acids, often referred to as simply amino acids, commonly found in proteins with their symbols and also their types as neutral, acidic or basic. Ten ∝-amino acids from this list cannot be synthesised in human body and have to be obtained through diet. These are called **essential amino acids** and are marked with asterisk (*) in Table 14.1.

Use your brain power

Tryptophan and histidine have the structures (I) and (II) respectively. Classify them into neutral/ acidic/basic ∝-amino acids and justify your answer.(Hint : Consider involvement of lone pair in resonance).



(I)

(II)

Can you think ?

Compare the molecular masses of the following compounds and explain the observed melting points.

Formula	Molecular mass	Melting point
$CH_3-\underset{\underset{NH_2}{\vert}}{CH}-COOH$	89	293.5^0C
$C_5H_{11}-NH_2$	87	-55^0C
C_3H_7-COOH	88	-7.9^0C

∝-Amino acids are high melting, water soluble crystalline solids, unlike simple amines or carboxylic acids. These properties are due to a peculiar structure called **zwitter ion structure** of ∝-amino acids. An ∝-amino acid molecule contains both acidic carboxyl (-COOH) group as well as basic amino ($-NH_2$) group. Proton transfer from acidic group to basic group of amino acid forms a salt, which is a dipolar ion called zwitter ion (Fig. 14.15).

Amino acid can exist in different forms depending upon the pH of the aqueous solution in which it is dissolved. Consider, for example, zwitter ion and the other forms of alanine (Fig. 14.16).

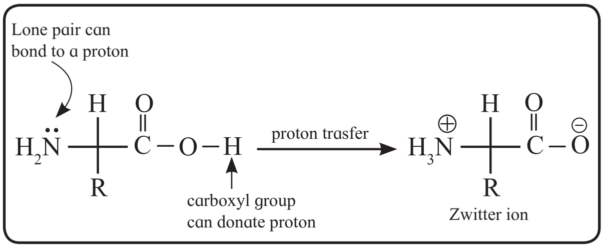


Fig. 14.15 : Zwitter ion

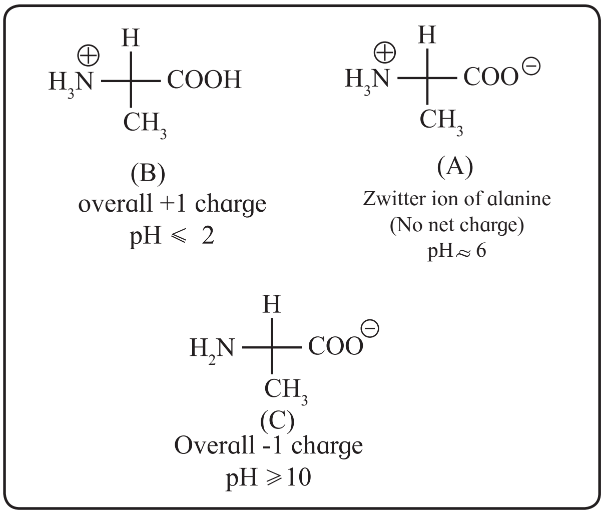


Fig. 14.16 : Three forms of alanine

Do you know ?

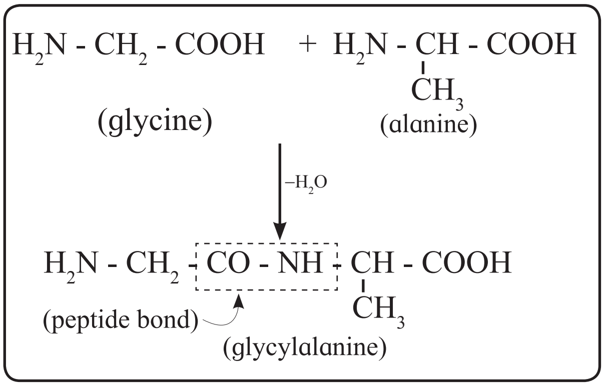
At the physiological pH of 7.4, neutral ∝-amino acids are primarily in their zwitterionic forms. On the other hand, at this pH acidic ∝-amino acids exist as anion (due to deprotonation of the carboxyl group), while basic ∝-amino acids exist as cation (due to protonation of the amino groups). Ionic structures of constituent ∝-amino acids result in ionic nature of proteins.

Can you recall ?

- What does the enzyme pepsin do?
- What are the initial and final products of digestion of proteins?

14.3.2 Peptide bond and protein :

Proteins are known to break down into peptides in stomach and duodenum under the influence of enzymes, pepsin being one of them which is secreted by stomach. Polypeptides are further broken down to ∝-amino acids. This implies that proteins are formed by connecting ∝-amino acids to each other. The bond that connects ∝-amino acids to each other is called **peptide bond**. Consider, for example, linking of a molecule of glycine with that of alanine. One way of doing this is to combine carboxyl group of glycine with ∝-amino group of alanine. This results in elimination of a water molecule and formation of a **dipeptide** called **glycylalanine** in which the two amino acid units are linked by a peptide bond (Fig. 14.17). It can be seen that a peptide bond or peptide linkage is same as what is described as **secondary amide** in organic chemistry. Combination of a third molecule of an ∝-amino acid with a dipeptide would result in formation of a **tripeptide**. Similarly linking of four, five or six ∝-amino acids results in formation of tetrapeptide, pentapeptide or hexapeptide respectively. When the number of ∝-amino acids linked by peptide bonds is more than ten, the products are called **polypeptides**. The -CHR- units linked by peptide bonds are referred to as '**amino acid residues**'. Proteins are polypeptides having more than hundred amino acid residues linked by peptide bonds. It may be, however, noted that distinction between proteins and polypeptides is not sharp. The two ends of a polypeptide chain of protein are not identical. The end having free carboxyl group is called **C-terminal** while the other end having free amino group is called **N-terminal**. In the dipeptide glycylalanine glycine residue is N-terminal and alanine residue is C-terminal.



$$H_2N-CH_2-COOH + H_2N-\underset{\displaystyle CH_3}{CH}-COOH \xrightarrow{-H_2O} H_2N-CH_2-\boxed{CO-NH}-\underset{\displaystyle CH_3}{CH}-COOH$$

Fig. 14.17 : Peptide bond

Use your brain power

- Write the structural formula of dipeptide formed by combination of carboxyl group of alanine and amino group of glycine.
- Name the resulting dipeptide.
- Is this dipeptide same as glycyalanine or its structural isomer?

14.3.3 Types of proteins :

Depending upon the molecular shape proteins are classified into two types.

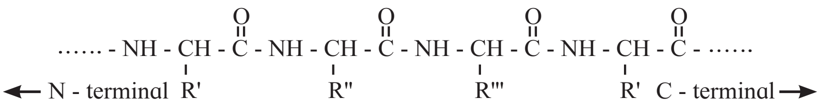
a. Globular proteins : Molecules of globular proteins have spherical shape. This shape results from coiling around of the polypeptide chain of protein. Globular proteins are usually soluble in water. For example : insulin, egg albumin, serum albumin, legumelin (protein in pulses)

b. Fibrous proteins : Molecules of fibrous proteins have elongated, rod like shape. This shape is the result of holding the polypeptide chains of protein parallel to each other. Hydrogen bonds and disulfide bonds are responsible for this shape. Fibrous proteins are insoluble in water. For example : keratin (present in hair, nail, wool), myosin (protein of muscles).

The shapes of protein molecules are the result of **four level structure of proteins**.

14.3.4 Structure of proteins :

Proteins are responsible for a variety of functions in organisms. Proteins of hair, muscles, skin give shape to the structure, while enzymes are proteins which catalyze physiological reactions. These diverse functions of proteins can be understood by studying the **four**



$$\leftarrow \text{N - terminal} \quad \cdots\text{ - NH - }\underset{R'}{\underset{|}{\text{CH}}}\text{ - }\overset{O}{\overset{\|}{\text{C}}}\text{ - NH - }\underset{R''}{\underset{|}{\text{CH}}}\text{ - }\overset{O}{\overset{\|}{\text{C}}}\text{ - NH - }\underset{R'''}{\underset{|}{\text{CH}}}\text{ - }\overset{O}{\overset{\|}{\text{C}}}\text{ - NH - }\underset{R'}{\underset{|}{\text{CH}}}\text{ - }\overset{O}{\overset{\|}{\text{C}}}\text{ - }\cdots \quad \text{C - terminal} \rightarrow$$

a. Representation by structural formula

...... Ala - Gly - Ser - Tyr - Gly - Gly - Lys ......

← N - terminal C - terminal →

b. Representation with amino acid symbols

Fig. 14.18 : Representation of primary structure of protein

level structure of proteins, namely primary, secondary, tertiary and quaternary structure of proteins.

a. Primary structure of proteins : Primary structure of proteins is **the sequence of constituent ∝-amino acid residues linked by peptide bonds**. Any change in the sequence of amino acid residue results in a different protein. Primary structure of proteins is represented by writing the three letter symbols of amino acid residuces as per their sequence in the concerned protein. The symbols are separated by dashes. According to the convention, the N-terminal amino acid residue as written at the left end and the C-terminal amino acid residue at the right end (Fig. 14.18).

Problem 14.3

Chymotrypsin is a digestive enzyme that hydrolyzes those amide bonds for which the carbonyl group comes from phenylalanine, tyrosine or tryptophan. Write the symbols of the amino acids and peptides smaller than pentapeptide formed by hydrolysis of the following hexapeptide with chymotrypsin.

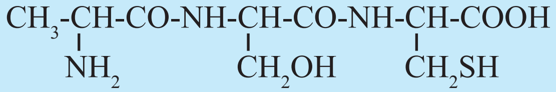
Gly-Tyr-Gly-Ala-Phe-Val

Solution : In the given hexapeptaide hydroylsis by chymotripsin can take place at two points, namely, Phe and Tyr. The carbonyl group of these residues is towards right side, that is, toward the C-terminal. Therefore the hydrolysis products in required range will be :

Gly-Tyr, Gly-Ala-Phe and Val

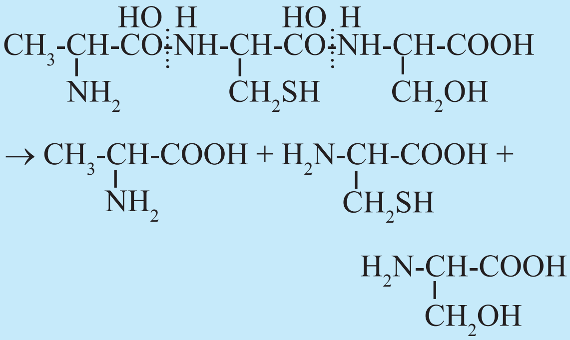
(a dipeptide) (a tripeptide) (∝-amino acid)

Problem 14.4 : Write down the structures of amino acids constituting the following peptide.



$$CH_3\text{-}\underset{NH_2}{\underset{|}{CH}}\text{-CO-NH-}\underset{CH_2OH}{\underset{|}{CH}}\text{-CO-NH-}\underset{CH_2SH}{\underset{|}{CH}}\text{-COOH}$$

Solution : The given peptide has two amide bonds linking three amino acids. The structures of these amino acids are obtained by adding one H_2O molecule across the amide bond as follows :



$$CH_3\text{-}\underset{NH_2}{\underset{|}{CH}}\text{-CO}\overset{HO\ H}{\vdots}\text{NH-}\underset{CH_2SH}{\underset{|}{CH}}\text{-CO}\overset{HO\ H}{\vdots}\text{NH-}\underset{CH_2OH}{\underset{|}{CH}}\text{-COOH}$$

$$\rightarrow CH_3\text{-}\underset{NH_2}{\underset{|}{CH}}\text{-COOH} + H_2N\text{-}\underset{CH_2SH}{\underset{|}{CH}}\text{-COOH} +$$

$$H_2N\text{-}\underset{CH_2OH}{\underset{|}{CH}}\text{-COOH}$$

b. Secondary structure of proteins :

The three-dimensional arrangement of localized regions of a protein chain is called the secondary structure of protein. Hydrogen bonding between N-H proton of one amide linkage and C=O oxygen of another gives rise to the secondary structure. Two types of secondary structures commonly found in proteins are **∝-helix** and **β-pleated sheet**.

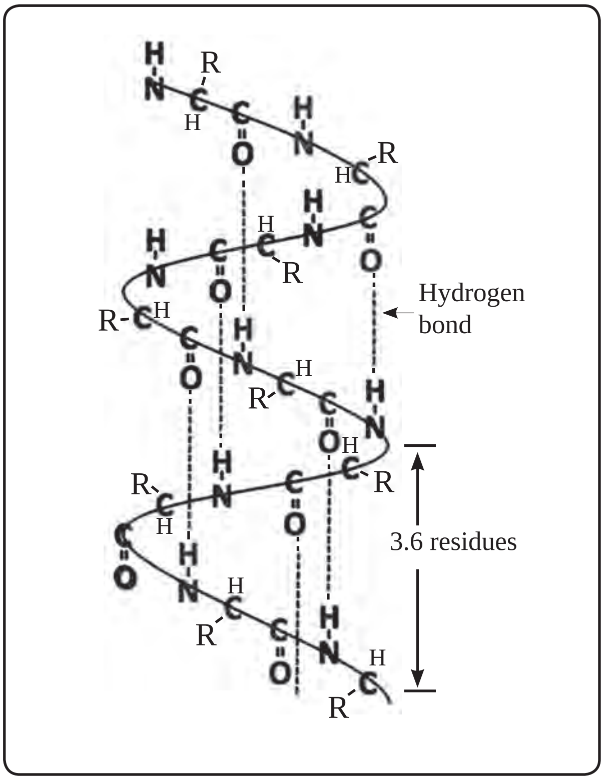


Fig. 14.19 : Backbone of ∝ - Helix

∝-Helix : The ∝-helix forms when a polypeptide chain twists into a **right handed or clockwise spiral** (Fig. 14.19). Some characteristic features of ∝-helical structure of protein are:

- Each turn of the helix has 3.6 amino acids.
- A C=O group of one amino acid is hydrogen bonded to N-H group of the fourth amino acid along the chain.
- Hydrogen bonds are parallel to the axis of helix while R groups extend outward from the helix core.

Myosin in muscle and ∝-keratin in hair are proteins with almost entire ∝-helical secondary structure.

Do you know ?

In collagen, the protein of connective tissue, the polypeptide chains have **unusual left-handed helix structure**. Three strands of these chains wind around each other in a right-handed triple helix.

β-Pleated sheet : The secondary structure is called β-pleated sheet when **two or more polypeptide chains, called strands, line up side-by-side** (Fig. 14.20). The β-pleated sheet structure of protein consists of extended strands of polypeptide chains held together by hydrogen bonding. The characteristics of β-pleated sheet structure are :

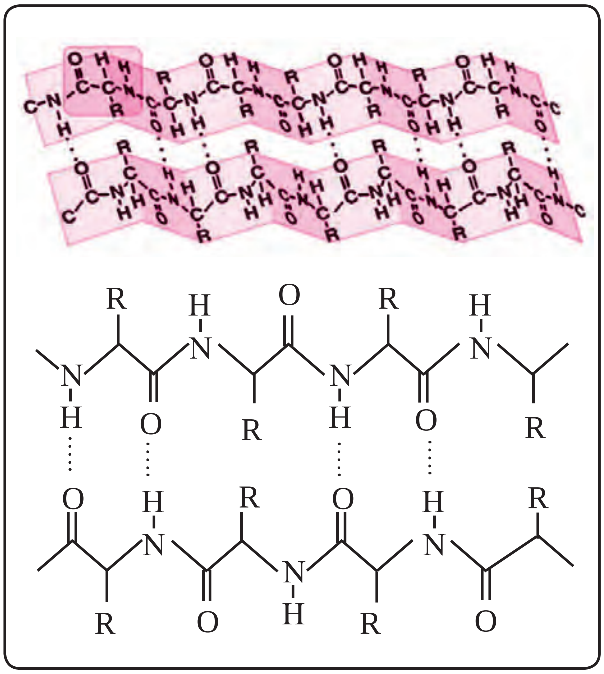


Fig. 14.20 : β - pleated sheet

- The C=O and N-H bonds lie in the planes of the sheet.
- Hydrogen bonding occurs between the N-H and C=O groups of nearby amino acid residues in the neighbouring chains.
- The R groups are oriented above and below the plane of the sheet.

The β-pleated sheet arrangement is favoured by amino acids with small R groups.

Most proteins have regions of ∝-helix and β-pleated sheet, in addition to other random regions that cannot be characterised by either of these secondary structures. For example: Spider dragline silk protein is strong due to β-pleated sheet region, yet elastic due to ∝-helical regions in it.

c. Tertiary structure of proteins : The three-dimensional shape adopted by the entire polypeptide chain of a protein is called its tertiary structure. It is the result of folding of the chain in a particular manner that the structure is itself stabilized and also has attractive interaction with the aqueous environment of the cell. The **globular** and **fibrous** proteins represent two major molecular shapes resulting from the tertiary structure. The forces that stabilize a particular tertiary structure include **hydrogen bonding**, **dipole-dipole attraction** (due to polar bonds in the side chains), **electrostatic attraction** (due to the ionic groups like $-COO^{\ominus}$, $NH_3^{\oplus}$ in the side chain) and also **London dispersion forces**. Finally, **disulfide bonds** formed by oxidation of nearby -SH groups (in cysteine residues) are the **covalent bonds** which stabilize the tertiary structure (Fig. 14.21).

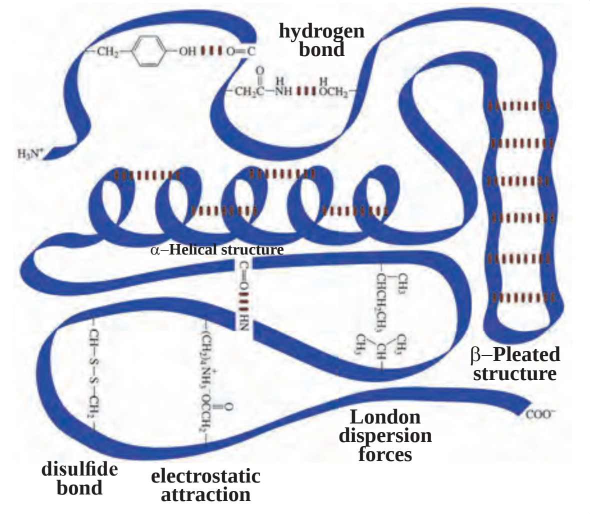


Fig. 14.21 : Tertiary structure of protein

d. Quaternary structure of proteins : When two or more polypeptide chains with folded **tertiary structures come together into one protein complex**, the resulting shape is called quaternary structure of the protein. Each individual polypeptide chain is called a subunit of the overall protein. For example: **Haemoglobin** consists of **four subunits** called haeme held together by intermolecular forces in a compact three dimensional shape. Haemoglobin can do its function of oxygen transport only when all the four subunits are together. Figure 14.22 summerizes the four levels of protein structure.

