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Textbook of Engineering Chemistry

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Jaya Shree Anireddy



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Textbook of Engineering Chemistry

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John Wiley & Sons (Asia) Pte Ltd, 1 Fusionopolis Walk #07-01 Solaris, South Tower, Singapore 138628

John Wiley & Sons Canada Ltd, 22 Worcester Road, Etobicoke, Ontario, Canada, M9W 1L1

First Edition: 2018

ISBN: 978-81-265-7632-6

www.wileyindia.com

Printed at:

Preface to this Edition

Engineering is a discipline that involves application of scientific knowledge and principles to develop and design structures, systems, devices, materials and processes for improving day-to-day lives and providing solution to global problems. It is thus imperative for engineering students to acquire an indepth understanding of science, and more so of chemistry which plays an integral role in design and development of materials. Engineering Chemistry course for the first-year undergraduate engineering students is designed to provide students with a background of important concepts and principles considered most relevant in engineering context. The course also aims to bridge the theoretical concepts and their practical engineering applications, thus highlighting the role of chemistry in the field of engineering.

Objective

This book is structured keeping in view the objective of the course, and is intended as a textbook for first-year students of all engineering disciplines. It aims to impart students an in-depth knowledge of various aspects of chemistry and their application to Molecular Structure and Theories of Chemical Bonding; Water and its Treatment; Electrochemistry and Corrosion; Stereochemistry, Reaction Mechanism and Synthesis of Drug Molecules; and Spectroscopic Techniques and Application. The primary focus of this textbook is to introduce the students to the concepts and applications areas of chemistry in engineering. The chapters are structured in a style which would facilitate a comprehensive understanding of chemistry for the first year students. The language of the textbook is rendered to be student friendly as it is the international practice today in the preparation of textbooks. Each chapter begins with learning objectives and ends with key terms, objective-type and review questions and numerical problems along with answer key to further the understanding of the students and make them self-reliant.