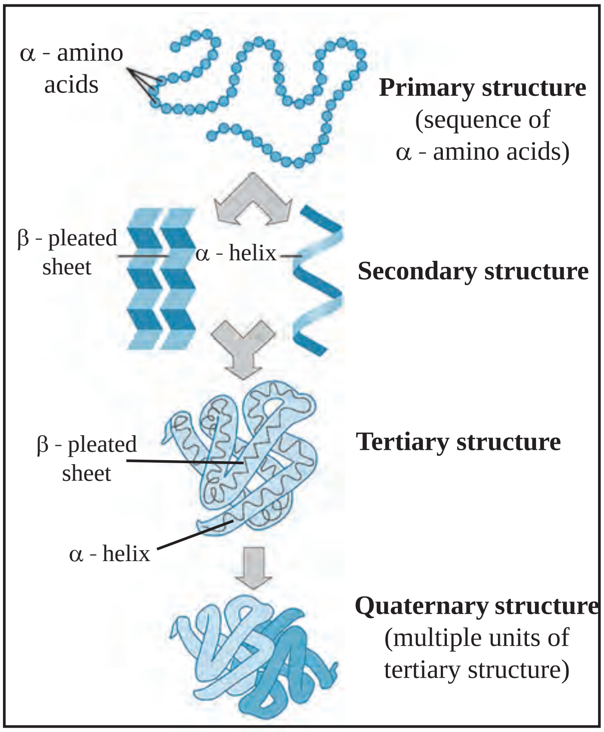


Fig. 14.22 : Four levels of protein structure

Use your brain power

A protein chain has the following amino acids residues. Show and label the interactions that can be present in various pairs from these giving rise to tertiary level structure of protein.

$-HN-\underset{|\atop CH_2OH}{CH}-CO-$, $-HN-\underset{|\atop CH_2-Ph}{CH}-CO-$,

$-HN-\underset{|\atop CH_2-CO-NH_2}{CH}-CO-$, $-HN-\underset{|\atop CH_2-CH-Me_2}{CH}-CO-$,

Can you tell ?

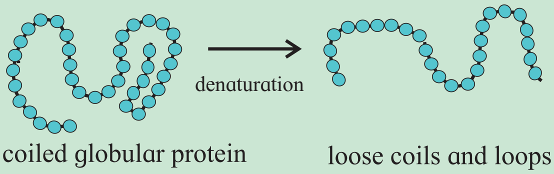
What is the physical change observed when (a) egg is boiled, (b) milk gets curdled on adding lemon juice ?

14.3.5 Denaturation of proteins

High temperature, acid, base and even agitation can disrupt the noncovalent interactions responsible for a specific shape of protein. This is denaturation of protein. **Denaturation is the process by which the molecular shape of protein changes without breaking the amide/peptide bonds that form the primary structre.**

Do you know ?

Globular proteins are typically folded with hydrophobic side chains in the interior and polar residues on the outside, and thereby are water soluble. Denaturation exposes the hydrophobic region of globular proteins and makes them water insoluble.



Denaturation results in disturbing the secondary, tertiary or quaternary structure of protein. This causes change in properties of protein and the biological activity is often lost.

14.3.6 Enzymes :

Can you recall ?

- Which parameter, equilibrium constant or activation energy, decides the rate of a chemical reaction?
- What is the influence of a catalyst on activation energy?

A very large number of chemical reactions take place in our bodies. These are brought about at the physiological pH of 7.4 and the body temperature of 37^0 C with the help of biological catalysts called enzymes. For example : insulin, an enzyme secreted by pancreas, controls blood sugar level; amylase, an enzyme present in saliva, hydrolyzes starch. Chemically enzymes are proteins. Every living cell contains at least 1000 different enzymes. Most enzymes catalyse only one reaction or one group of similar reactions. Thus, enzyme catalysis is **highly specific**. You have learnt that a mineral acid can catalyse hydrolysis of many types of compounds such as esters, acetals and amides. In contrast, an enzyme that catalyses hydrolysis of amide will not work on ester or acetal.

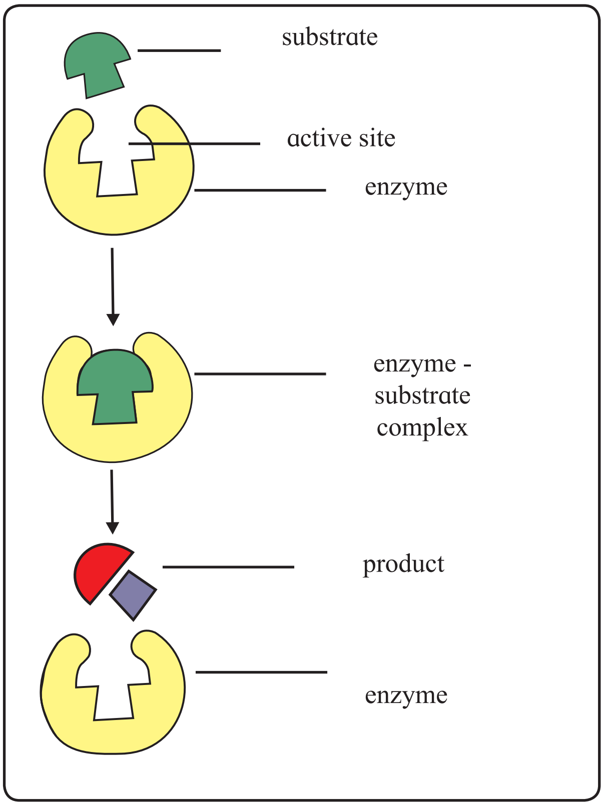


Fig. 14.23 : Enzyme catalysis

Mechanism of enzyme catalysis

Action of an enzyme on a substrate is described as **lock-and-key mechanism** (Fig.14.23). Accordingly, the enzyme has active site on its surface. A substrate molecule can attach to this active site only if it has the right size and shape. Once in the active site, the substrate is held in the correct orientation to react and forms the products of reaction.

The products leave the active site and the enzyme is then ready to act as catalyst again. Formation of enzyme-substrate complex has very low activation energy. That is how the rate of the reaction is very high. Some enzymes are so **efficient** that one enzyme molecule can catalyse the reaction of 10000 substrate molecules in one second.

Several enzymes have been isolated from organisms (such as bacteria), purified and crystallised,and amino acid sequences of many of them have been determined. In many **industrial processes** specific reactions are carried out by use of enzymes extracted from organisms, and also by use of **new enzymes** made using genetic engineering.

Some examples of **industrial application** of enzyme catalysis are :

- Conversion of glucose to sweet-tasting fructose, using glucose isomerase.
- Manufacture of new antibiotics, using pencillin G acylase.
- Manufacture of laundry detergents, using proteases.
- Manufacture of esters used in cosmetics, using genetically engineered enzyme.

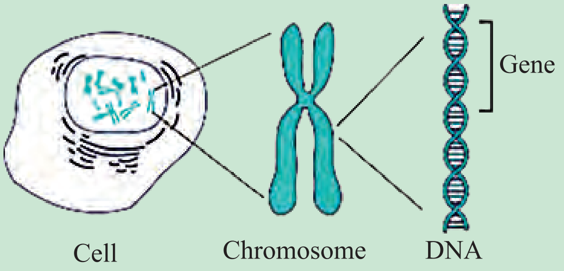
14.4 Nucleic acids :

Can you tell ?

- What is the single term that answers all the following questions ?
- What decides whether you are blue eyed or brown eyed ?
- Why does wheat grain germinate to produce wheat plant and not rice plant ?
- Which acid molecules are present in nuclei of living cells ?

Do you know ?

Synthesis of protein, the fundamental structural material of body, is the process in which genetic information is transferred. DNA governs this process. DNA is present in the chromosomes of the cell nucleus. Each chromosome has a different type of DNA. An individual chromosome is composed of many **genes**. Gene is a portion of DNA molecule responsible for synthesis of a single protein. **DNA stores the genetic information**, while **RNA translates** this into synthesis of proteins needed by cells for proper function and development.

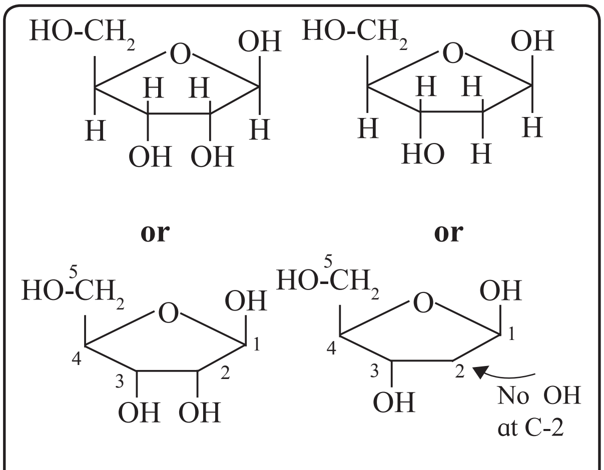


One of the most remarkable properties of living cells is their ability to produce their replicas through thousands of generations. This becomes possible because certain type of information is passed unchanged from one generation to the next. Such information is called **genetic information** and its transfer to new cells is accomplished by **nucleic acids**.

There are two types of nucleic acids : **ribonucleic acids (RNA) and deoxyribonucleic acids (DNA)**. RNA are found mainly in the fluid of living cells (cytoplasm) while DNA are found primarily in the nuclei of living cells.

Knowledge of structure of nucleic acids is essential to understand their biological functions. In this chapter we are going to look at the **structural aspects of nucleic acids**.

14.4.1 Nucleotides : Nucleic acids are unbranched polymers of **repeating monomers** called nucleotides. In other words, nucleic acids have a polynucleotide structure. DNA molecules contain several million nucleotides while RNA molecules contain a few thousand



D - Ribose
(present in RNA)

2 - Deoxy-D-ribose
(present in DNA)

Fig 14.24 : Sugar Components of nucleic acids

nucleotides.

The nucleotide monomers consist of three components : a **monosaccharide**, a **nitrogen-containing base** and a **phosphate group**.

Nucleotides of both RNA and DNA contain five-membered ring monosaccharide (furanose), often called simply sugar component. In RNA, the sugar component of nucleotide unit is D-ribose, while in DNA, it is 2-deoxy-D-ribose (Fig. 14.24).

Total five nitrogen - containing bases are present in nucleic acids. Three bases with one ring (**cytosine**, **uracil** and **thymine**) are derived from the parent compound **pyrimidine**. Two bases with two rings (**adenine** and **guanine**) are derived from the parent compound **purine**. Each base in designated by a one-letter symbol (Fig. 14.25). Uracil (U) occurs only in RNA while thymine (T) occurs only in DNA.

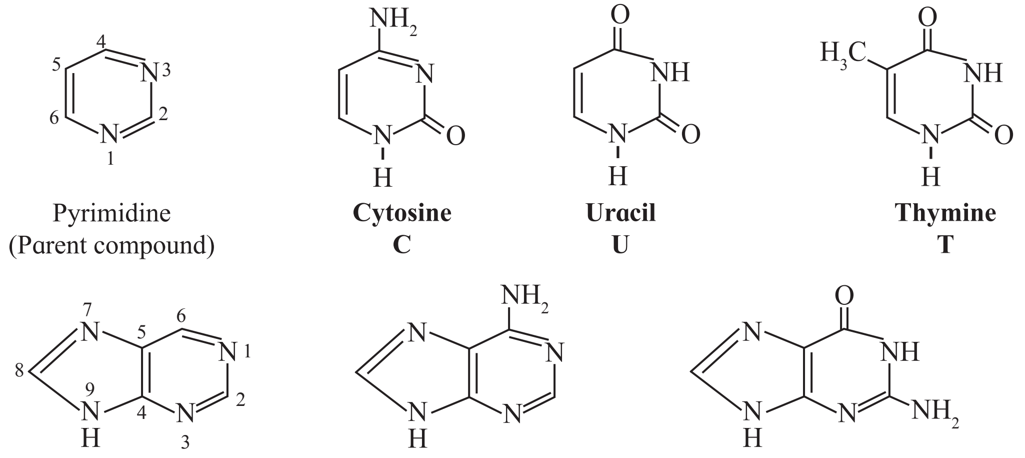
Remember...

RNA contains : D-ribose, A, G, C, U

DNA contains : D-2-deoxyribose, A, G, C, T

A **nucleoside** is formed by joining the anomeric carbon of the furanose with nitrogen of a base. While numbering the atoms in a nucleoside, primes (') are used for furanose numbering to distinguish them from the atoms of the base (Fig. 14.26). With pyrimidine bases, the nitrogen atom at the 1 position bonds with the 1' carbon of the sugar. With purine bases, the nitrogen atom at the 9 position bonds with 1' carbon of the sugar.

Nucleotides are formed by adding a phosphate group to the 5'-OH of a nucleoside (Fig. 14.27). Thus, **nucleotides are monophosphates of nucleosides**. Abridged names of some nucleotides are AMP, dAMP, UMP, dTMP and so on. Here, the first capital letter is derived from the corresponding base.



Pyrimidine
(Parent compound)

Cytosine
C

Uracil
U

Thymine
T

Purine
(Parent compound)

Adenine
A

Guanine
G

Fig 14.25 : Bases in nucleic acids

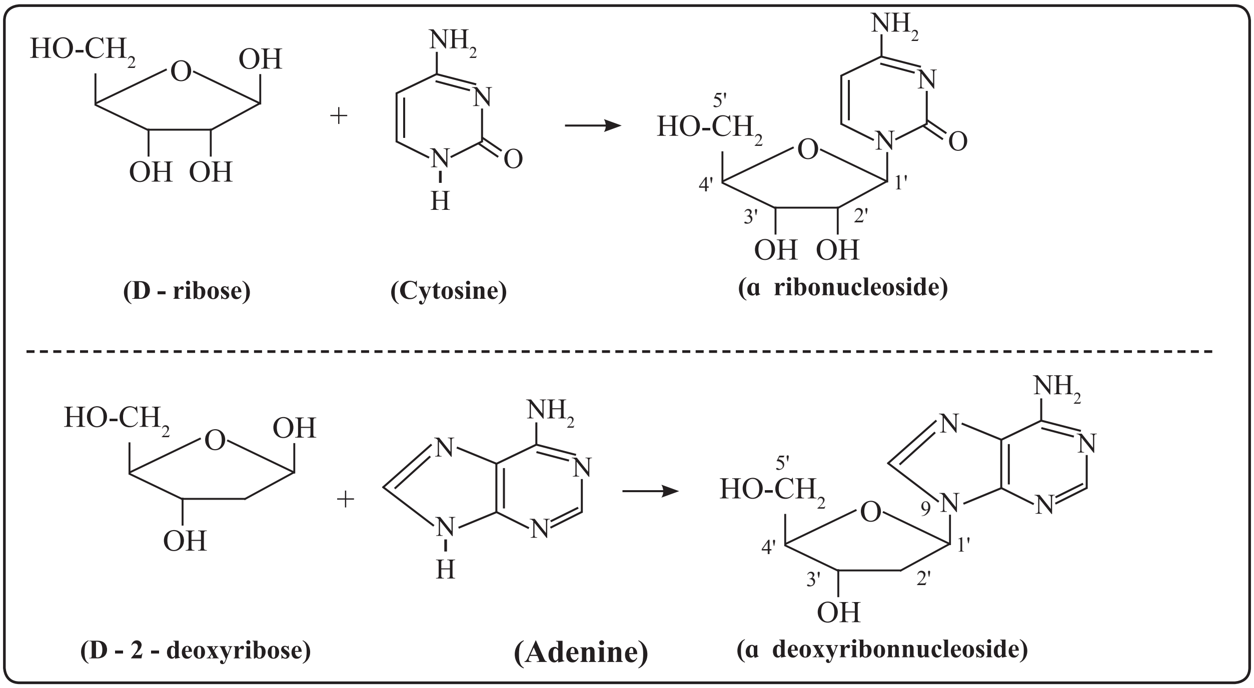


Fig 14.26 : Formation of nucleoside

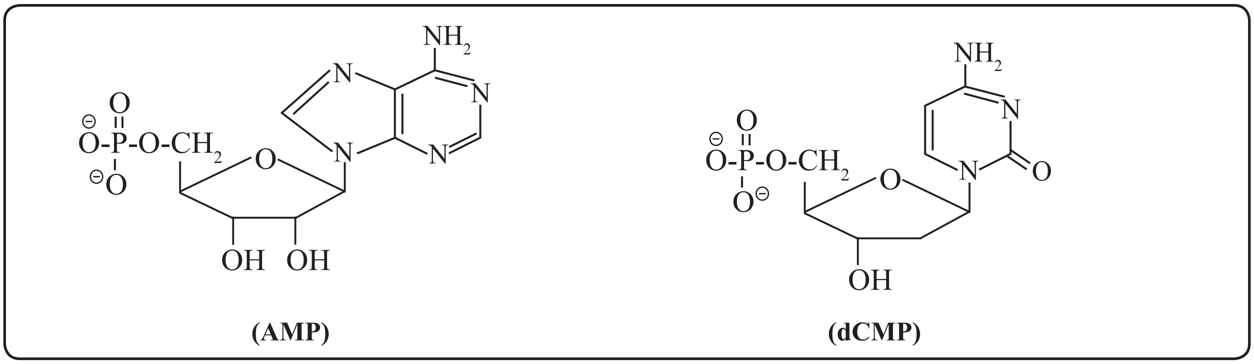


Fig 14.27 : Structures of nucleotides

Use your brain power

Draw structural formulae of nucleosides formed from the following sugars and bases.
i. D-ribose and guanine
ii. D-2-deoxyribose and thymine

MP stands for monophosphate. Small letter 'd' in the beginning indicates deoxyribose in the nucleotide.

14.4.2 Structure of nucleic acids : Nucleic acids, both DNA and RNA, are polymers of nucleotides, formed by joining the 3' - OH group of one nucleotide with 5'-phosphate of another nucleotide (Fig. 14.28). Two ends of polynucleotide chain are distinct from each other. One end having free phosphate group of 5' position is called 5' end. The other end is 3' end and has free OH- group at 3' position.

The polynucleotide structure of nucleic acids can be represented schematically as in Fig. 14.29 (a and b).

The primary structure of nucleic acids is the sequence of the nucleotides in it. This, in turn, is determined by the identity of the bases in the nucleotides. Different nucleic acids have distinct primary structure. **It is the sequence of bases in DNA which carries the genetic information of the organism.** The polynucleotide chains of nucleic acids are named by the sequence of the bases, beginning at the 5' end and using the one letter symbols of the bases. For example the

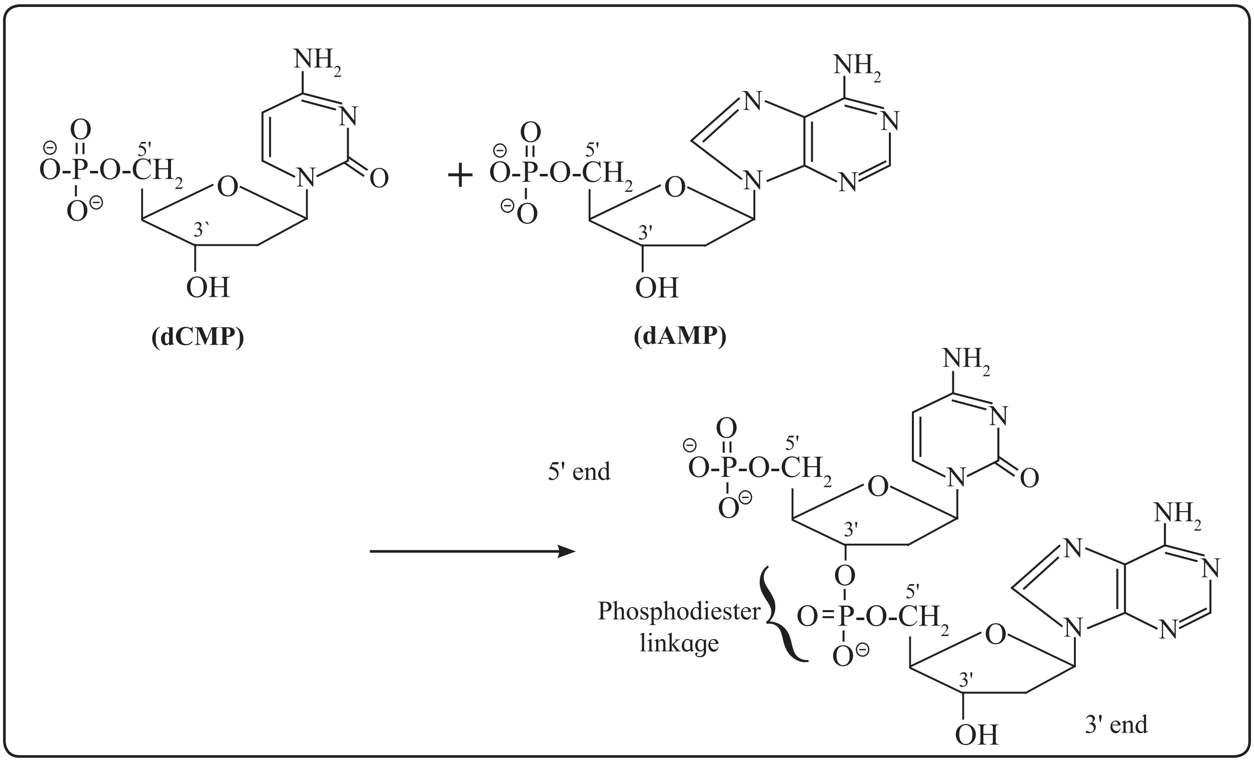


Fig 14.28 : Formation of a dinucleotide

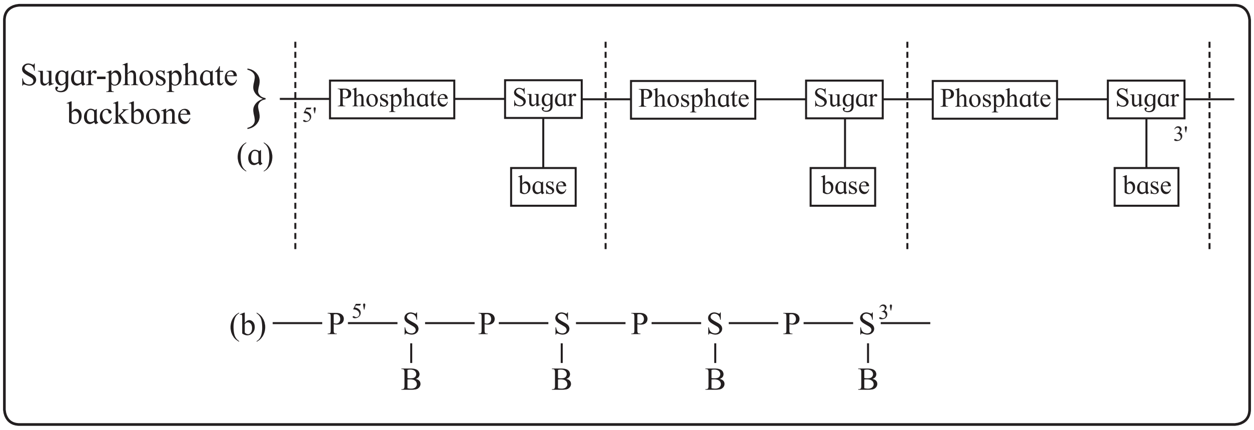
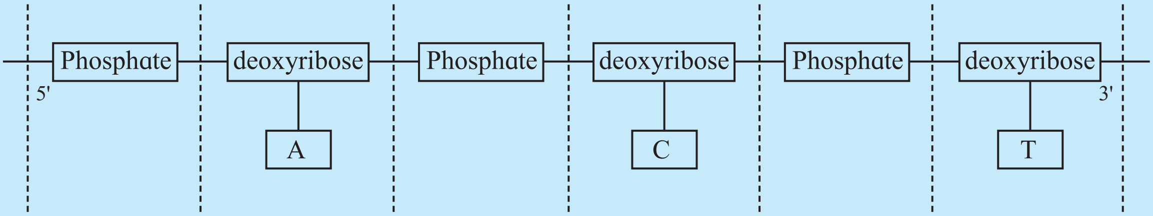


Fig 14.29 : Polynucleotide structure of nucleic acids : Schematic representations (a) and (b)

Problem 14.5 : Draw a schematic representation of trinucleotide segment 'ACT' of a DNA molecule.

Solution : In DNA molecule sugar is deoxyribose. The base 'A' in the given segment is at 5' end while the base 'T' at the 3' end. Hence the schematic representation of the given segment of DNA is



name CATG means there are four nucleotides in the segment containing the bases cytosine, adenine, thymine and guanine, in the indicated order from the 5' end.

Remember...

- A nucleic acid contains a backbone consisting of alternating sugar and phosphate groups.
- Backbone of all types of DNA contains the sugar 2-deoxy-D-ribose while that of RNA contains the sugar D-ribose.
- The identity and sequence of bases distinguish one polynucleotide from the other.
- A polynucleotide has one free phosphate group at the 5' end.
- A polynucleotide has a free OH group at the 3' end.

14.4.3 DNA double helix : James Watson and Francis Crick put forth in 1953 a double helix model for DNA structure, which was later verified by electron microscopy. Salient features of the Watson and Crick model of DNA are :

- DNA consists of two polynucleotide strands that wind into a **right-handed double helix**.
- The two strands run in opposite directions; one from the 5' end to the 3' end, while the other from the 3' end to the 5' end.
- The sugar- phosphate backbone lies on the outside of the helix and the bases lie on the inside, perpendicular to the axis of the helix.
- The double helix is stabilized by hydrogen bonding between the bases of the two DNA strands. This gives rise to a ladder-like structure of DNA double helix.
- Adenine always forms two hydrogen bonds with thymine, and guanine forms three hydrogen bonds with cytosine. Thus **A - T and C - G are complementary base pairs** and the two strands of the double helix are complementary to each other.

It may be noted that RNA exists as single stranded structure.

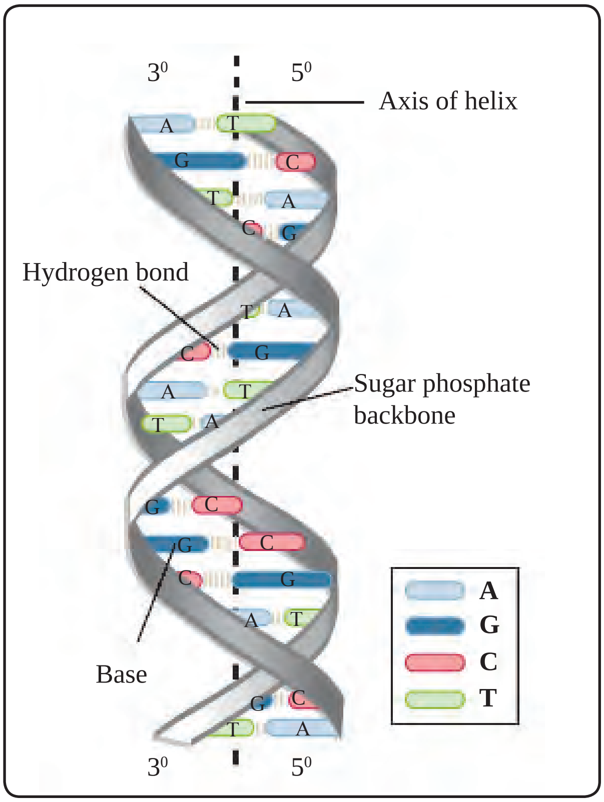
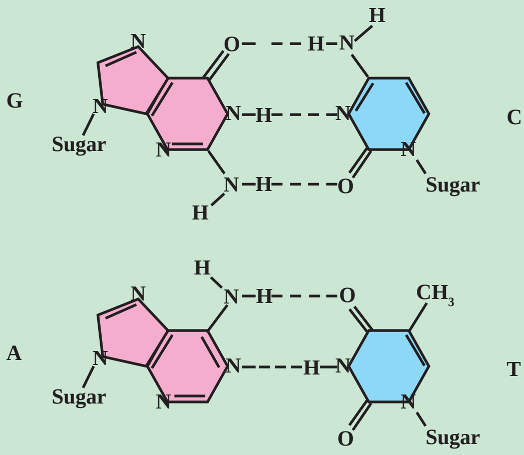


Fig. 14.30 : DNA double helix

Do you know ?

Hydrogen bonding between complementary base pairs.



Problem 14.6 : Write the sequence of the complementary strand of the following portion of a DNA molecule : 5' - ACGTAC-3'

Solution : The complementary strand runs in opposite direction from the 3' end to the 5' end. It has the base sequence decided by complementary base pairs A - T and C - G.

Original strand 5' - A C G T A C - 3'
↓ ↓ ↓ ↓ ↓ ↓
Complementary strand 3' - T G C A T G - 5'

Exercises

1. Select the most correct choice.

i. CH_2OH-CO-$(CHOH)_4$-CH_2OH is an example of

a. Aldohexose b. Aldoheptose
c. Ketotetrose d. Ketoheptose

ii. Open chain formula of glucose does not contain

a. Formyl group

b. Anomeric hydroxyl group

c. Primary hydroxyl group

d. Secondary hydroxyl group

iii. Which of the following does not apply to CH_2NH_2 - $COOH$

a. Neutral amino acid

b. L - amino acid

c. Exists as zwitter ion

d. Natural amino acid

iv. Tryptophan is called essential amino acid because

a. It contains aromatic nucleus.

b. It is present in all the human proteins.

c. It cannot be synthesised by human body.

d. It is essential constituent of enzymes.

v. A disulfide link gives rise to the following structure of protein.

a. Primary

b. Secondary

c. Tertiary

d. Quaternary

vi. RNA has

a. A - U base pairing

b. P-S-P-S backbone

c. double helix

d. G - C base pairing

2. Give scientific reasons :

i. The disaccharide sucrose gives negative Tollens test while the disaccharide maltose gives positive Tollens test.

ii. On complete hydrolysis DNA gives equimolar quantities of adenine and thymine.

iii. α - Amino acids have high melting points compared to the corresponding amines or carboxylic acids of comparable molecular mass.

iv. Hydrolysis of sucrose is called inversion.

v. On boiling egg albumin becomes opaque white.

3. Answer the following

i. Some of the following statements apply to DNA only, some to RNA only and some to both. Lable them accordingly.

   a. The polynucleotide is double stranded. (……..)

   b. The polynucleotide contains uracil. (……..)

   c. The polynucleotide contains D-ribose (……..).

   d. The polynucleotide contains Guanine (……..).

ii. Write the sequence of the complementary strand for the following segments of a DNA molecule.

   a. 5' - CGTTTAAG - 3'

   b. 5' - CCGGTTAATACGGC - 3'

iii. Write the names and schematic representations of all the possible dipeptides formed from alanine, glycine and tyrosine.

iv. Give two evidences for presence of formyl group in glucose.

4. Draw a neat diagram for the following:

i. Haworth formula of glucopyranose

ii. Zwitter ion

iii. Haworth formula of maltose

iv. Secondary structure of protein

v. AMP

vi. dAMP

vii. One purine base from nucleic acid

viii. Enzyme catalysis

Activity :

- **Draw structure of a segment of DNA comprising at least ten nucleotides on a big chart paper.**
- **Make a model of DNA double stranded structure as group activity.**

15. INTRODUCTION TO POLYMER CHEMISTRY

Can you recall ?

i. Classify the following materials as bio-degradable and non-bio-degradable : Thermocol, glass, wood, cotton clothes, paper bags, polythene bags, nylon ropes, fruit peels.

ii. Give examples of man made materials we use in our daily life.

iii. Which material is used in manufacture of toys, combs ?

iv. Write examples of thermosetting plastic articles.

v. List various properties of plastic.

15.1 Introduction : Today the overall development in polymer science and technology has enriched human life. The world would be at totally different place without polymers such as artificial fibres, plastics and elastomers. From the throwaway candy wrapper to the artificial heart, polymers touch our lives as does no other class of material.

In short we are living in the world of polymers. Polymer chemistry emerged as a separate branch of chemistry during the last several decades due to the voluminous knowledge built up in this field and the ever increasing applications in everyday life.

Chemically polymers are complex, giant macromolecules made from the repeating units which are derived from small molecules called 'monomers'. The term 'polymer' originates from Greek word 'poly' meaning many and 'mer' meaning part or unit. Interlinking of many units constitutes polymers.

Polymers are high molecular mass macromolecules (10^3 - 10^7 u).

Both inorganic as well as organic polymers are known. In this chapter we will study some aspects of organic polymers. You have learnt in Chapter 14 about carbohydrates, proteins and nucleic acids which are important organic biopolymers playing crucial role in living world.

In this chapter we will consider mainly man made organic polymers with reference to aspects such as types, preparation and applications.

Do you know ?

Nobel prizes for pioneering work in 'Polymers' :

- The polymeric substances, that we know today as macromolecules, were considered hundred years ago as associated molecules. Staudinger received Nobel prize (1953) for his work which established macromolecular nature of polymers.
- In 1963 Natta received Nobel prize for recognizing stereospecific regularity in vinyl polymers.
- In 1974 Flory received Nobel prize for elucidating the three step mechanism of chain-reaction in polymerization involving initiation, propagation and termination.

15.2 Classification of polymers : Polymers are classified in number of ways on the basis of their source, chemical structures, mode of polymerization, molecular forces, type of monomers and biodegradability.

15.2.1 Classification of polymers on the basis of source or origin : Poylmers are divided into three categories : a. Natural b. Synthetic c. Semisynthetic

a. Natural polymers : The polymers obtained from natural source are said to be natural polymers. They are further subdivided into two types.

i. Plant polymers : These are obtained from plants. For example, cotton and linen are obtained from cotton plant and flax plant respectively. Natural rubber is another example of natural polymer which is manufactured from the latex obtained from bark of rubber trees.

ii. Animal polymers : These are derived from animal sources. For example, wool is obtained from hair of sheep. Silk is obtained from silkworm.

b. Synthetic Polymers : These are man- made polymers. These polymers are artificially prepared by polymerization of one monomer or copolymerization of two or more monomers. Nylon, terylene, neoprene are synthetic polymers. These are further divided into three subtypes, namely, fibres, synthetic rubbers and plastics.

c. Semisynthetic polymers : These are derived from natural polymers. These are also called regenerated fibres.Cellulose derivatives such as cellulose acetate rayon, cellulose nitrate, viscose rayon, cuprammonium rayon are a few examples of this category.

Semisynthetic polymers are used in preparation of non-inflammable photographic films, cinema films, varnishes, etc.

Use your brain power

- Differentiate between natural and synthetic polymers.

15.2.2 Classification of polymers on the basis of structure : Depending upon how the monomers are linked together, that is, the chain configuration, polymers are classified in three general types : a. linear b. branched and c. three dimensional cross - linked polymers (Fig. 15.1). The nature of linking the monomers depends upon the nature and number of functional groups in them.

a. Linear or straight chain polymers : When the monomer molecules are joined together in a linear arrangement the resulting polymer is straight chain polymer. It is obtained from bifunctional monomers or alkenes. (Fig. 15.1(a)). For example : PVC, high density polythene.

b. Branched chain polymers : The second most common arrangement is that of branched chain. Monomer having 3 functional groups or already having side chains give rise to branched chain polymers. (Fig. 15.1 (b)). For example : low density polythene.

c. Cross-linked polymers : Third type of arrangement is said to be cross linked or network polymers where cross links are produced between linear chains as shown in Fig. 15.1 (c). Cross linking results from polyfunctional monomers. For example, bakelite, melamine.

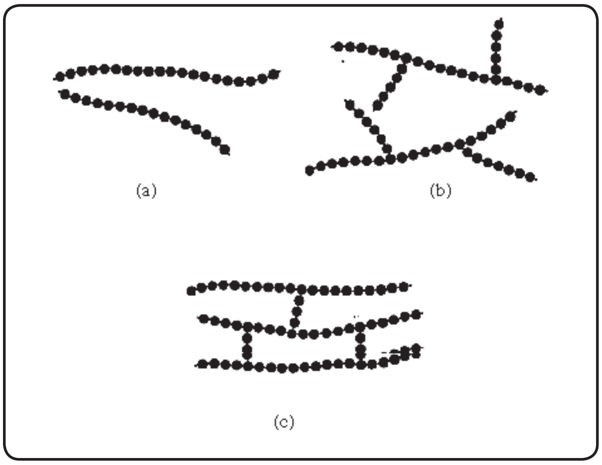


Fig. 15.1 : Different chain configurations of polymers

15.2.3 Classification of polymers on the basis of mode of polymerization : Polymerization is the fundamental process by which low molecular mass compounds are converted into high molecular weight compounds by linking together of repeating structural units with covalent bonds. This process is illustrated below.

$$\text{Low molecular mass material (Possessing reactive groups)} \xrightarrow[\text{and/or pressure and/or catalyst}]{\text{High temprature}} \text{High molecular mass material}$$

There are three modes of polymerization according to the types of reactions taking place between the monomers.

a. Addition polymerization (or chain growth polymerization)

b. Condensation polymerization (or step growth polymerization)

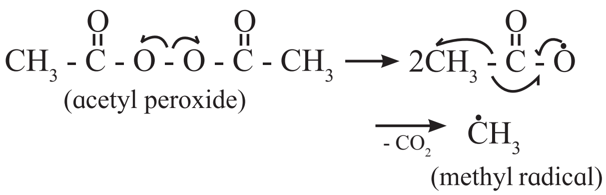
c. Ring opening polymerization

a. Addition polymerization : Addition polymerization is a process of formation of polymers by addition of monomers without loss of any small molecules. The repeating unit of an addition polymer has the same elemental composition as that of original monomer.

Compounds containing double bond undergo addition polymerization. It is also referred as vinyl polymerization, since majority of monomers are from vinyl category. For example : vinyl chloride (CH_2=CHCl), acrylonitrile (CH_2=CHCN). Formation of polyethylene from ethylene is well known example of addition polymerization. Addition polymerization produces high molecular mass polymeric materials without formation of any intermediate low molecular mass polymeric materials.

Free radical mechanism is most common in addition polymerisation. It is also called chain reaction which involves three distinct steps chain initiation, chain propagation and chain termination.

Step 1 : Chain initiation : The chain reaction is initiated by a free radical. An initiator (catalyst) such as benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. can be used to produce free radical. For example acetyl peroxide generates methyl radical as shown below :



$$CH_3-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-\dot{O} \xrightarrow[-CO_2]{} \dot{C}H_3$$

The free radical (say $\dot{R}$) so formed attaches itself to the olefin (vinyl monomer) and produces a new radical, made up of two parts, namely, the attached radical and the monomer unit.

$$\dot{R} + CH_2 = CHY \longrightarrow R-CH_2-\dot{C}HY$$

(free radical) (vinyl monomer) (new radical)

Step 2 : Chain propagation : The new radical formed in the initiation step reacts with another molecule of vinyl monomer, forming another still bigger sized radical, which in turn reacts with another monomer molecule. The repetition of this sequence takes place very rapidly. It is called chain propagation.

$$R-CH_2-\dot{C}HY + nCH_2 = CHY \longrightarrow R \left(CH_2-CHY \right)_n CH_2-\dot{C}HY$$

This step is very rapid and leads to high molecular mass radical.

Step 3 : Chain termination : Ultimately, at some stage, termination of the growing chain takes place. It may occur by several processes. One mode of termination is by combination of two growing chain radicals.

$$2\ R \left(CH_2-CHY \right)_n CH_2-\dot{C}HY \longrightarrow R \left(CH_2CHY \right)_{n+1} \left(CHYCH_2 \right)_{n+1} R$$

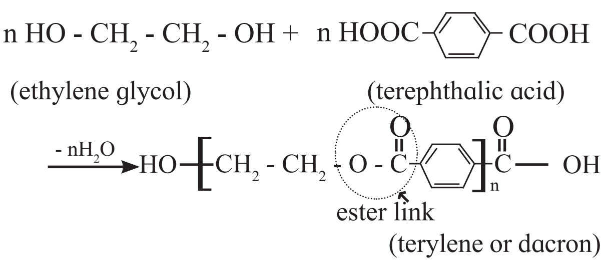
(polymer)

Internet my friend

Study audiovisual free radical mechanism of addition polymerization. (Refer/search for free radical polymerization.Animation (IQOG-CSIC) on youtube channel)

b. Condensation polymerization :

Consider the formation of terylene, a poly ester polymer, from ethylene glycol and terephthalic acid.