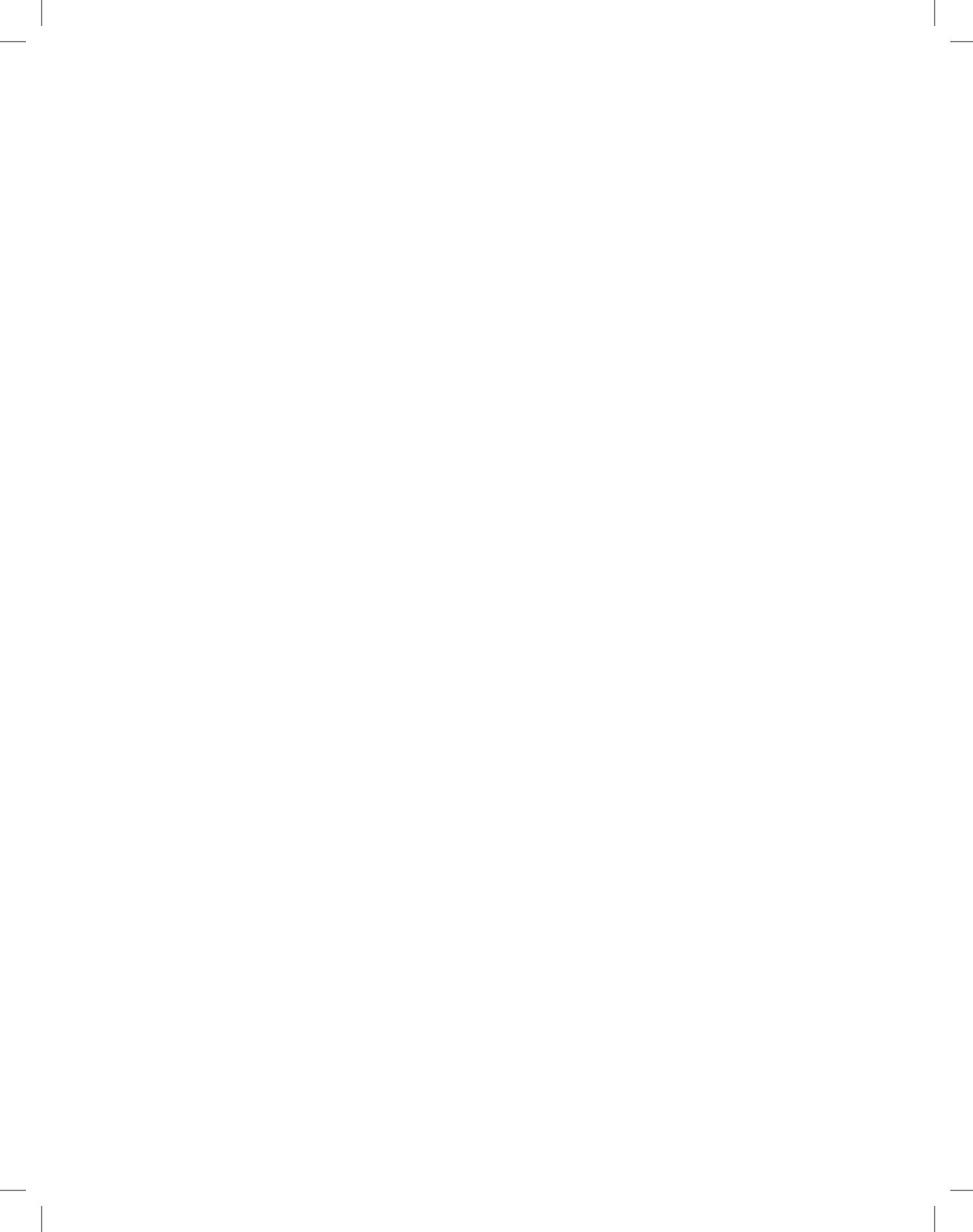
About the Author



Dr. A. Jaya Shree, Professor of Chemistry, Chairman, BOS for Chemistry, JNTUH, and Head, Centre for Chemical Sciences and Technology, Institute of Science and Technology, JNTUH, Hyderabad has 26 years of professional experience with active research and teaching commitments. She obtained her Ph.D degree from Osmania University in 1992 with UGC/CSIR NET fellowship. She is fellow of professional bodies like Royal Society of Chemistry, London, Telangana Academy of Sciences, Indian Chemical Society (ICS), Kolkata and member, American Chemical Society (USA), The Indian Science Congress Association, Indian Council of Chemists, Indian Association of Chemistry Teachers (IACT, TIFR), etc. She is a recipient of best teacher award from the Government of Telangana State for the year 2016.

Dr. A. Jaya Shree has guided 9 research scholars for Ph.D, and currently supervising 10 full time research scholars for Ph.D. degree at Centre for Chemical Sciences and Technology, Institute of Science and

Technology, JNTUH. She has published more than 100 scientific papers in peer reviewed journals. She has attended more than 75 National and International conferences and presented scientific papers in conferences organized at USA, China, Dubai and India etc. She has organized various national and international conferences and seminars. She has also designed and organized five UGC sponsored Refresher Courses in Chemistry at Academic Staff College, JNTUH. She has been nominated as member of Board of Governors, Academic Council and Board of Studies for various affiliated colleges of JNTU, Hyderabad.



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1

Molecular Structure and Theories of Chemical Bonding

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Formation of ionic bond and properties of ionic compounds.
- Nature of covalent bond and properties of covalent compounds.
- Nature and properties of coordinate or dative bond.
- Quantum theory of chemical bonding.
- Valence bond theory of chemical bonding and its limitations.
- Molecular orbital theory and its application to explain formation of homonuclear and heteronuclear molecules.
- Hybridization and shapes of some molecules.
- Various theories explaining bond formation in coordination complexes.
- Relation between coordination number and geometry of coordination compounds.
- Formation of octahedral, tetrahedral and square planar complexes
- Nature of metallic bond.

A chemical bond, which apparently exists between atoms in a molecule, is a *force* that holds bonded atoms together. Basically, it is the same kind of electrostatic attraction that binds the electrons of an atom to its positively charged nucleus. Chemical bonding occurs between two atoms when their electrons are simultaneously attracted by two nuclei and it causes the energy of the combining atoms to become lower than when they are apart.

There is no single satisfactory theory which would explain the concept of bonding in all types of compounds and also predict their structures, energies and properties. Initially the concept of a chemical bond was explained by a few classical models which assume that electrons and ions behave as point charges that attract and repel according to the laws of classical mechanics and electrostatics. However, these models apply only to certain classes of compounds and explain only a restricted range of phenomena. Since the development of quantum theory in 1920s, the chemical bond has been explained by quantum mechanical models. We shall look into the different models proposed and different kinds of bonds.

The first ever theory to explain the formation of chemical bond was proposed by Kossel and Lewis and is known as the electronic theory of valency. The theory was based on the following observations:

- The electrons in the outermost shell/orbit of an atom are called valence shell electrons. These are responsible for most of the properties of the elements.
- Elements which have two or eight electrons in the outermost shell, that is, have their octet complete are stable and do not combine chemically either with each other or other elements.

According to the theory then, the formation of a chemical bond between two or more atoms can thus be explained as tendency of elements to attain stable configuration of electrons in the outermost shell. The combining atoms may rearrange their electrons either by complete transfer of electrons from one atom to another or by sharing of electrons. This leads to two types of bond formation discussed as follows.

1.1 Ionic Bond

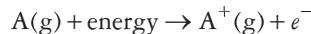
A classical model which explains the bonding in an important class of compounds, namely, ionic solids is called the *ionic bond* or *electrovalent bond*. This model proposes that when one or more outermost electrons from one atom are transferred to another atom, it results in the formation of positive and negative ions. The electrostatic attraction binding together the unlike ions so formed is called *ionic bonding*. The ionic bonding forces act in all directions around a particular ion, that is, they are not directional.

Before we discuss the formation of ionic bond, there are some terms we need to define and understand. These are as follows:

- Ionization energy:** It is the minimum energy required to remove an electron from a gaseous atom or molecule in its ground state. It is a measure of how strongly the electron is held to an atom. Higher the value of ionization energy, greater is the difficulty in removal of electrons. The ionization energy for removal of the first electron is called *first ionization energy* and that for removal of second electron is called *second ionization energy* and so on.
- Electron affinity:** It is the measure of change of energy when an electron is added to a neutral atom in gaseous state to form a negative ion. Higher the electron affinity of an atom, greater is its tendency to accept an electron.
- Lattice energy:** It is the energy released when one mole of crystal of ionic solid is formed from gaseous ions. The tendency to form ionic compounds increases with increase in lattice energy. The magnitude of lattice energy is determined by:
 - Size of the ions:** Smaller ions have lesser internuclear distance and hence higher lattice energy.
 - Charge on ions:** Higher charge on the ions causes greater attractive forces between ions and hence higher lattice energy.

Ionic bond formation requires that the element forming positive ion should have low ionization energy and that forming negative ion should have high electron affinity. Hence, an ionic bond is generally formed between electropositive elements of Groups 1, 2, 13, which readily lose electrons and electronegative elements of Groups 15, 16, 17, which readily gain electrons. The formation of ionic bond between an electropositive element A and an electronegative element X, can be considered to proceed in three steps:

- Formation of gaseous cations:**



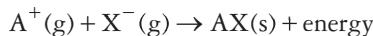
The energy required for this step is the ionization energy (I.E.). For bond formation, the atom forming the cation should have low ionization energy.

- Formation of gaseous anions:**



The energy released from this step is the electron affinity (E.A.). For bond formation, the electron affinity of the atom forming the anion should be high.

- Binding of ions of opposite charges to form ionic solid:**



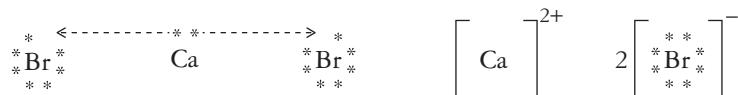
Since the ionic bond is non-directional, the formation of ion pair does not stop at this stage. The ion pair will each attract other oppositely charged ions from all directions and result in a cluster of ions arranged in a particular manner called a *crystal lattice*. The energy released in this step is the lattice energy.

When the ions come together to form a crystalline array, large amount of energy is released (the lattice energy) even if the sum of energies involved in Steps (1) and (2) is positive. This is because the total energy released (Step 3) is more than the total energy released in Steps (1) and (2) and is the driving force behind the formation of ionic compounds. Although for sake of clarity, the formation of an ionic solid is shown in these three steps, it all actually happens at once. As a result of packing of the ions in a crystal, every cation has anion(s) as its neighbor, and every anion has cation(s) around it, and there is a strong overall attractive interaction among the various oppositely charged ions in the crystal.