In this reaction an alcoholic OH group in ethylene glycol condenses with a carboxyl group in terephthalic acid by eliminating a water molecule to form an ester linkage.

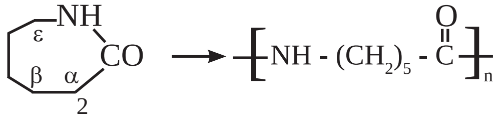
The process of formation of polymers from polyfunctional monomers with the elimination of some small molecules such as water, hydrochloric acid, methanol, ammonia is called condensation polymerization.

In this type of polymerization the chain growth occurs by a series of condensation steps. Therefore it is also referred to as **step growth polymerization**. This process is continued until a high molecular mass polymer is obtained.

Remember...

Repeating units of condensation polymer do not have the same elemental composition as that of monomer.

c. Ring opening polymerization : The third type of polymerization is ring opening polymerization. Cyclic compounds like lactams, cyclic ethers, lactones, etc. polymerize by ring opening polymerization. Strong acid or base catalyze this reaction. For example : polymerization of ε-caprolactam. (For more details see section 15.3.5 (b).



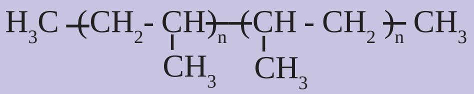
Elemental composition of the repeating unit in the polymer resulting from ring opening polymerization is same as that of the monomers, as in the case of addition polymerization. Addition polymerizations are often very rapid. But ring opening polymerization proceeds by addition of a single monomer unit (but never of larger units) to the growing chain molecules. In this sense, ring opening polymerization is a step growth polymerization similar to condensation polymerization.

Use your brain power

What is the type of polymerization in the following examples ?

(i)

$2n\ CH_2 = CH - CH_3 \xrightarrow{\dot{C}H_3}$



$$H_3C \text{-}\!\left(CH_2 - \underset{CH_3}{\underset{|}{CH}}\right)_n\!\!-\!\left(\underset{CH_3}{\underset{|}{CH}} - CH_2\right)_n\!\!- CH_3$$

(ii)

$nHO\text{-}(CH_2)_x\text{-}OH + nHOOC - (CH_2)_y - COOH$

$\longrightarrow HO\text{-}\!\left[(CH_2)_x\text{-}O\text{-}CO - (CH_2)_y - CO\right]_n\!\text{-} OH$

15.2.4 Classification of polymers on the basis of intermolecular forces :

Mechanical properties of polymers such as tensile strength, toughness, elasticity differ widely depending upon the intermolecular forces. Polymers are classified into various categories on the basis of intermolecular forces as follows.

a. Elastomers : Elasticity is a property by which a substance gets stretched by external force and restores its original shape on release of that force. Elastomers, the elastic polymers, have weak van der Waals type of intermolecular forces which permit the polymer to be stretched. A few crosslinks between the chains help the stretched polymer to retract to its original position on removal of applied force. For example : vulcanized rubber, buna-S, buna-N, neoprene, etc.

b. Fibres : Polymeric solids which form threads are called fibres. The fibres possess high tensile strength which is a property to have resistance to breaking under tension. This characteristic is due to the strong intermolecular forces like hydrogen bonding and strong dipole-dipole forces. Due to these strong intermolecular forces the fibres are crystalline in nature. For example : polyamides (nylon 6, 6), polyesters (terylene), etc.

c. Thermoplastic polymers : Plasticity is a property of being easily shaped or moulded. Thermoplastic polymers are capable of repeated softening on heating and hardening on cooling. These polymers possess moderately strong intermolecular forces that are intermediate between elastomers and fibres. For example : polythene, polystyrene, polyvinyls, etc. :

d. Thermosetting polymers : Themosetting polymers are rigid polymers. During their formation they have property of being shaped on heating; but they get hardened while hot. Once hardened these become infusible; cannot be softened by heating and therefore cannot be remoulded. This characteristic is the result of extensive cross linking by covalent bonds formed in the moulds during hardening/setting process while hot. For example : bakelite, urea formaldehyde resin, etc.

15.2.5 Classification of polymers on the basis of type of different monomers : Polymers are divided into two classes :

a. Homopolymers : The polymers which have only one type of repeating unit are called homopolymers. Usually they are formed from a single monomer. In some cases the repeating unit is formed by condensation of two distinct monomers. For example : polythene, polypropene, Nylon 6, polyacrylonitrile, Nylon 6, 6.

b. Copolymers : The polymers which have two or more types of repeating units are called copolymer. They are formed by polymerization of two or more different types of monomers in presence of each other. The different monomer units are randomly sequenced in the copolymer. For example : Buna-S, Buna-N.

Problem 15.1 : Refer to the following table listing for different polymers formed from respective monomer. Identify from the list whether it is copolymer or homopolymer.

Sr. No.	Monomer	Polymers
1.	Ethylene	Polyethylene
2.	Vinyl chloride	Polyvinyl chloride
3.	Isobutylene	Polyisobutylene
4.	Acrylonitrile	Polyacrylonitrile
5.	Caprolactum	Nylon 6
6.	Hexamethylene diammonium adipate	Nylon 6, 6
7.	Butdiene + styrene	Buna-S

Solution : In each of first five cases, there is only one monomer which gives corresponding homopolymer. In the sixth case hexamethylene diamine reacts with adipic acid to form the salt hexamethylene diammonium adipate which undergoes condensation to form Nylon 6, 6. Hence nylon 6, 6 is homopolymer. The polymer Buna-S is formed by polymerization of the monomers butadiene and styrene in presence of each other. The repeating units corresponding to the monomers butadiene and styrene are randomly arranged in the polymer. Hence Buna-S in copolymer.

Fig. 15.2 Shows all the classes of polymers in the form of a tree diagram.

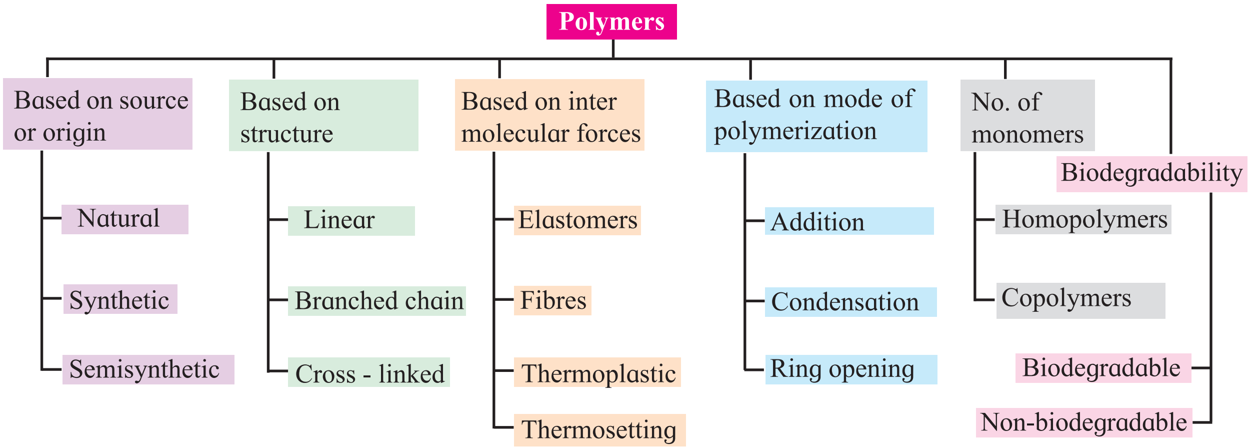


Fig. 15.2 : Classification of polymers

15.2.6 Classification of polymers on the basis of biodegradability :

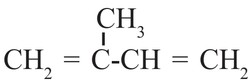
Most of the synthetic polymers are not affected by microbes. These are called non-biodegradable polymers. These, in the form of waste material which stays in the environment for very long time and pose pollution hazards. Most natural fibres in contrast are biodegradable. In attempt to tackle the environmental problem, scientists have developed bio-degradable synthetic polymers. More details will be described in section 15.5.

15.3 Some important polymers :

15.3.1 Rubber :

Elastomers are popularly known as **rubbers**. For example, balloons, shoesoles, tyres, surgeon's gloves, garden hose, etc. are made from elastomeric material or rubber.

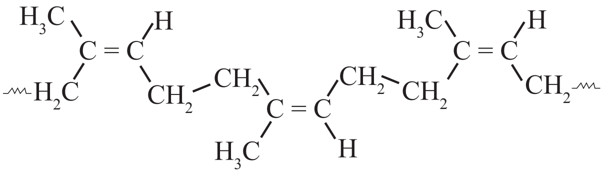
Natural rubber : Monomer of natural rubber is isoprene (2-methyl - 1, 3-butadiene).



$$CH_2 = \overset{CH_3}{C}\text{-}CH = CH_2$$

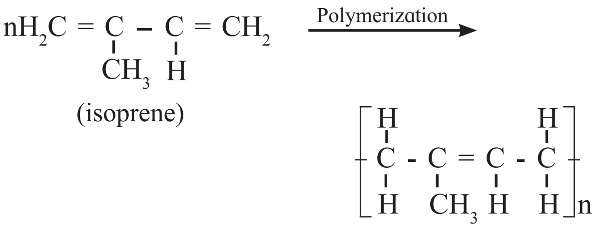
(isoprene)

Natural rubber is a high molecular mass linear polymer of isoprene. Its molecular mass varies from 130, 000u to 340, 000u (that is number of monomer units varies from 2000 to 5000).



Natural rubber

Reaction involved in formation of natural rubber by the process of addition polymerization is as follows.



(isoprene)

(polyisoprene/rubber)

Properties of Natural rubber :

1. Polyisoprene molecule has cis configuration of the C = C double bond. It consists of various chains held together by weak van der Waals forces and has coiled structure.

2. It can be stretched like a spring and exhibits elastic property.

Vulcanization of rubber : To improve the physical properties of natural rubber, a process of vulcanization is carried out. In 1839 Charles Goodyear, an American inventor invented the process of vulcanization.

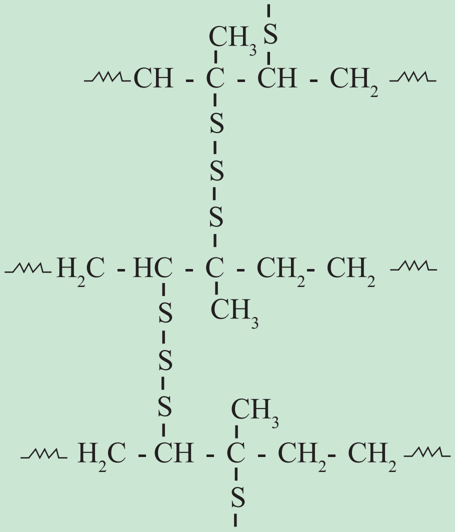
The process by which a network of cross links is introduced into an elastomers is called vulcanization. The profound effect of vulcanization enhances the properties like tensile strength, stiffness, elasticity, toughness; etc. of natural rubber. Sulfur vulcanization is the most frequently used process. Sulfur forms crosslinks between polyisoprene chains which results in improved properties of natural rubber.

Do you know ?

Vulcanizing is carried out by heating raw rubber with sulfur powder in presence of some organic compounds called accelerators at about 150 ^{0}C. (The most common accelerator is ZBX or zincbutyl xanthate). By increasing amount of sulfur the rubber can be hardened. For example when the amount of sulfur is raised to 40-45 % a non-elastic hard material known as **ebonite** is obtained.

One or more sulfur atoms cross-link two polyisoprene chains. Cross-linking takes place by opening of a double bond and produces three dimensional vulcanised rubber.

Probable 3-D structure of vulcanized rubber is



Use your brain power

- From the cis-polyisoprene structure of natural rubber explain the low strength of van der Waals forces in it.
- Explain how vulcanization of natural rubber improves its elasticity ? (Hint : consider the intermolecular links.)

Do you know ?

Natural Rubber first came into the market in early 19 th century. It was entirely recovered from wild *Hevea brasiliensis* trees which usually grew on the banks of Amazon river and its tributaries in South America. The amount of hydrocarbon present in Hevea Tree is very high (35%). As per the demand the production of natural rubber increased by leaps and bounds and at present 1.5 million tons of natural rubber is sent to the market.

The latex is collected from a mature Hevea tree by making deep cuts on the bark and by allowing the latex stream in a pot attached below the cut. The latex is an emulsion like milk.

When a coagulant like acetic acid is added to the latex the rubber hydrocarbon gets coagulated in the amorphous solid form.

15.3.2 Polythene :

Can you recall ?

How is ethylene prepared ?

Polythene is the simplest and most commonly used hydrocarbon thermoplastic and has following structure.

$$-\!\left[CH_2 - CH_2\right]\!-_n$$

The IUPAC name of polyethylene is polythene. Polythene is of two kinds, namely low density polythene (LDP) and high density polythene (HDP) .

a. Low density polyethylene (LDP) :

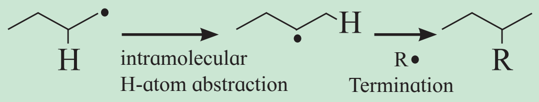
LDP is obtained by polymerization of ethylene under high pressure (1000 - 2000 atm) and temperature (350 - 570 K) in presence of traces of O_2 or peroxide as initiator.

$$CH_2 = CH_2 \xrightarrow[\text{peroxide at 350 - 370K, 1000 - 2000 atm}]{\text{Traces of } O_2} LDP$$

The mechanism of this reaction involves free radical addition and H-atom abstraction. The latter results in branching. As a result the chains are loosely held and the polymer has low density.

Do you know ?

In the H-atom abstraction, process involved in formation of LDP; the terminal carbon radical abstracts H-atom from an internal carbon atom in the form of an internal carbon radical. Termination step in addition polymerization gives rise to branching of these internal carbons.



Properties of LDP : LDP films are extremely flexible, but tough, chemically inert and moisture resistant. It is poor conductor of electricity with melting point 110 ^{0}C.

Uses of LDP : LDP is mainly used in preparation of pipes for agriculture, irrigation, domestic water line connections as well as insulation to electric cables. It is also used in submarine cable insulation. It is used in producing extruded films, sheets, mainly for packaging and household uses like in preparation of squeeze bottles, attractive containers etc.

b. High density polyethylene (HDP) : It is essentially a linear polymer with high density due to close packing.

$$CH_2 = CH_2 \xrightarrow[\text{6 - 7 atm, catalyst}]{\text{333 K - 343 K}} HDP$$

HDP is obtained by polymerization of ethene in presence of Zieglar-Natta catalyst which is a combination of triethyl aluminium with titanium tetrachloride at a temperature of 333K to 343K and a pressure of 6-7 atm.

Properties of HDP : HDP is crystalline, melting point in the range of 144 - 150 ^{0}C. It is much stiffer than LDP and has high tensile strength and hardness. It is more resistant to chemicals than LDP.

Uses of HDP : HDP is used in manufacture of toys and other household articles like buckets, dustbins, bottles, pipes etc. It is used to prepare laboratory wares and other objects where high tensile strength and stiffness is required.

Internet my friend

Where is polythene manufactured in India ?

15.3.3 Teflon : Chemically teflon is polytetrafluoroethylene. The monomer used in preparation of teflon is tetrafluoroethylene, ($CF_2 = CF_2$) which is a gas at room temperature.

Tetrafluoroethylene is polymerized by using free radical initiators such as hydrogen peroxide or ammonium persulphate at high pressure.

$$nCF_2 = CF_2 \xrightarrow[\text{Peroxide}]{\text{Polymerization}} \left[CF_2 - CF_2 \right]_n$$

(Tetrafluoroethene) (Teflon)

Properties : Telflon is tough, chemically inert and resistant to heat and attack by corrosive reagents.

C - F bond is very difficult to break and remains unaffected by corrosive alkali, organic solvents.

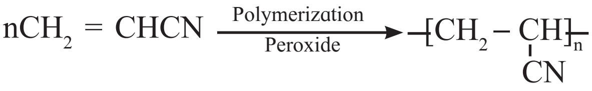
Uses : Telflon is used in making non-stick cookware, oil seals, gaskets, etc.

Internet my friend

Collect the information of Teflon coated products used in daily life and in industries.

15.3.4 Polyacrylonitrile :

Polyacrylonitrile is prepared by addition polymerization of acrylonitrile by using peroxide initiator.



$$nCH_2 = CHCN \xrightarrow[\text{Peroxide}]{\text{Polymerization}} -\!\!\left[CH_2 - \underset{\displaystyle CN}{\underset{|}{CH}}\right]_n\!\!-$$

(Acrylonitrile) (Polyacrylonitrile)

Polyacrylonitrile resembles wool and is used as wool substitute and for making orlon or acrilan.

Do you know ?

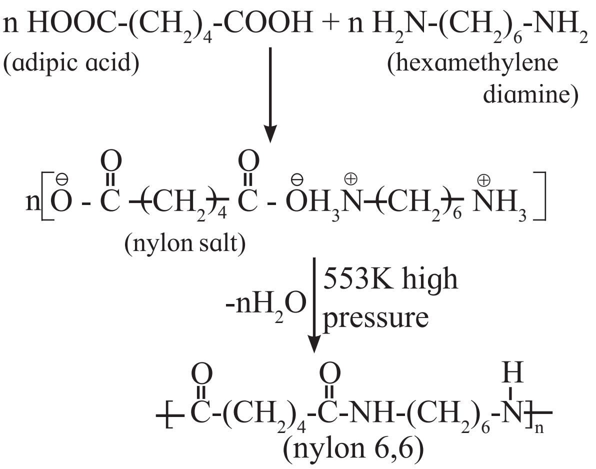
Orlon is used to make blankets, shawls, sweat shirts, sweaters.

15.3.5 Polyamide polymers :

Polyamide polymers are generally known as nylons. Nylon is the generic name of the synthetic linear polyamides obtained by the condensation polymerization between dicarboxylic acids and diamines, the self condensation of an amino acid or by the ring opening polymerization of lactams.

Polyamides contain - CO - NH - groups as the inter unit linkages. Two important polyamide polymers are nylon 6, 6 and nylon 6.

a. Nylon 6,6 : The monomers adipic acid and hexamethylendiamine on mixing forms nylon salt, which upon condensation polymerization under conditions of high temperature and pressure give the polyamide fibre nylon 6,6.



$$n\,HOOC\text{-}(CH_2)_4\text{-}COOH + n\,H_2N\text{-}(CH_2)_6\text{-}NH_2$$

(adipic acid) (hexamethylene diamine)

$$\downarrow$$

$$n\left[\overset{\ominus}{O} - \overset{O}{\overset{\|}{C}} -\!(CH_2)_4\!- \overset{O}{\overset{\|}{C}} - \overset{\ominus}{O}H_3\overset{\oplus}{N}\!-\!(CH_2)_6\!-\!\overset{\oplus}{N}H_3\right]$$

(nylon salt)

$$\downarrow^{\text{553K high pressure}}_{-nH_2O}$$

$$-\!\!\left[\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}(CH_2)_6\text{-}\overset{H}{\overset{|}{N}}\right]_n\!\!-$$

(nylon 6,6)

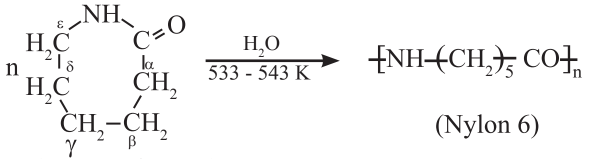
The numerals 6,6 in the name of this polymer stand for the number of carbon atoms in the two bifunctional monomers, namely, adipic acid and hexamethylenediamine.