The formation of ionic bond explains the bonding in a number of compounds, particularly crystalline solids formed by Groups 1 and 2 elements with highly electronegative elements such as the halogens. For example, let us consider the formation of the ionic compound KCl. This involves the formation of the ions K^+ and Cl^- . Here K has an electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. The ionization energy of K to form K^+ is +418 kJ/mol and the electron affinity for the formation of Cl^- is -361 kJ/mol. The lattice energy of KCl is -715 kJ/mol. The ionic bond formation may be represented as:



Similarly, the formation of $CaBr_2$ and LiF may be represented as follows:



However, the formation of ionic bond cannot explain bond formation in a large number of compounds and is thus limited in its application.



Properties of Ionic Compounds

The compounds resulting from the non-directional ionic bond, namely, ionic compounds are characterized by the following properties:

1. All ionic compounds adopt a three-dimensional (3D) structure in which the ions are close to various oppositely charged ions, that is, they are highly crystalline solids.
2. They are thermally stable and have high density, high melting and boiling points due to stronger electrostatic force of attraction between oppositely charged ions.
3. They are hard and brittle.

4. Being highly polar, they are soluble in polar solvents.
5. They have low electrical conductivity as solids but are good conductors in molten state or solution state due to availability of free ions.

Concept Check

- What are the types of elements involved in formation of ionic bond?
 - Explain the formation of ionic bond in the compound Al_2O_3 .
 - What is lattice energy and what does it signify?
 - Why is ionic bond considered to be non-directional?
 - Although the sum total of energy involved in the formation of cation Na^+ and anion Cl^- is positive, how is the formation of ionic bond in NaCl justified? The following reactions are provided:
- (a) Formation of the sodium ions (ionization):
- $$\text{Na(g)} + \text{Energy} \rightarrow \text{Na}^+(\text{g})$$
- $$(\Delta H = +496 \text{ kJ/mol})$$
- (b) Formation of the chloride ions (electron affinity):
- $$\text{Cl(g)} + e^- \rightarrow \text{Cl}^-(\text{g}) + \text{Energy}$$
- $$(\Delta H = +348 \text{ kJ/mol})$$
- Why are crystals of ionic compounds hard and brittle?

1.2 Covalent Bond

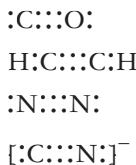
Another theory which is very successful in explaining the bonding in many compounds is the shared electron pair theory. According to this theory, when two atoms come together, the valence electrons of each of the atoms will be attracted and shared by the nuclei of both the atoms; as a result, a net strong bonding occurs between the two atoms and is called the covalent bond. *This bond is formed between two atoms by mutual sharing of their outer electrons so as to complete their octets or duplets (in case of hydrogen which has only one shell).* Typical covalent bond strength is about 250–400 kJ/mol and is of the same order of magnitude as ionic bond.

A covalent bond is represented by Lewis electron-dot formula, where only the valence electrons of each bonded atom are depicted as dots around the atom symbols. Atom symbol represents the nucleus plus the electrons of the filled inner shell orbitals. The shared pair of electrons is shown between the atoms involved in covalent bonding, while the covalent bond is shown as a horizontal line between the atoms. Such a covalent bond is known as a single bond.

For example, an isolated hydrogen atom possesses only one electron, but *two* hydrogen atoms can share their electrons so that the resulting covalent bond gives each atom an inert gas electron configuration; the formation of H_2 can be depicted as:



When one pair of electrons is shared between two atoms, it constitutes one covalent bond. However, two or three pairs of electrons could also be shared in order to complete the octet in the bonding atoms to produce double and triple bonds. Such a covalent bond is called multiple bond. Since multiple bonds place more electron density between the two nuclei, the latter are held toward each other more closely and tightly; multiple bonds are, therefore, shorter and stronger than single bonds. For example, the multiple covalent bond between the atoms in molecules like CO , C_2H_2 , N_2 , CN^- can be represented as:



In many molecules, not all of the electron pairs comprising the octet on an atom are shared between atoms. The unshared electron pairs are called *lone pairs* (e.g., N in NH₃ and O in H₂O). Although lone pairs are not directly involved in bond formation, they have an important role in determining the shape of the molecule.