Nylon 6,6 is high molecular mass (12000-50000 u) linear condensation polymer. It possesses high tensile strength. It does not soak in water. It is used for making sheets, bristles for brushes, surgical sutures, textile fabrics, etc.

Do you know ?

- When an amino group and carboxyl group present in the same molecule react intramolecularly the resulting amide is cyclic and is called **lactam**.
- A cyclic ester formed by intramolecular reaction of hydroxyl and carboxyl groups is called **lactone**.

b. Nylon 6 : When epsilon (ε)-caprolactam is heated with water at high temperature it undergoes ring opening polymerization to give the polyamide polymer called nylon 6.

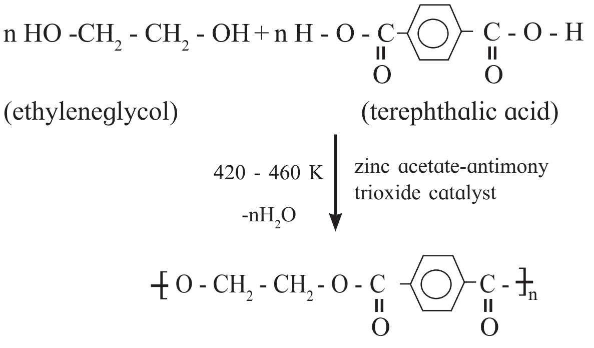


(ε - caprolactam)

(Nylon 6)

The name nylon 6 is given on the basis of six carbon atoms present in the monomer unit. Due to its high tensile strength and luster nylon 6 fibres are used for manufacture of tyre cords, fabrics and ropes.

15.3.6 Polyesters : The polyester polymers have ester linkage joining the repeating units. Commercially the most important polyester fibre is 'terylene' (also called dacron). It is obtained by condensation polymerization of ethylene glycol and terephthalic acid in presence of catalyst at high temperature.



(terylene or dacron)

Terylene has relatively high melting point (265⁰C) and is resistant to chemicals and water. It is used for making wrinkle free fabrics by blending with cotton (terycot) and wool (terywool), and also as glass reinforcing materials in safety helmets. PET is the most common thermoplastic which is another trade name of the polyester polyethyleneterephthalate. It is used for making many articles like bottles, jams, packaging containers.

Polycarbonates are also a kind of polyester polymers. These are high melting thermosetting resins.

15.3.7 Phenol - formaldehyde and related polymers :

a. Bakelite : Bakelite, the thermosetting polymer obtained from reaction of phenol and formaldehyde is the oldest synthetic polymer. Phenol and formaldehyde react in presence of acid or base catalyst to form thermosetting/moulding powder (novolac) in two stages. In the third stage, various articles are shaped from novolac by putting it in appropriate moulds and heating at high temperature (138⁰C to 176⁰C) and at high pressure. The reactions involved are represented in the Fig. 15.3.

During the third stage of thermosetting in the moulds, many crosslinks are formed which results in formation of rigid polymeric material, called bakelite which is insoluble and infusible and has high tensile strength. It can also serve as substitute for glass. Bakelite is used for making articles like telephone instrument, kitchenware, electric insulators.

b. Melamine-formaldehyde polymer : Decorative table tops like formica and plastic dinner-ware are made from heat and moisture resistant themosetting plastic called melamine - formaldehyde resin. The reactions are shown in Fig. 15.4. Melamine and formaldehyde undergo condensation polymerisation to give cross linked melamine formaldehyde.

Internet my friend

Find applications of bakelite in day to day life.

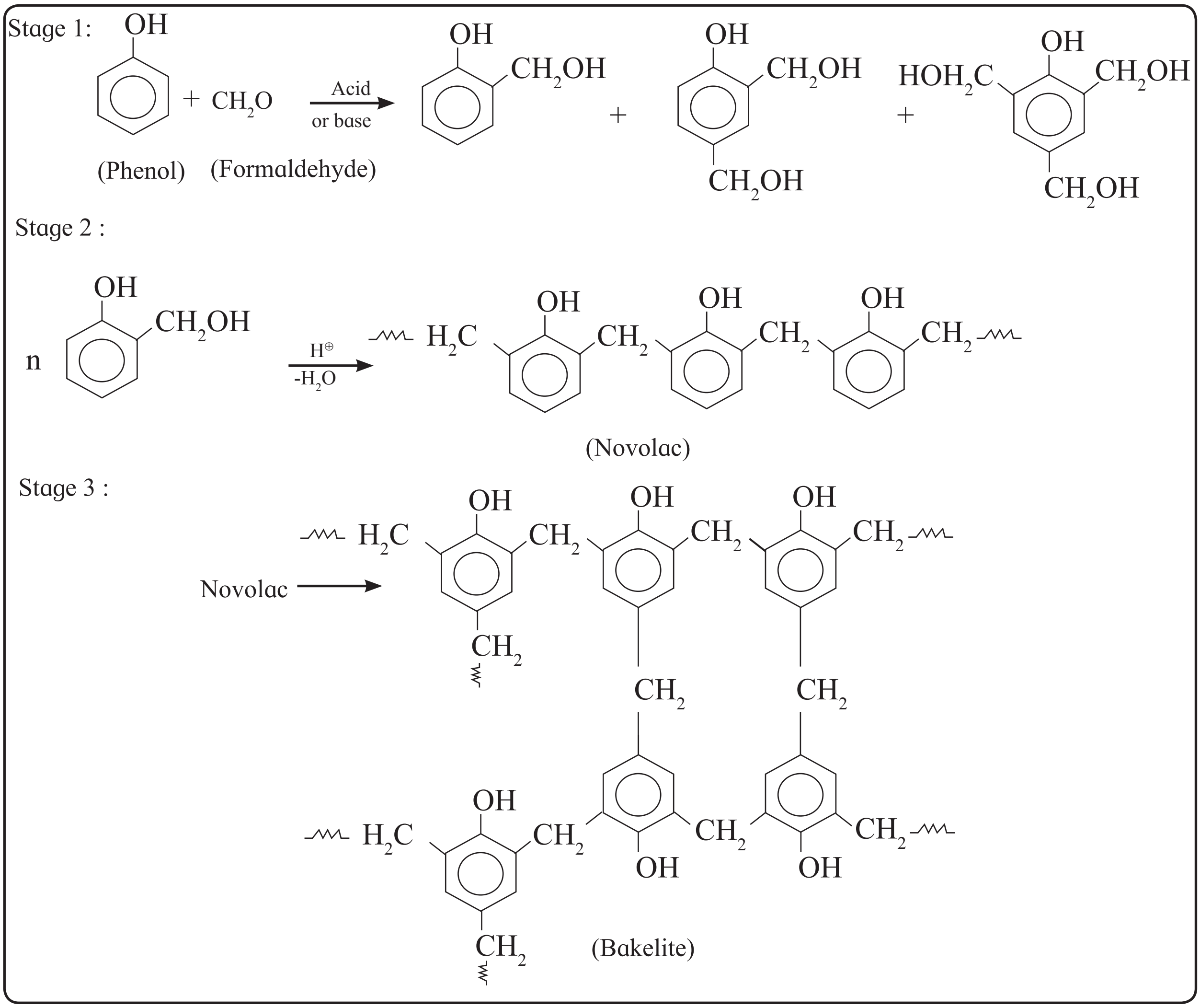


Fig. 15.3 Preparation of Bakelite

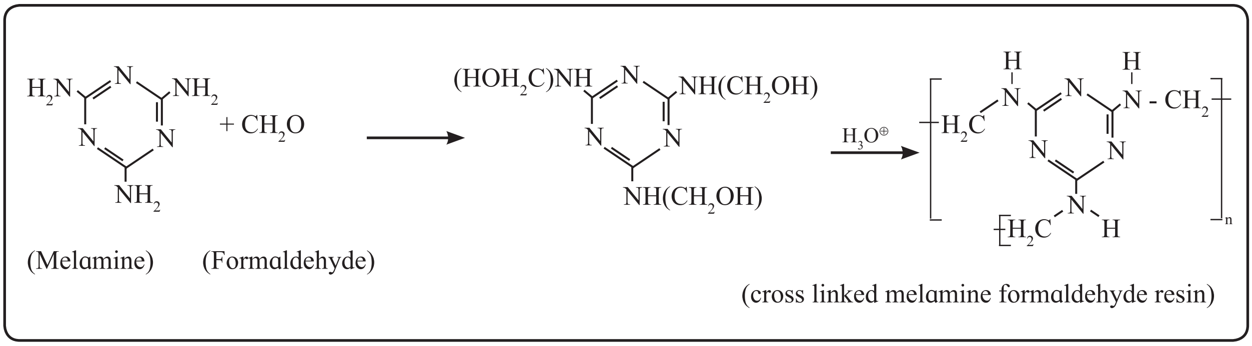
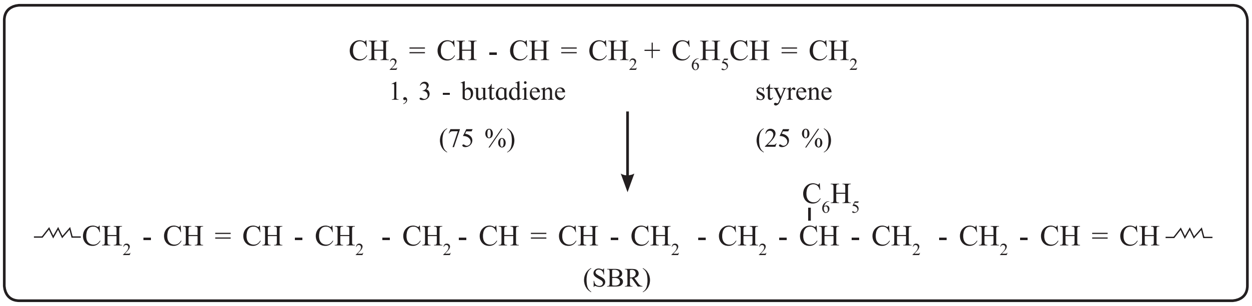
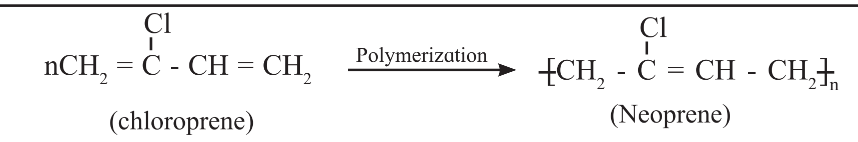


Fig. 15.4 Formation of cross linked melamine formaldehyde resin



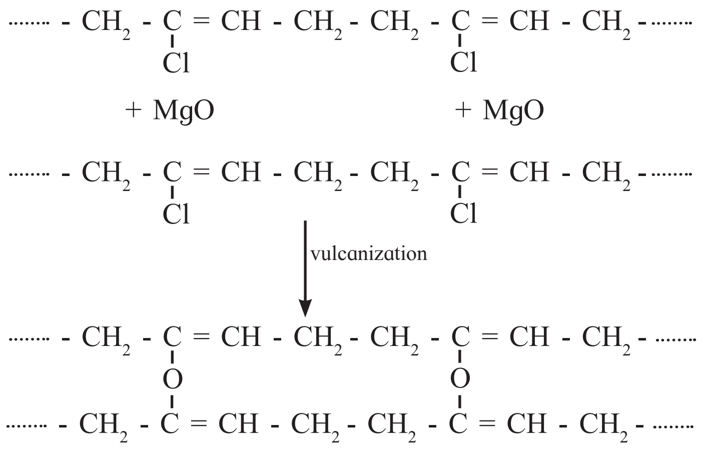
$$\begin{array}{c}
CH_2 = CH - CH = CH_2 + C_6H_5CH = CH_2 \\
\text{1, 3 - butadiene} \qquad\qquad \text{styrene} \\
(75\ \%) \qquad\qquad (25\ \%) \\
\downarrow \\
\sim CH_2 - CH = CH - CH_2 - CH_2 - CH = CH - CH_2 - CH_2 - \underset{}{\overset{C_6H_5}{\overset{|}{CH}}} - CH_2 - CH_2 - CH = CH \sim \\
\text{(SBR)}
\end{array}$$

Fig. 15.5 Formation of SBR (Buna - S)



$$nCH_2=\overset{Cl}{C}-CH=CH_2 \xrightarrow{\text{Polymerization}} \left[CH_2-\overset{Cl}{C}=CH-CH_2\right]_n$$

(a) : Polymerization



(b) : Vulcanization of neoprene

Fig. 15.6 Neoprene and vulcanization

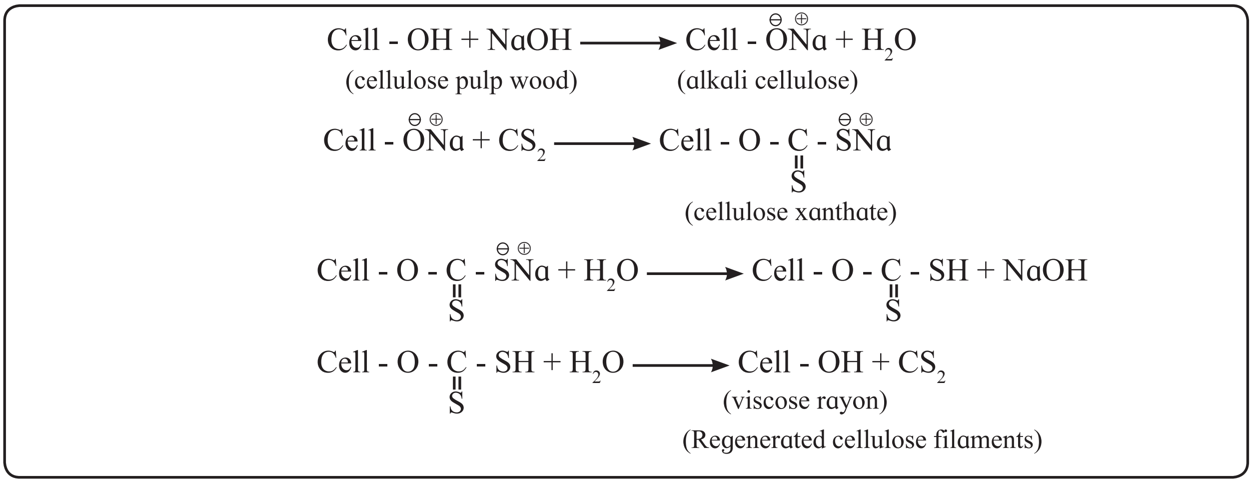
15.3.8 Buna-S rubber : Buna-S is an elastomer which is a copolymer of styrene with butadiene (Fig.15.5). Its trade name is SBR (styrene-butadiene rubber). The copolymer is usually obtained from 75 parts of butadiene and 25 parts of styrene subjected to addition polymerization by the action of sodium. It is vulcanized with sulfur.

Buna-S is superior to natural rubber with regard to mechanical strength and has abrasion resistance. Hence it is used in tyre industry.

15.3.9 Neoprene : Neoprene, a synthetic rubber, is a condensation polymer of chloroprene (2-chloro-1,3-butadiene). Chloroprene polymerizes rapidly in presence of oxygen. Vulcanization of neoprene takes place in presence of magnesium oxide. The reactions involved can be represented in Fig. 15.6.

Neoprene is particularly resistant to petroleum, vegetable oils, light as well as heat. Neoprene is used in making hose pipes for transport of gasoline and making gaskets. It is used for manufacturing insulator cable, jackets, belts for power transmission and conveying.

15.3.10 Viscose rayon : Viscose rayon is a semisynthetic fibre which is regenerated cellulose. Cellulose in the form of wood pulp is transformed into viscose rayon. Cellulose is a linear polymer of glucose units and has molecular formula $(C_6H_{10}O_5)_n$. A modified representation of the molecular formula of cellulose Cell-OH, is used in the reactions involved in viscose formation, as shown in Fig. 15.7. Cellulose in the form of wood pulp is treated with concentrated NaOH solution to get fluffy alkali cellulose. It is then converted to xanthate by treating with carbon disulphide. On mixing with dilute NaOH it gives viscose solution which is extruded through spinnerates



$$\underset{\text{(cellulose pulp wood)}}{\text{Cell - OH} + \text{NaOH}} \longrightarrow \underset{\text{(alkali cellulose)}}{\text{Cell - }\overset{\ominus\,\oplus}{\text{ONa}}} + H_2O$$

$$\text{Cell - }\overset{\ominus\,\oplus}{\text{ONa}} + CS_2 \longrightarrow \underset{\text{(cellulose xanthate)}}{\text{Cell - O - }\underset{\text{S}}{\underset{\|}{\text{C}}}\text{ - }\overset{\ominus\,\oplus}{\text{SNa}}}$$

$$\text{Cell - O - }\underset{\text{S}}{\underset{\|}{\text{C}}}\text{ - }\overset{\ominus\,\oplus}{\text{SNa}} + H_2O \longrightarrow \text{Cell - O - }\underset{\text{S}}{\underset{\|}{\text{C}}}\text{ - SH} + \text{NaOH}$$

$$\text{Cell - O - }\underset{\text{S}}{\underset{\|}{\text{C}}}\text{ - SH} + H_2O \longrightarrow \text{Cell - OH} + CS_2$$

(viscose rayon)

(Regenerated cellulose filaments)

Fig. 15.7 : Formation of viscose rayon

of spining machine into acid bath when regenerated cellulose fibres precipitate.

Use your brain power

- Write structural formulae of styrene and polybutadiene.

15.4 Molecular mass and degree of polymerization of polymers : A polymer is usually a complex mixture of molecules of different molecular masses. Hence, molecular mass of a polymer is an average of the molecular masses of constituent molecules. Molecular mass of polymer depends upon the degree of polymerization (DP). DP is the number of monomer units in a polymer molecule.

Most of the mechanical properties of polymers depend upon their molecular mass. Low molecular mass polymers are liable to be brittle and have low mechanical strength. If a polymer is allowed to attain very high molecular mass it becomes tough and unmanageable. Both these ends are undesirable. A polymer must possess a molecular mass more than certain minimum value in order to exhibit the properties needed for a particular application. This minimum molecular mass corresspond to the critical degree of polymerization. But the polymerization process has to be controlled after certain stage. For polymers containing hydrogen bonding the critical degree of polymerization is lower than those containing weak intermolecular forces.

Can you tell ?

1. Classify the following polymers as addition or condensation.

   i. PVC ii. Polyamides iii. Polystyrene iv. Polycarbonates v. Novolac

2. Complete the following table :

Condensation polymers	Repeating unit	Name of monomer	Formula of monomer	Uses
1. Nylon 6				
2. Nylon 6, 6				
3. Terylene				
4. Melamine				

Problem 15.2 : The critical degree of polymerization is low for nylon 6 while high for polythene. Explain.

Solution : Nylon 6 is a polyamide polymer, and has strong intermolecular hydrogen bonding as inter molecular forces. On the other hand polythene chains have only weak van der Waals forces as intermolecular interaction. Because of the stronger intermolecular forces the critical DP is lower for nylon 6 than polythene.

15.5 Biodegradable polymers :

Can you recall ?

- Name some materials which undergo degradation after use.
- List the materials which do not decay even after a long time.
- How is the environment affected by non decaying substances ?
- Which bonds are broken during digestion of proteins and carbohydrates ?
- What happens to disposed natural wastes such as stale food, fruit peels, torn cotton cloth ?

Inspite of large number of useful applications, polymers are blamed for creating environmental pollution. To strike the golden mean, certain new biodegradable synthetic polymers have been developed.