The conditions for the formation of a covalent bond between two electronegative elements are as follows:

1. The combining atoms should have 1, 2 or 3 electrons less than stable noble gas configuration in the valence shell.
2. Electronegativity difference between the two atoms should be zero or very small.
3. The approach of the atoms towards one another should be accompanied by decrease of energy.



Polar and Non-Polar Covalent Bonds

When a covalent bond is formed by the sharing of a pair of electrons between two identical atoms, the amount of “pull” experienced by electrons from each atom is the same, the electrons are shared equally and the bond is completely non-polar. For example, the covalent bond between the atoms of diatomic molecules such as H₂ (H–H), F₂ (F–F), Cl₂ (Cl–Cl), Br₂ (Br–Br) and I₂ (I–I). When the bonding atoms differ greatly in electronegativity then the sharing is not equal and the bond becomes polar. For example, H–Cl and H–F.

Electronegativity (E.N.) describes the ability of an atom to compete for electron with the other atom to which it is bonded. The American physical chemist Linus Pauling devised a scale for electronegativity for the elements of the periodic table which varies from 0 to 4. Electronegativity decreases from the top to bottom in a group and increases from left to right along a period. If the difference in electronegativity between the bonding atoms is greater, then greater is the polarity of the covalent bond. The electron pair is closer to the atom with larger electronegativity.

Atoms with widely different electronegativity values (by 1.9 or more) tend to form ionic bonds. True non-polar covalent bonds form only when diatomic molecules are formed from two identical atoms; otherwise the covalent bond formed is polar. In fact, there is no sharp distinction between ionic and polar bonds.

Roughly, the bond formed is ionic if the difference in electronegativity between the atoms is greater than 2.0 ($|\Delta\text{E.N.}| > 2.0$), bond is polar covalent if electronegativity difference is between 0 and 2.0

($0 < |\Delta E.N.| < 2.0$) and it is non-polar covalent bond if there is no difference in the electronegativity values ($|\Delta E.N.| = 0$).

Properties of Covalent Compounds

The covalent compounds are characterized by the following properties:

1. Covalent bond is directional in nature because it is localized in between the nuclei of atoms.
2. Compounds containing covalent bonds under normal conditions of pressure and temperature exist as gases or liquids of low boiling point, since these compounds exist as individual molecules and the intermolecular forces are generally weak. However, a few covalent compounds also exist in solid states (e.g., urea, sugar, etc.).
3. Covalent compounds have relatively low melting and boiling points. Due to the presence of weak intermolecular forces between the molecules, lesser amount of energy is required to break the bond.
4. These compounds are generally poor or non-conductors of electricity since they do not give ions in solutions or in diffused state.
5. They are soluble in non-polar solvents such as benzene, carbon tetrachloride, etc., but insoluble in polar solvents like water.
6. As the bond is rigid and directional, covalent compounds show isomerism.
7. The reactions of covalent compounds involve breaking of covalent bonds in reacting molecules and forming of new covalent bonds in product molecules. Hence the reactions are relatively slow because a lot of energy is required to break the covalent bond.

Expanded Octet

The octet rule (bonds are formed by atoms in order to achieve the eight electrons configuration in the valence shell) applies quite well to the elements of second row of the periodic table, Li through F; but beyond this, it is generally applicable only to the non-transition elements. This is because, for the second period elements, the only available orbitals are the s^2p^6 set which when filled comprises the octet.

For elements in the third period (Na through Cl) and beyond, the higher empty orbitals ($3d$), being closer in energy to $3p$ level, can be used to accommodate additional shared pairs beyond the octet. Hence the elements such as S, Cl, P, and Si form compounds in which five or six electron pairs surround the central atom. These pairs may all be shared with other atoms, or some of them may remain as lone pairs. Examples of molecules in which the central atom contains an expanded octet are the phosphorus pentahalides and sulphur hexafluoride.