Aliphatic polyesters and polyamides with large proportion of polar linkages are one of the important classes of biodegradable polymers. Some important examples are discussed below.

Disposed natural wastes are usually attacked by soil microbes and get degraded to humus. But most synthetic polymers and plastics cannot be degraded by microbes and stay in the environment for very long period of time posing pollution problems. To overcome this problem biodegradable polymers are being developed. These polymers contain functional groups similar to those in biopolymers such as proteins. Aliphatic polyesters are also an important class of biodegradable polymers.

Can you recall ?

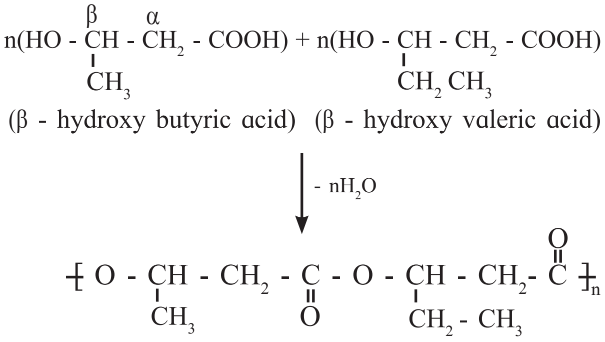
- What are the structural formulae of glycine and ε - amino caproic acid ?

Use your brain power

- Represent the copolymerization reaction between glycine and ε - amino caproic acid to form the copolymer nylon 2- nylon 6.
- What is the origin of the numbers 2 and 6 in the name of this polymer ?

15.5.1 PHBV :

PHBV is a copolymer of two bifunctional β- hydroxy carboxylic acids, namely, β- hydroxybutyric acid (3 - hydroxybutanoic acid) and β- hydroxyvaleric acid (3 - hydroxypentanoic acid). Hydroxyl group of one monomer forms ester link by reacting with carboxyl group of the other. Thus PHBV is an aliphatic polyester with name poly β- hydroxy butyrate - co - β- hydroxy valerate (PHBV). PHBV is degraded by microbes in the environment.



$$n(HO-\underset{CH_3}{\overset{\beta}{CH}}-\overset{\alpha}{CH_2}-COOH) + n(HO-\underset{CH_2CH_3}{CH}-CH_2-COOH)$$

(β - hydroxy butyric acid) (β - hydroxy valeric acid)

$$\xrightarrow{-nH_2O} \left[O-\underset{CH_3}{CH}-CH_2-\underset{\underset{O}{\|}}{C}-O-\underset{CH_2-CH_3}{CH}-CH_2-\overset{\overset{O}{\|}}{C} \right]_n$$

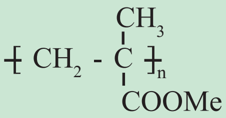
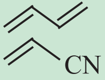
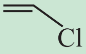
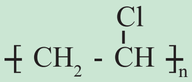
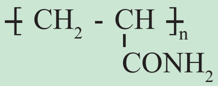
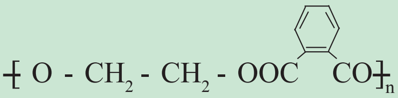
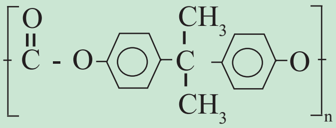
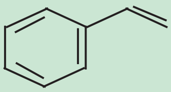
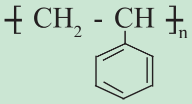
(PHBV)

15.5.2 Nylon 2 - nylon 6 :

Nylon 2 - nylon 6 is a polyamide copolymer of two amino acids, namely, glycine and ε - amino caproic acid. It is a biodegradable polymer.

15.6 Commercially important polymers : Apart from the polymers already discussed in this chapter, many more polymers are used extensively. Structures and applications of some of them are given in the Table 15.1.

Table 15.1 : Commercially important polymers

Trade name	Monomer	Polymer structure	Applications
Perspex/acrylic glass	methyl methacrylate 	 $-[CH_2-\overset{CH_3}{\underset{COOMe}{C}}-]_n$	lenses, paint, security barrier, LCD screen, shatter resistant glass
Buna N	Butadiene and acrylonitrile 	 $-[H_2C-CH=CH-CH_2-CH_2-\underset{CN}{CH}-]_n$	adhesives, rubber belts, shoe soles, O-rings, gaskets
PVC (polyvinyl chloride)	vinyl chloride 	 $-[CH_2-\overset{Cl}{CH}-]_n$	water pipes, rain coats, flooring
Polyacrylamide	acrylamide 	 $-[CH_2-\underset{CONH_2}{CH}-]_n$	Polyacrylamide gel used in electrophoresis
Urea-formaldehyde resin	a. urea b. formaldehyde	$-[NH-CO-NH-CH_2-]_n$	unbreakable dinner ware, decorative laminates
Glyptal	a. ethyleneglycol b. phthalic acid		paints and lacquers
Polycarbonate	a. bisphenol b. phosgene		electrical and telecommunication hardware, food grade plastic containers
Thermocol (made from airfilled thin walled beads of polystyrene	Styrene 		non-biodegradable styrene can leach when heated. Therefore it is banned.

Exercises

1. Choose the correct option from the given alternatives.

i. Nylon fibres are ----

A. Semisynthetic fibres

B. Polyamide fibres

C. Polyester fibres

D. Cellulose fibres

ii. Which of the following is naturally occurring polymer ?

A. Telfon B. Polyethylene

C. PVC D. Protein

iii. Silk is a kind of ---- fibre

A. Semisynthetic

B. Synthetic

C. Animal

D. Vegetable

iv. Dacron is another name of ----

A. Nylon 6 B. Orlon

C. Novolac D. Terylene

v. Which of the following is made up of polyamides ?

A. Dacron B. Rayon

C. Nylon D. Jute

vi. The number of carbon atoms present in the ring of ε - caprolactam is

A. Five B. Two

C. Seven D. Six

vii. Terylene is ----

A. Polyamide fibre

B. Polyester fibre

C. Vegetable fibre

D. Protein fibre

viii. PET is formed by ----

A. Addition B. Condensation

C. Alkylation D. Hydration

ix. Chemically pure cotton is ----

A. Acetate rayon

B. Viscose rayon

C. Cellulose nitrate

D. Cellulose

x. Teflon is chemically inert, due to presence of ....

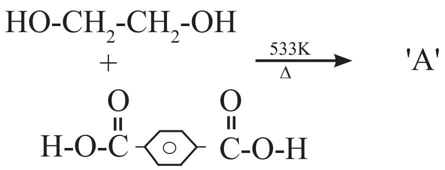
A. C-H bond B. C-F bond

C. H- bond D. C=C bond

2. Answer the following in one sentence each.

i. Identify 'A' and 'B' in the following reaction ----

a.



b. $H_2N\text{-}(CH_2)_6\text{-}NH_2 + HOOC\text{-}(CH_2)_4COOH \xrightarrow[533K]{N_2}$ ‘B’

ii. Complete the following statements

a. Caprolactam is used to prepare--------

b. Novolak is a copolymer of -------- and ---------

c. Terylene is ----------polymer of terephthalic acid and ethylene glycol.

d. Benzoyl peroxide used in addtion polymerisation acts as ----------

e. Polyethene consists of polymerised ----------

iii. Draw the flow chart diagram to show classification of polymers based on type of polymerisation.

iv. Write examples of Addition polymers and condensation polymers.

v. Name some chain growth polymers.

vi. Define the terms :

1) Monomer

2) Vulcanisation

3) Synthetic fibres

vii. What type of intermolecular force leads to high density polymer ?

viii. Give one example each of copolymer and homopolymer.

ix. Identify Thermoplastic and Thermosetting Plastics from the following -----

1. PET

2. Urea formaldehyde resin

3. Polythene

4. Phenol formaldehyde

3. Answer the following.

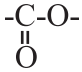
i. Write the names of classes of polymers formed according to intermolecular forces and describe briefly their structural characteristics.

ii. Write reactions of formation of :

a. Nylon 6 b. Terylene

iii. Write structure of natural rubber and neoprene rubber along with the name and structure of thier monomers.

iv. Name the polymer type in which following linkage is present.



$-\underset{\overset{\|}{O}}{C}-O-$

v. Write structural formula of the following synthetic rubbers :

a. SBR rubber

b. Buna-N rubber

c. Neoprene rubber

vi. Match the following pairs :

Name of polymer	Monomer
1. Teflon	a. $CH_2=CH_2$
2. PVC	b. $CF_2=CF_2$
3. Polyester	c) $CH_2=CHCl$
4. Polythene	d) C_6H_5OH and HCHO
5. Bakelite	e) Dicarboxylic acid and polyhydoxyglycol

vii. Draw the structures of polymers formed from the following monomers

1. nHOOC-R-COOH + nHO-R'-OH
2. $H_2N-(CH_2)_5-COOH$

viii. Name and draw structure of the repeating unit in natural rubber.

ix. Classify the following polymers as natural and synthetic polymers

a. Cellulose b. Polystyrene

c. Terylene d. Starch

e. Protein f. Silicones

g. Orlon (Polyacrylonitrle)

h. Phenol-formedehyde resins

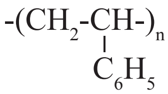
x. What are synthetic resins? Name some natural and synthetic resins.

xi. Distinguish between thermosetting and thermoplastic resins. Write example of both the classes.

xii. Write name and formula of raw material from which bakelite is made.

4. Attempt the following :

i. Identify condensation polymers and addition polymers from the following.

a. 

$-(CH_2-\underset{C_6H_5}{\underset{|}{C}H}-)_n$

b. $-(CH_2-CH=CH-CH_2)_n$

c. $-(CO(CH_2)_4-CONH(CH_2)_6NH-)_n$

d. 

ii. Write the chemical reactions involved in manufacture of Nylon 6,6

iii. Explain vulcanisation of rubber. Which vulcanizing agents are used for the following synthetic rubber.

a. Neoprene b. Buna-N

iv. Write reactions involved in the formation of --- 1) Teflon

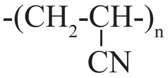
2) Bakelite

v. What is meant by LDP and HDP? Mention the basic difference between the same with suitable examples.

vi. Write preparation, properties and uses of Teflon.

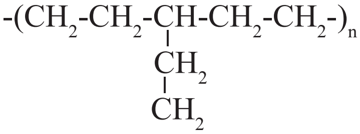
vii. Classify the following polymers as straight chain, branched chain and cross linked polymers.

a.



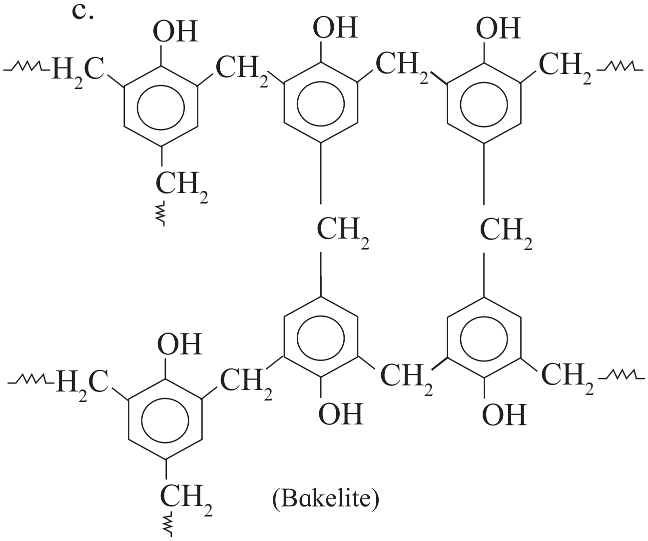
$-(CH_2-\underset{\substack{|\\ CN}}{CH}-)_n$

b.



$-(CH_2-CH_2-\underset{\substack{|\\ CH_2\\ |\\ CH_2}}{CH}-CH_2-CH_2-)_n$

c.



(Bakelite)

5. Answer the following.

i. How is polythene manufactured ? Give their properties and uses.

ii. Is synthetic rubber better than natural rubber ? If so, in what respect?

iii. Write main specialities of Buna-S, Neoprene rubber?

iv. Write the structure of isoprene and the polymer obtained from it.

v. Explain in detail free radical mechanism involved during preparation of addition polymer.

Activity :

i. Collect the information of the process like extrusion and moulding in Textile Industries.

ii. Make a list of polymers used to make the following articles

a. Photographic film

b. Frames of spectacles

c. Fountain pens

d. Moulded plastic chains

e. Terywool or Terycot fabric

iii. Prepare a report on factors responsible for degradation of polymers giving suitable example.

iv. Search and make a chart/note on silicones with reference to monomers, structure, properties and uses.

v. Collect the information and data about Rubber industry, plastic industry and synthetic fibre (rayon) industries running in India.

16. GREEN CHEMISTRY AND NANOCHEMISTRY

Can you recall ?

1. What do you mean by environment?
2. Which are the factors affecting the environment?
3. What is pollution? Which are the types of pollution?
4. Why it occurs?

16.1 Introduction

Chemistry plays an important role to improve the quality of our life. Unfortunately, due to this achievement our health and global environment are under threat. Also, due to increase in human population and the industrial revolution, energy crisis and environmental pollution are highlighted major global problems in the 21st century. To minimize the problems of energy crisis and pollution, we have to adapt **green chemistry**.

Do you know ?

Paul T. Anastas (Born on May 16, 1962) is the director of Yale university's Center for green chemistry and green engineering. He is known as father of green chemistry.

Green Chemistry is an approach to chemistry that aims to maximize efficiency and minimize hazardous effects on human health and environment. The concept of green chemistry was coined by **Paul T. Anastas**.

Definition : Green Chemistry is the use of chemistry for pollution prevention by environmentally conscious design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

To reduce the impact of energy crisis, pollution and to save natural resources, we need to implement 12 principles of green chemistry enunciated by Paul Anastas whereever possible.

16.2 Sustainable development : Green chemistry plays an important role in sustainable development. We can achieve sustainable development by adapting the twelve principles of green chemistry. **Sustainable development** is development that meets the needs of the present, without compromising the ability of future generations to meet their own need. Sustainable development has been continued to evolve as that protecting the world's resources.

16.3 Principles of green chemistry :

1. Prevention of waste or by products :

To give priority for the prevention of waste rather than cleaning up and treating waste after it has been created.

Illustration : To develop the zero waste technology (ZWT). In terms of ZWT, in a chemical synthesis, waste product should be zero or minimum. It also aims to use the waste product of one system as the raw material for other system. For example : 1. bottom ash of thermal power station can be used as a raw material for cement and brick industry. 2. Effluent coming out from cleansing of machinery parts may be used as coolant water in thermal power station.

2. Atom economy : Atom economy is a measure of the amount of atoms from the starting materials that are present in the useful products at the end of chemical process. Good atom economy means most of the atoms of the reactants are incorporated in the desired products and only small amounts of unwanted byproducts are formed and hence lesser problems of waste disposal.

Illustration : The concept of atom economy gives the measure of the unwanted product produced in a particular reaction.

$$\% \text{ atom economy} = \frac{\text{Formula weight of the desired product}}{\text{sum of formula weight of all the reactants used in the reaction}} \times 100$$

For example : conversion of Butan-1-ol to 1 - bromobutane

$$CH_3CH_2CH_2CH_2OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2CH_2CH_2\text{-}Br + NaHSO_4 + H_2O$$

$$\% \text{ atom economy} = \frac{\text{mass of } (4C + 9H + 1Br) \text{ atoms}}{\text{mass of } (4C + 12H + 5O + 1Br + 1Na + 1S)\text{atoms}} \times 100$$

$$= \frac{137 \text{ u}}{275 \text{ u}} \times 100$$

$$= 49.81 \%$$

3. Less hazardous chemical synthesis :

Designed chemical reactions and synthesis routes should be as safe as possible. So that we can avoid formation of hazardous waste from chemical processes.

Illustration : Earlier DDT (Dichlorodiphenyl trichloroethane) was used as insecticide and which was effective in controlling diseases like typhoid and malaria carrying mosquitos. It was realized that DDT is harmful to living things. Nowadays benzene hexachloride (BHC) is used as insecticide. One of the ϒ-isomer (gamma) of BHC is called gammexane or lindane.

4. Desigining Safer Chemicals : This principle is quite similar to the previous one. To develop products that are less toxic or which require less toxic raw materials.

Illustration : In Chemical industries workers are exposed to toxic environment. In order to prevent the workers from exposure to toxicity, we should think of designing safer chemicals.

For example : Adipic acid is widely used in polymer industry. Benzene is the starting material for the synthesis of adipic acid but benzene is carcinogenic and benzene being volatile organic compound (VOC) pollutes air. In green technology developed by Drath and Frost, adipic acid is enzymatically synthesised from glucose.

5. Use Safer solvent and auxilaries :

Choose the safer solvent available for any given step of reaction. Minimize the total amount of solvents and auxilary substances used, as these make up a large percentage of the total waste created.

Illustration : The main aim behind this principle is to use green solvents. For example, water, supercritical CO_2 in place of volatile halogenated organic solvents, for example, CH_2Cl_2, $CHCl_3$, CCl_4 for chemical synthesis and other purposes. Solvents as chemicals that dissolve solutes and form solutions, facilitate many reactions. Water is a safe benign solvent while dichloromethane is hazardous. Use of toxic solvent affects millions of workers every year and has implications for consumers and the environment as well. Many solvents are used in high volumes and many are volatile organic compounds. Their use creates large amounts of waste, air pollution and other health impacts. Finding safer, more efficient alternatives or removing solvents altogether is one of the best ways to improve a process or product.

6. Design for energy efficiency : Chemical synthesis should be designed to minimize the use of energy. It is better to minimize the energy by carrying out reactions at room temperature and pressure.

This can be achieved by use of proper catalyst, use of micro organisms for organic synthesis, use of renewable materials, ... ,etc.

Illustration : The biocatalyst can work at the ambient condition. Similarly, in chemical synthesis, refluxing conditions require less energy, improving the technology of heating system, use microwave heating, ... , etc.

7. Use of renewable feedstocks : The perspective of this principle is largely toward petrochemicals. Use chemicals which are made from renewable (plant based) sources rather than other (for example : Crude Oil).

Illustration : Overexploitation of nonrenewable feed stocks will deplete the resources and future generation will be deprived. Moreover, use of these nonrenewable resources puts burden on the environment.

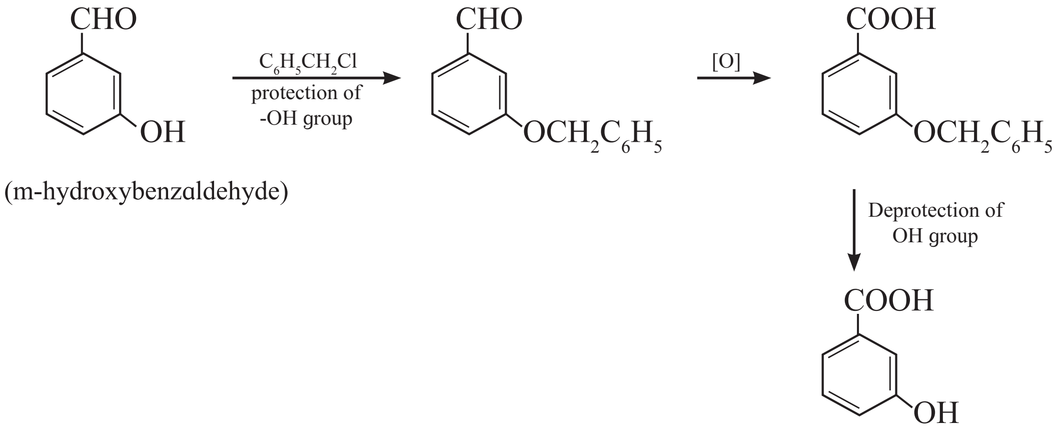
On the other hand, use of renewable resources for example agricultural or biological product ensures the sharing of resources by future generation. This practice generally does not put much burden on environment. The products and waste are generally biodegradable.

8. Reduce derivatives : [Minimization of steps]

A commonly used technique in organic synthesis is the use of protecting or blocking group. Unnecessary derivatization (for example installation / removal of use of protecting groups) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

Illustration : In organic synthesis, we need very often protection of some functional groups. Finally, we again need their deprotection. It is explained in the following example of synthesis of m-hydroxybenzoic acid from m-hydroxy benzaldehyde.

Obviously, in such cases, atom economy is also less. The green chemistry principle aims to develop the methodology where unnecessary steps should be avoided, if practicable biocatalytic reactions very often need no protection of selective group.



(m-hydroxybenzaldehyde)

(m-hydroxybenzoic acid)

9. Use of catalysis : Use of catalyst in the chemical reaction speeds up its rate. Catalyst helps to incease selectivity, minimize waste and reduce reaction times and energy demands.

Complete the chart

Reaction	Name of Catalyst used
1. Hydrogenation of oil (Hardening)	....
2. Haber's process of manufature of ammonia	....
3. Manufacture of HDPE polymer	....
4. Manufacture of H_2SO_4 by contact process	....
5. Fischer-Tropsch process (synthesis of gasoline)	....

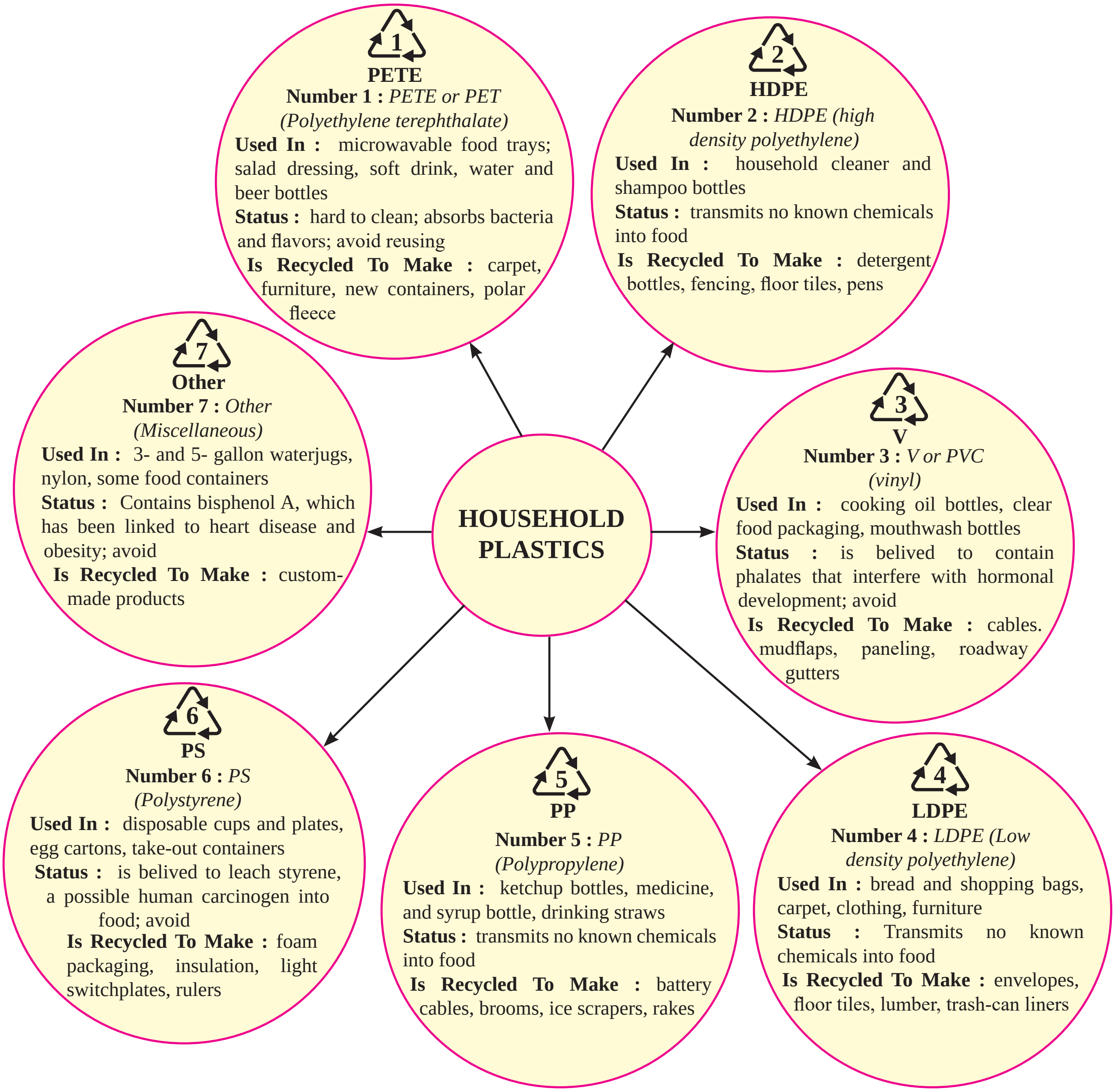
Do you know ?

Does plastic packaging impact the food they wrap ?

Phthalates leach into food through packaging so you should avoid microwaving food or drinks in plastic and not use plastic cling wrap and store your food in glass container whenever possible. Try to avoid prepackaging, processed food so that you will reduce exposure to harmful effect of plastic.

10. Design for degradation : Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative or environmentally persistent.

Illustration : The aim behind this principle is that the waste product should degrade automatically to clean the environment. Thus, the biodegradable polymers and pesticides are always preferred. To make separation easier for the consumer an international plastic recycle mark is printed on larger items.



HOUSEHOLD PLASTICS

1
PETE
Number 1 : *PETE or PET (Polyethylene terephthalate)*
Used In : microwavable food trays; salad dressing, soft drink, water and beer bottles
Status : hard to clean; absorbs bacteria and flavors; avoid reusing
Is Recycled To Make : carpet, furniture, new containers, polar fleece

2
HDPE
Number 2 : *HDPE (high density polyethylene)*
Used In : household cleaner and shampoo bottles
Status : transmits no known chemicals into food
Is Recycled To Make : detergent bottles, fencing, floor tiles, pens

3
V
Number 3 : *V or PVC (vinyl)*
Used In : cooking oil bottles, clear food packaging, mouthwash bottles
Status : is belived to contain phalates that interfere with hormonal development; avoid
Is Recycled To Make : cables. mudflaps, paneling, roadway gutters

4
LDPE
Number 4 : *LDPE (Low density polyethylene)*
Used In : bread and shopping bags, carpet, clothing, furniture
Status : Transmits no known chemicals into food
Is Recycled To Make : envelopes, floor tiles, lumber, trash-can liners

5
PP
Number 5 : *PP (Polypropylene)*
Used In : ketchup bottles, medicine, and syrup bottle, drinking straws
Status : transmits no known chemicals into food
Is Recycled To Make : battery cables, brooms, ice scrapers, rakes

6
PS
Number 6 : *PS (Polystyrene)*
Used In : disposable cups and plates, egg cartons, take-out containers
Status : is belived to leach styrene, a possible human carcinogen into food; avoid
Is Recycled To Make : foam packaging, insulation, light switchplates, rulers

7
Other
Number 7 : *Other (Miscellaneous)*
Used In : 3- and 5- gallon waterjugs, nylon, some food containers
Status : Contains bisphenol A, which has been linked to heart disease and obesity; avoid
Is Recycled To Make : custom-made products

Use this chart to sort plastic materials in daily life

11. Real-time Analysis Pollution Prevention: Analytical methods need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.

Illustration : Analytical methodologies should be developed or modified, so that continuous monitoring of the manufacturing and processing units is possible. This is very much important for the chemical industries and nuclear reactors.

12. Safer chemistry for Accident prevention:

We need to develop chemical processes that are safer and minimize the risk of accidents.

Illustration : The substances to be used in a chemical reaction should be selected in such a way that they can minimize the occurrence of chemical accidents, explosions, fire and emission. For example, if the chemical process works with the gaseous substances, then the possibility of accidents including explosion is relatively higher compared to the system working with non volatile liquid and solid substances.

16.4 The role of Green chemistry : The green chemistry approach recognizes that the Earth does have a natural capacity for dealing with much of the waste and pollution that society generates, it is only when that capacity is exceeded that we become unsustainable.

To promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products.

The green chemistry helps to reduce capital expenditure, to prevent pollution. Green chemistry incorporates pollution prevention practices in the manufacture of chemicals and promotes pollution prevention and industrial ecology. Green chemistry is a new way of looking at chemicals and their manufacturing process to minimize any negative environmental effects. Right now the green chemistry revolution is beginning and it is an exciting time with new challenges for chemists involved with the discovery, manufacture and use of chemicals.

Green chemistry helps to protect the presence of ozone in the stratosphere essential for the survival of life on the earth. Green chemistry is useful to control green house effect (Global warming). So we should think about save environment and save earth.

Can you recall ?

1. What are the shapes of a bacillus and coccus? (Refer to chapter from Biology, Std. XI)
2. Which instrument is used to observe the cells ? (Refer to chapter 5 from Biology, Std. XI)
3. What is the size range of molecules of lipids and proteins ?

16.5 Introduction to nano chemistry : From clothes, sunglasses you wear to computer hard drives and even cleaning products, nanotechnology plays a big part in the manufacture of many materials. We have been using Lasers in DVD, CD players for a long time which contain nanosize components. Look at Fig. 16.1 which shows comparative scales from macro-materials to atoms.

Also observe another Fig. 16.2 which depicts the materials in nature, as well as devices that are man made. In both figures some objects like tennis ball (Fig. 16.1), ant, human hair (Fig. 16.2) we can see with our own eyes whereas bacteria, virus, red blood cell, we can not observe with naked eye. These are known as nanomaterials.

a. What is nanoscience ?

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales where properties differ significantly from those at a larger scale.

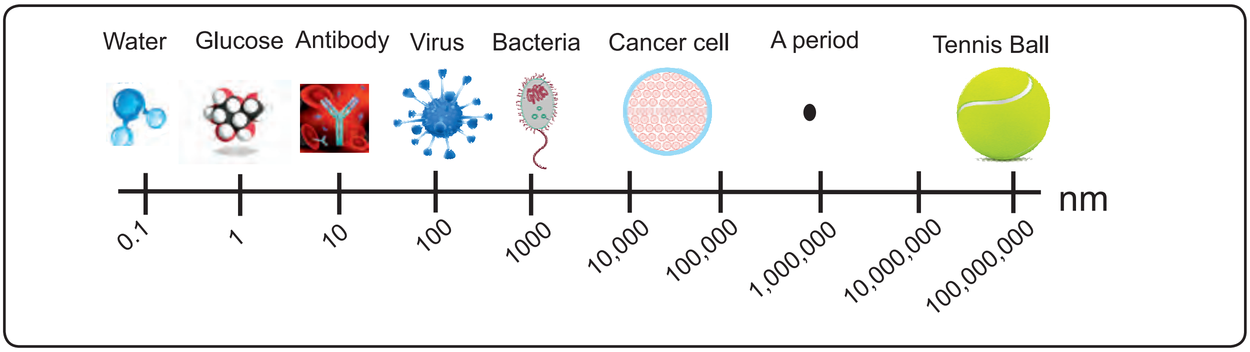


Fig. 16.1 Macro-materials to atoms

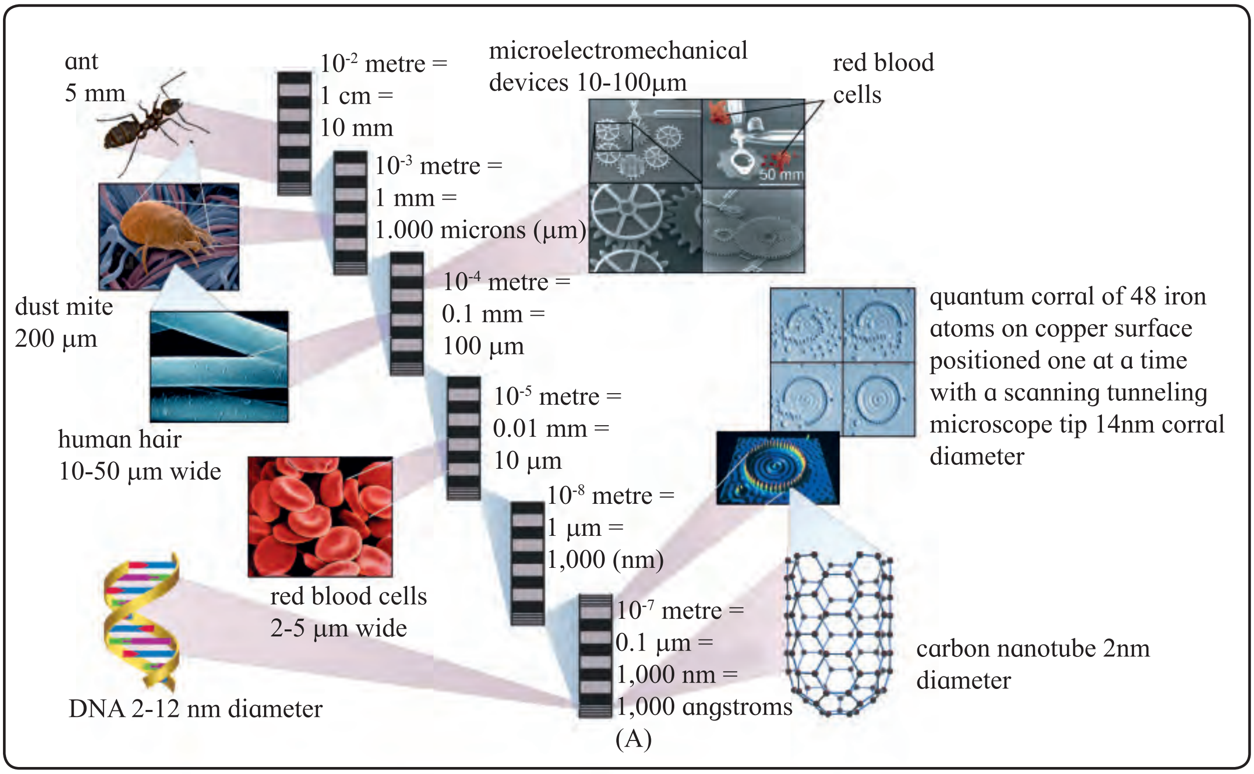


Fig. 16.2 Scale of nanomaterials

b. How do we define nanotechnology ?

Nanotechnology is the design, characterization, production and application of structures, device and system by controlling shape and size at nanometer scale.

c. Why Nano ?

The nanometer scale : ‘Nano’ in Greek means dwarf but in actual case ‘nano’ is even smaller than dwarf. Conventionally, the nanometer scale is defined as 1-100 nm. One nanometer is one billionth of a meter. (that is 1nm = 10^{-9}m).

The materials we see around us are bulk materials that possess macroscopic physical properties. Grain of sand that is micron-sized material also possesses same bulk properties. But material synthesized at nanoscale (1nm - 100nm) possesses unique optical, structural, thermal, catalytic, magnetic and electrical properties. These properties change as a function of size and are very different from their bulk materials.

d. What is a nanomaterial ?

The nanomaterial is a material having structural components with atleast one dimension in the nanometer scale that is 1-100 nm. Nanomaterials are larger than single atoms but smaller than bacteria and cells. These may be nanoparticles, nanowires and nanotubes according to dimensions. Nanostructured materials may be large organic molecules, inorganic cluster compounds and metallic or semiconductor particles.

What are zero, one and two dimensional nanoscale system ?

i. Zero-Dimensional Nanostructures : For example, Nanoparticles.

A zero dimensional structure is one in which all three dimensions are in the nanoscale.

ii. One-Dimensional Nanostructures : For example, Nanowires and Nano rods.

A one dimensional nanostructure is one in which two dimensions are in the nanoscale.

iii. Two-Dimensional Nanostructures : For example, Thin films.

A two-dimensional nanostructure is one in which one dimension is in the nanoscale.

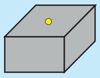
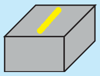
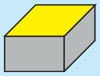
Nanomaterial Dimension	Nanomaterial Type	Example
All three dimensions < 100 nm	Nanoparticles, Quantum dots, nanoshells, nanorings, microcapsules	
Two dimensions < 100 nm	Nanotubes, fibres, nanowires	
One dimension < 100 nm	Thin films, layers and coatings	

Fig. 16.3 Illustration of zero, one, two dimensions

e. Definition of Nanochemistry : It is the combination of chemistry and nanoscience. It deals with designing and synthesis of materials of nanoscale with different size and shape, structure and composition and their organization into functional architectures. Nanochemistry is used in chemical, physical, materials science as well as engineering, biological and medical applications.

Do you know ?

A very highly useful application of nanochemistry is 'medicine'. A simple skin care product of nanochemistry is sunscreen. Sunscreen contains nanoparticles of Zinc oxide, (ZnO) and Titanium dioxide, (TiO_2). These chemicals protect the skin against harmful UV (ultraviolet) rays by absorbing or reflecting the light and prevent the skin from damage.

Internet my friend

Find out similar applications in medicine related to wounds, healing process. Also find out applications of TiO_2 and ZnO in other areas.

16.6 Characteristic features of Nanoparticles : What makes the science at nanoscale special is that at such a small scale, different laws dominate over those that we experience in our everyday life.

16.6.1 Colour : It is an optical property that is different at nanoscale. Elemental gold as we know, has nice shining yellow colour. However, if you had only 100 gold atoms arranged in cube, its colour would be much more red.

Fig. 16.4 Formation of gold nanoparticles solution

16.6.2 Surface area : High surface-to-volume ratio is a very important characteristic of nanoparticles. If a bulk material is sub divided into a group of individual nanoparticles, the total volume remains the same, but the collective surface area is largely increased. With large surface area for the same volume, these small particles react much faster because more surface area provides more number of reaction sites, leading to more chemical reactivity. Explanation of increase in surface area with decrease in particle size.

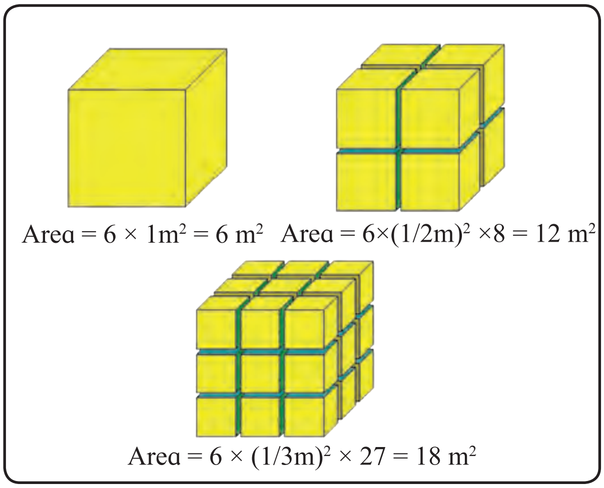


Fig. 16.5 : Surface area of nanoparticles

Fig. 16.5 shows the surface areas when a cube of $1m^3$ were progressively cut into smaller cube until cube of $1nm^3$ formed.

16.6.3 Catalytic activity : Due to increase in surface area with decrease in particle size, nanomaterial-based catalysts show increased catalytic acitivity. Usually they are heterogeneous catalysts that means catalysts are in solid form and the reactions occur on the surface of the catalyst. Nanoparticle catalysts can be easily separated and can be recycled. Example, Pd, Pt metal nanoparticles used in hydrogenation reactions.