Concept Check

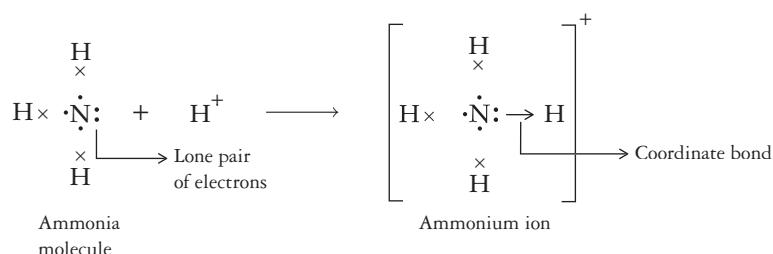
- State the important conditions for the formation of a covalent bond.
- Draw Lewis electron-dot diagrams for MgF_2 , CO_2 , PCl_3 and CCl_4 .
- What is the difference between polar and non-polar covalent bonds? Are all covalent bonds polar?
- Why is H_2O more polar than H_2S ?
- Why are melting and boiling points of covalent molecules low in spite of covalent bond energy being very high?
- Why solutions of covalent compounds do not conduct electricity?
- The octet rule is not satisfied in certain compounds. Give two examples and justify.

1.3 Coordinate or Dative Bond

During the formation of a bond by sharing of electrons between atoms, when both electrons of the shared pair are provided by one of the combining atoms then the bond formed is called *a coordinate bond* or *a dative bond*. The atom which provides the electron pair is termed as the donor atom, while the atom which accepts it, is termed as the acceptor atom. An arrow pointing from donor towards the acceptor atom represents a coordinate bond. Once a coordinate bond is formed, it cannot be distinguished from a normal covalent bond. The formation of such bonds is illustrated in the following examples:

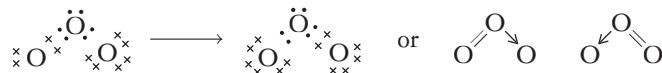
Formation of Ammonium (NH_4^+) Ion

During the formation of ammonium ion, nitrogen is the donor atom, while H^+ is the acceptor ion as shown:



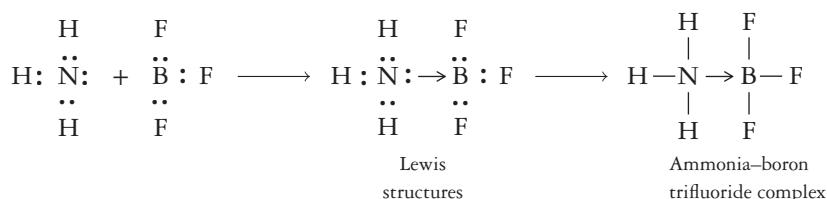
Formation of Ozone (O_3) Molecule

A molecule of oxygen contains two oxygen atoms joined by a covalent double bond. The electronic configuration of oxygen atom is $1s^2 2s^2 2p^4$; it is two electrons short of neon configuration. Thus, the two atoms of oxygen share two electrons each to attain stable octet configuration and form a double bond between them. If another atom of oxygen having six electrons comes closer to the oxygen molecule, then the oxygen molecule may share a lone pair of electrons from either of the two oxygen atoms with the new atom. As a result, a coordinate bond is formed between one of the oxygen atoms of the oxygen molecule, and the third oxygen atom as shown:



Formation of Coordinate Bond between Two Molecules

Sometimes, two or more stable molecules combine to form a molecular complex in which the constituent molecules are held together by a “coordinate bond”. One typical example is the complex formed by coordinate bond between the molecules of NH_3 and BF_3 . The electron-dot structures of these molecules are:



The nitrogen atom has a complete octet around it, but boron has only six electrons around it. The nitrogen atom donates its lone pair of electrons to boron so that it also acquires the octet. This sharing gives rise to a coordinate bond between N and B atoms. Coordinate bonds are involved in the formation of transition metal complexes, namely, the coordination compounds.

Concept Check

- What is a coordinate bond? Why is it formed in certain compounds only? Explain with examples.
- Coordinate bond can be formed between neutral molecules. Explain with an example.

1.4 Quantum Theory of Chemical Bonding

Although the Lewis structures give an idea of the valence electrons around the atom, it does not precisely locate the position of the electrons in the chemical bond. The behavior of electrons in molecules and compounds is predicted by the valence bond theory in terms of the quantum mechanical model.