TiO_2, ZnO are used in photocatalysis. Gold in bulk form is unreactive, but gold nanoparticles are found to be very good catalyst for various organic reactions.

Internet my friend

Find out various applications or use of gold nanoparticles.

16.6.4 Thermal properties : melting point

The melting point of nanomaterial changes drastically and depends on size. For example, sodium clusters (Na_n) of 1000 atoms appeared to melt at 288 K while cluster of 10,000 atoms melted at 303 K and bulk sodium melts at 371K.

16.6.5 Mechanical properties

Mechanical strength : Nanosized copper and palladium clusters with diameter in the size range of 5-7 nm can have hardness upto 500% greater than bulk metal.

16.6.6 Electrical conductivity : Electrical conductivity is observed to change at nanoscale. For example, carbon nanotube can act as a conductor or semiconductor in behaviour.

16.7 Synthesis of nanomaterials

16.7.1 : There are two approaches to the synthesis of nanomaterials. Bottom up and Top down. Fig. 16.6 shows schematic illustration of the preparation methods of nanoparticles.

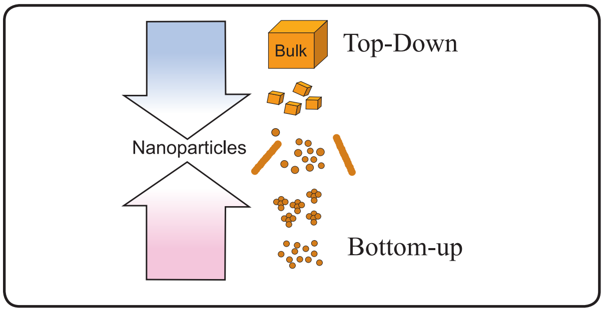


Fig. 16.6 : Schematic illustration of the preparation of nanoparticles

In the bottom approach, molecular components arrange themselves into more complex assemblies atom by atom, molecule by molecule and cluster by cluster from the bottom. Example : synthesis of nanoparticles by colloidal dispersion.

In the top-down approach, nanomaterials are synthesized from bulk material by breaking the material. The bulk solids are dis-assembled into finer pieces until they are constituted of only few atoms.

16.7.2 Wet chemical synthesis of Nanomaterials : Sol-gel process : Sols are dispersions of colloidal particles in a liquid. Colloids are solid particles with diameters of 1-100nm. A gel is interconnected rigid network with pores of submicrometer dimensions and polymeric chains whose average length is greater than a micrometer.

A sol-gel process is based on inorganic polymerization reactions. It is generally carried out at room temperature and includes four steps : hydrolysis, polycondensation, drying and thermal decomposition. This method is widely employed to prepare oxide materials.

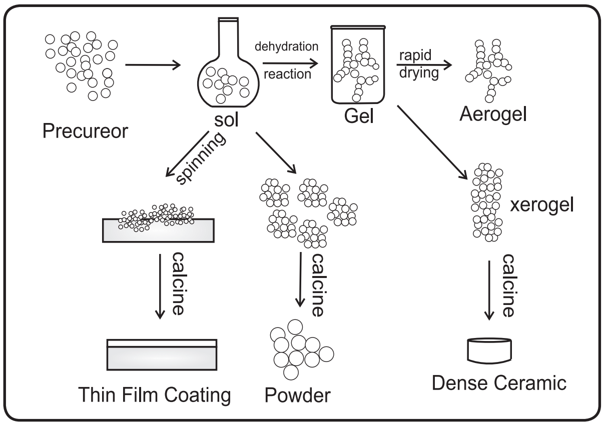


Fig. 16.7 : Schematic representation of sol-gel process of synthesis of nanoparticles

The rections involved in the sol-gel process can be described as follows :

$MOR + H_2O \longrightarrow MOH + ROH$ (hydrolysis)

metal alkoxide

$MOH + ROM \longrightarrow M\text{-}O\text{-}M + ROH$

(condensation)

1. Formation of different stable solution of the alkoxide or solvated metal precursor.
2. Gelation resulting from the formation of an oxide or alcohol-bridged network. (gel) by a polycondensation reaction.
3. Aging of the gel means during that period gel transforms into a solid mass.
4. Drying of the gel : In this step, water and other volatile liquids are removed from the gel network.
5. Dehydration : The material is heated at temperatures upto 800 ^{0}C.

16.7.3 Analysis or characterization of nanomaterials :

The synthesized material is analyzed by various analytical tools or techniques. The name of the technique and its use is described in the following Table 16.1.

16.7.4 Photographs of instruments

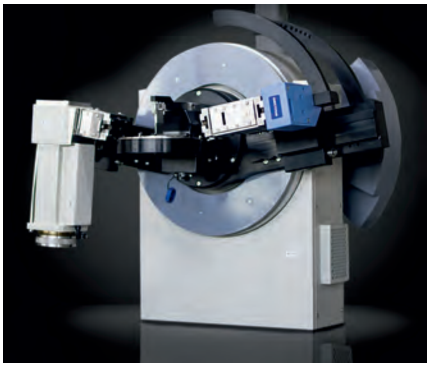


Fig. 16.8 Photograph of X-ray diffractometer

Table 16.1

Name of Technique	Instrument used	Information
1. UV-visible spectroscopy	UV-visible spectrophotometer	Preliminary confirmation of formation of nanoparticles
2. Xray Diffraction (XRD)	Xray diffractometer	particle size, crystal structure, geometry
3. Scanning electron microscopy	Scanning electron microscope (SEM)	Structure of surface of material that is morphology
4. Transmission electron microscopy	Transmission electron microscope (TEM)	particle size
5. FTIR Fourier transform infrared spectroscopy	Fourier transform infrared spectrophotometer	Absorption of functional groups, Binding nature.

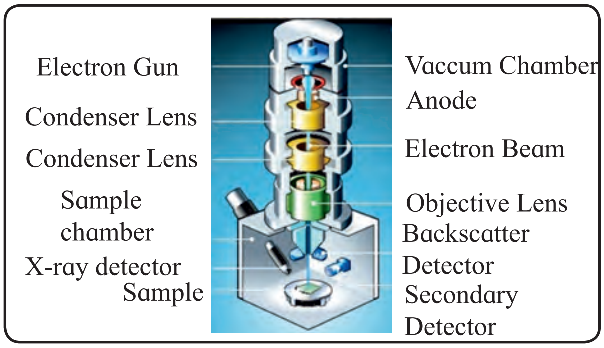


Fig. 16.9 Schematic diagram of scanning electron microscope

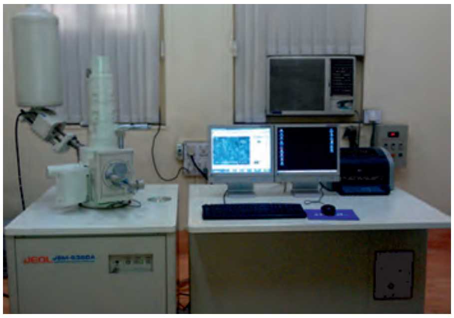


Fig. 16.10 Scanning electron microscope

16.8 History of nanotechnology :

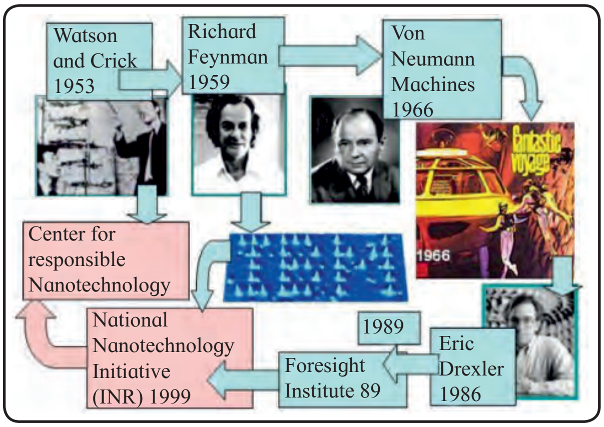


Fig. 16.13 : Scientists contributed to nanotechnology

Nanomaterials have been produced and used by humans for hundreds of years. However, understanding of certain materials as nanostructured materials is relatively recent. Due to the development of advanced tools that is sophisticated instruments, it has been possible to reveal the information at nanoscale.

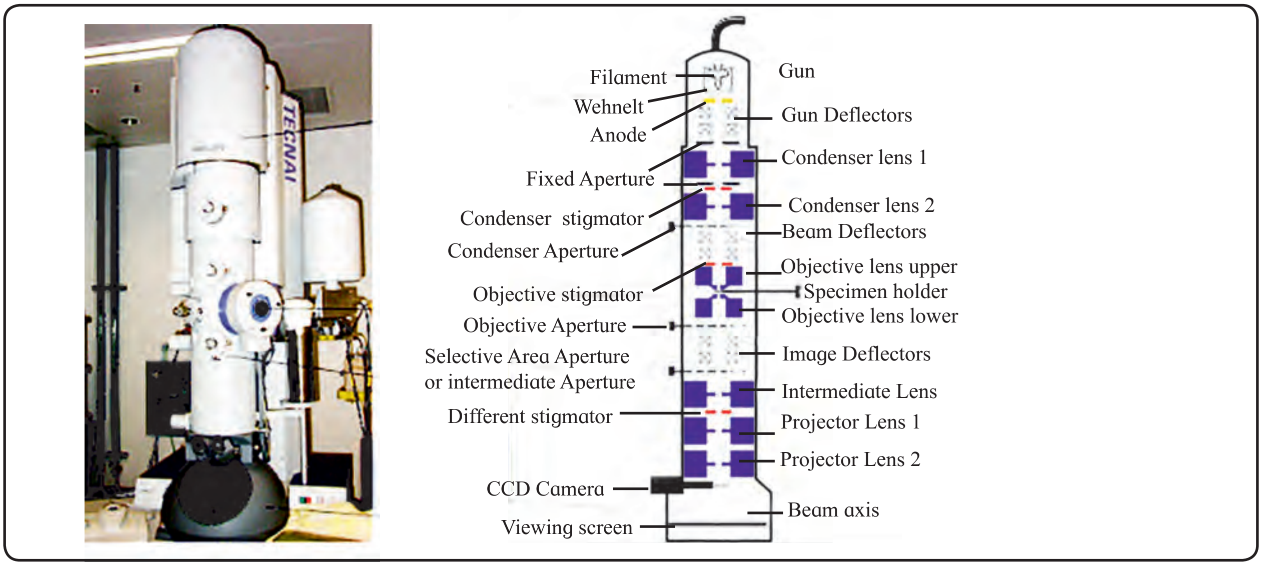


Fig. 16.11Transmission electron microscope (TEM)

Fig. 16.12 FTIR specroscope

Fig. 16.14 Ruby red colour

a. Beautiful ruby red colour of some ancient glass paintings is due to gold and silver nanoparticles trapped in the glass matrix.

b. The decorative glaze or metallic film known as lustre found on some medieval pottery is due to certain spherical metallic nanoparticles.

c. Carbon black is a nanostructured material that is used in tyres of car to increase the life of tyre. (Discovery in 1900). Carbon nanotubes are made up of graphite sheets with nanosized diameter. They have highest strength.

d. Fumed silica, a component of silicon rubber, coatings, sealants and adhesives is also a nanostructured material.

Internet my friend

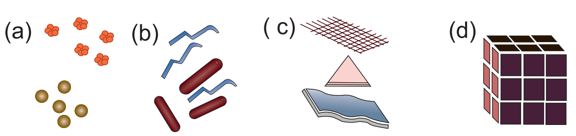
Find out more number of nanostructured materials in day to day used products.

Do you know ?

1. The term '**nanotechnology**' was defined by Tokyo science University Professor, Nario Taniguchi in 1974.
2. Invention of Scanning Tunneling Microscope (STM) in 1980, led to the discovery of fullerenes in 1986 and carbon nanotubes a few years later.

Internet my friend

Collect the information about the scientists who discovered SEM, STM, TEM instruments.



(a) 0D spheres and clusters, (b) 1D nanofibers, wires and rods (c) 2D films, plates and networks, (d) 3D nanomaterials

Fig. 16.15 Classification of nanomaterials

Can you think ?

Visualize the size effect : Size difference between the earth and an apple is equal to the size difference between atoms (30 nm) and an apple.

16.9 Applications of nanomaterials :

Nanochemistry has already contributed to number of innovative products in various disciplines because of their unique physical, chemical, optical, structural, catalytic properties and so on. Few applications are given below :

a. Nanoparticles can contribute to stronger, lighter, cleaner and smarter surfaces and systems. They are used in the manufacturing of scratchproof eyeglasses, transport, sunscreen, crack resistant paints and so on.

b. Used in electronic devices. For example, Magnetoresistive Random Acess memory (MRAM)

c. Nanotechnology plays an important role in water purification techniques.

Water contains waterborne pathogens like viruses, bacteria. 1.1 billion people are without access to an improved water supply. The provision of safe drinking water is currently high priority. Recently, cost effective filter materials coated with silver nanoparticles (AgNps) is an alternative technology. (For example : water purifier) Silver nanoparticles act as highly effective bacterial disinfectant, remove E.Coli from water.

d. Self cleaning materials : Lotus is an example of self cleaning. The lotus plant (*Nelumbo nucifera*) although grows in muddy water, its leaves always appear clean. The plants' leaves are superhydrophobic. Nanostructures on lotus leaves repel water which carries dirt as it rolls off. Lotus effect is the basis of self cleaning windows.

Do you know ?

Sol-gel processes are used in the motor vechicle industry to produce water repellent coatings for wind screens or exterior mirrors.

16.10 Nanoparticles and Nanotechnology :

Advantages :

1. Revolution in electronics and computing.

2. Energy sector - nanotechnology will make solar power more economical. Energy storage devices will become more efficient.

3. Medical field :

Manufacturing of smart drugs, helps cure faster and without side effects. Curing of life threatening diseases like cancer and diabetes.

Disadvantages : Despite the possibilities and the advancements that the nanotechnology offers to the world, there also exist certain potential risks involved with the disadvantages of it.

Nanotechnology has raised the standard of living but at the same time, it has increased the pollution which includes air pollution. The pollution caused by nanotechnology is known as nano pollution. This kind of pollution is very dangerous for living organisms.

Nanoparticles can cause lung damage. Inhaled particulated matter can be deposited throughout the human respiratory tract and then deposit in lungs.

The characteristics of nanoparticles that are relevant for health effects are size, chemical composition and shape.

Exercises

1. Choose the most correct option.

i. The development that meets the needs of present without compromising the ability of future generations to meet their own need is known as

a. Continuous development

b. Sustainable development

c. True development

d. Irrational development

ii. Which of the following is ϒ-isomer of BHC?

a. DDT　　b. lindane

c. Chloroform

d. Chlorobenzene

iii. The prefix 'nano' comes from

a. French word meaning billion

b. Greek word meaning dwarf

c. Spanish word meaning particle

d. Latin word meaning invisible

iv. Which of the following information is given by FTIR technique ?

a. Absorption of functional groups

b. Particle size

c. Confirmation of formation of nanoparticles

d. Crystal structure

v. The concept of green chemistry was coined by

a. Born Haber

b. Nario Taniguchi

c. Richard Feynman

d. Paul T. Anastas

2. Answer the following

i. Write the formula to calculate % atom economy.

ii. Name the ϒ-isomer of BHC.

iii. Ridhima wants to detect structure of surface of materials. Name the technique she has to use.

iv. Which nanomaterial is used for tyres of car to increase the life of tyres ?

v. Name the scientist who discovered scanning tunneling microscope (STM) in 1980.

vi. 1 nm = ...m ?

3. Answer the following

i. Define (i) Green chemistry (ii) sustainable development.

ii. Explain the role of green chemistry.

iii. Give the full form (long form) of the names for following instruments.

a. XRD b. TEM. c. STM

d. FTIR e. SEM

iv. Define the following terms :

a. Nanoscience

b. Nanotechnology

c. Nanomaterial

d. Nanochemistry

v. How nanotechnology plays an important role in water purification techniques?

vi. Which nanomaterial is used in sunscreen lotion ? Write its use.

vii. How will you illustrate the use of safer solvent and auxiliaries ?

viii. Define catalyst. Give two examples.

4. Answer the following

i. Explain any three principles of green chemistry.

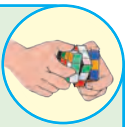
ii. Explain atom economy with suitable example.

iii. How will you illustrate the principle, minimization of steps ?

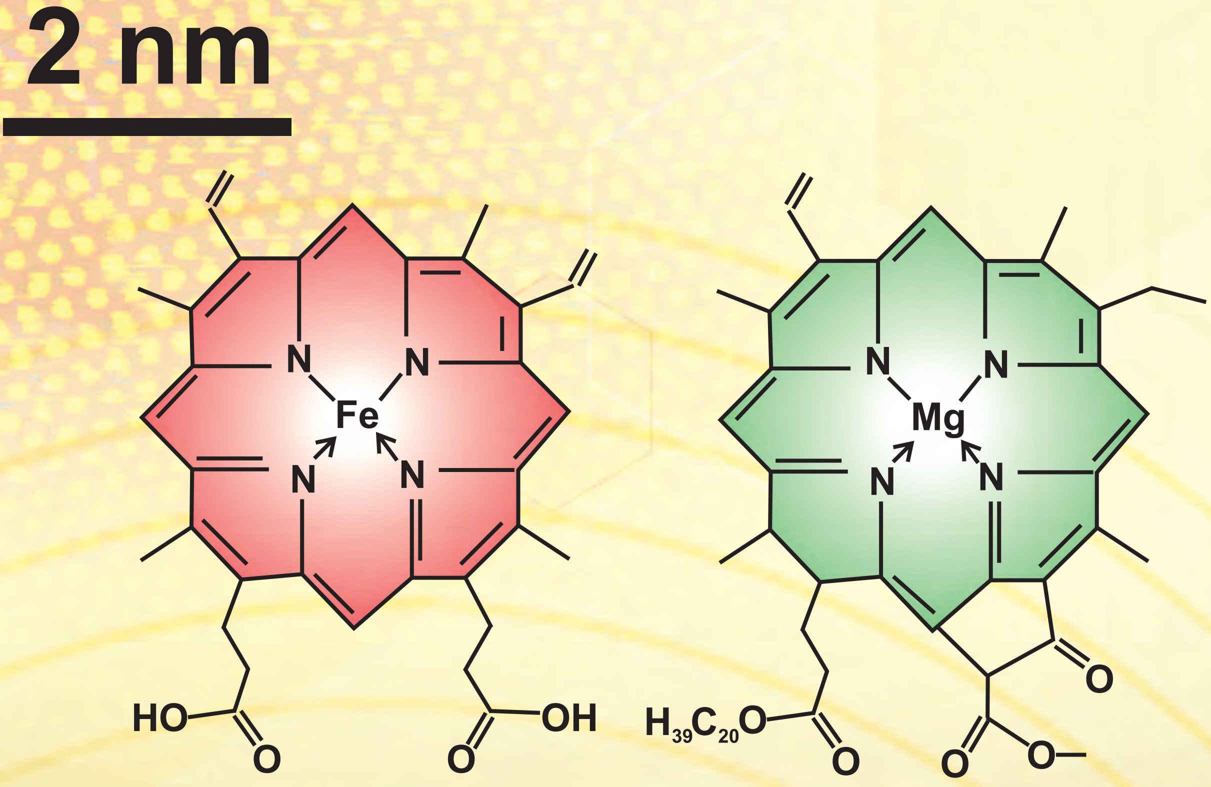
iv. What do you mean by sol and gel? Describe the sol-gel method of preparation for nanoparticles.

v. Which flower is an example of self cleaning ?

Activity :



- **Collect information about application of nanochemistry in cosmetics and pharmaceuticals**



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