The classical models used to explain the bonding between atoms considered the electrons as rigid particles whose position and momentum could be exactly determined at any point of time and whose behavior could be governed by laws of classical mechanics. However, many properties exhibited by atoms and molecules such as line spectra of atoms, photoelectric effect, blackbody radiation and others could not be satisfactorily explained by classical mechanics. This resulted in the development of quantum mechanics to explain the behavior of systems at atomic scale and smaller. The fundamental concepts on which quantum mechanics is based are the de Broglie's postulate, Heisenberg's uncertainty principle and the Schrodinger's wave equations with their solutions.

Based on experimental evidences like observation of diffraction pattern due to electrons similar to light waves, in 1924, de Broglie postulated that electrons not only behave like particles but also exhibit wave-like behavior (like light radiation). He suggested that electrons have an associated matter wave whose motion is governed by the equation $\lambda = h/p$, where p is the momentum of the entity when it behaves like a particle and is associated with a wave of wavelength λ .

Following de Broglie's postulate, in 1927 Heisenberg gave the *uncertainty principle* which stated that it is not possible to simultaneously determine the exact value of the momentum p_x as well as the corresponding position x of a particle-like electron. The precision of measurement is inherently limited by the measurement process itself such that

$$\Delta p_x \cdot \Delta x \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

where h is the Planck's constant and $h/4\pi = 0.527 \times 10^{-34} \text{ J}\cdot\text{s}$. In other words, the uncertainty in the energy (ΔE) times the uncertainty in the time (Δt) – or alternatively, the uncertainty in the position (Δx) multiplied by the uncertainty in the momentum (Δp) – is greater than or equal to a constant ($h/4\pi$). The implication is that in extremely small time elements, the uncertainty in the value of the energy of a particle is significant. Heisenberg declared, because one cannot know the precise position and momentum of a particle at a given instant, one cannot calculate the precise future motion of a particle, but only a range of possibilities for the future motion of the particle. Since experimental evidence suggested that atomic particles were also wave-like in nature, Schrodinger arrived at a wave equation to explain the

behavior of atomic particles in 1925 around the same time as Heisenberg. The Schrodinger's wave equation is a second derivative differential equation given as follows:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{b^2}(E - V)\psi = 0$$

where $\partial^2 \psi / \partial x^2$ is the second derivative with respect to x , ψ is the Schrodinger wave function, x is the position, E is the energy and V is the potential energy.

The solution to this equation is a wave that describes the quantum aspects of a system. By solving Schrodinger's equation, we get a wave function $\psi(x, t)$ which tells us the *probability* (square of the wave function, ψ^2) of finding the particle in some region in space as a function of time. The probability interpretation of the wave function imposes that the allowed energies of a particle moving in a potential $V(x)$ are restricted to certain discrete values, which are determined by the nature of the potential. This phenomenon is known as the quantization of energy. Quantum mechanical model of an atom considers that the electron cannot be at any single location, rather there is a region in space in which the probability of finding the electron has some arbitrary value which will always be less than unity. The shape of this volume of space is called an *orbital* and is defined by a mathematical function that relates the probability to the (x, y, z) coordinates of the molecule.

Concept Check

- Which theory states and relates the wave nature of electrons originally considered as particles?
- What is the important contribution of Hiesenberg's uncertainty principle in the understanding of location of electrons around atomic nucleus?
- What is the significance of Schrodinger's wave function ψ ?

1.5 Valence Bond Theory

Valence bond theory is one of the two basic theories, along with molecular orbital theory, developed to explain chemical bonding based on quantum mechanics. According to valence bond theory, a covalent bond is formed between two atoms in a molecule, when the half-filled valence atomic orbitals (AOs) of the two atoms containing unpaired electron overlap with one another and the electrons pair up in the overlap region. Due to the overlapping, electrons are localized between the atoms in the bond region. When the attractive forces (electron–nucleus of two different atoms) are stronger than the repulsive forces (electron–electron or nucleus–nucleus), energy is released; lowering of energy makes the molecule stable. This theory proposes that maximum overlap leads to the formation of the strongest possible bonds.

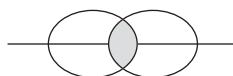
The postulates of the valence bond theory of covalent bonding are as follows:

1. A covalent bond is formed due to the overlap of the outermost half-filled atomic orbitals of the combining atoms. The extent of overlap determines the strength of this bond.
2. The two half-filled orbitals involved in the bond formation should contain electrons of opposite spins.
3. Completely filled orbitals do not take part in the bond formation.
4. The non-spherical orbitals such as *p* and *d* orbitals tend to form bonds in the direction of maximum overlap.

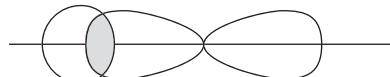
5. When two orbitals are of same energy, the orbital which is non-spherical (p or d orbital) forms stronger bonds than the spherically symmetrical orbital (s orbital).

This overlap of orbitals leads to the formation of two types of covalent bonds, namely, sigma (σ) and pi (π):

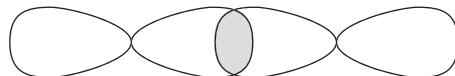
- Sigma (σ) bonds are formed when the orbitals of two shared electrons overlap head-to-head. The overlapping AOs can be of different types, for example, a σ bond may be formed by the $s-s$, $s-p$, $s-d$, $p-p$, $p-d$ or $d-d$ overlapping of AOs. Some of the possible overlaps leading to a σ bond are:
 - $s-s$ orbital overlap:



- $s-p$ orbital overlap:

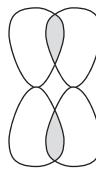


- $p-p$ orbital overlap:



For example in the case of H_2 molecule, H–H σ bond is formed by the $s-s$ orbital overlap of the two hydrogen atoms containing one unpaired electron each; while in an F_2 molecule, the F–F bond is formed by the overlap of p_x orbitals of the two F atoms containing an unpaired electron each. Since the nature of the overlapping orbitals is different in H_2 and F_2 molecules, the bond strength and bond lengths differ between H_2 and F_2 molecules.

- Pi (π) bonds are formed when two p_y or two p_z orbitals overlap laterally as shown below. It concentrates electron density between the nuclei, but above and below the internuclear axis:



Hybridization and Shapes of Molecules

Simple valence bond theory fails to explain the structure of molecules. For example, in a methane molecule (CH_4), if the covalent bonds between the hydrogen atoms and the carbon were formed by the overlap of $1s$ orbitals of four hydrogen atoms with the three $2p$ and one $2s$ orbitals of the carbon atom ($1s^2 2s^2 2p^2$), the H–C–H bond angles would be 90° for three of the hydrogen atoms and the fourth hydrogen atom would have a bond angle of 135° . Experimental evidence shows that all the bond angles in methane are 109.5° and the resulting shape is a regular tetrahedron. Thus, the formation of bonds by considering “pure” atomic orbitals cannot explain the different shapes observed in the molecules.

In 1931, L. Pauling proposed that the different atomic orbitals in the valence shell of the same atom combine or mix with each other resulting in more stable set of orbitals called hybridized orbitals. This process is known as *hybridization*.

Mathematically, the wave functions of the electrons in the orbitals of an atom are combined to give sets of equivalent wave functions called hybridized atomic orbitals. *Hybridization* is a simple mathematical

process used for modifying electron densities, to describe bonding geometries and electron densities in more complex molecules. The driving force for hybridization is the formation of a bonding geometry with the lowest net potential energy, which is accessible by energetically feasible means.

Hybridization results in a set of atomic orbitals which have equal energies (degenerate) and are intermediate between those of the basic orbitals used to construct them. These hybridized atomic orbitals can overlap more effectively with the atomic orbitals of other atoms in the molecule, thus providing an overall molecular structure which has stronger bonds and lower energy. The other inner atomic orbitals which are not used in constructing the hybrid orbitals remain unaffected by the hybridization process. The important characteristics of hybridization are:

1. The number of hybridized orbitals formed is equal to the number of atomic orbitals that get hybridized.
2. The hybridized orbitals are always equivalent in energy and shape.
3. The atomic orbitals involved in hybridization can be empty, half-filled or completely filled.
4. The hybridized orbitals have two lobes, one larger and one smaller; larger lobes are more effective in overlapping with other atomic orbitals and forming stable bonds. Smaller lobes are generally not shown since they are close to nucleus and do not effectively participate in bond formation.
5. The hybridized orbitals are directed in certain directions in space which will have stable arrangements. The type of hybridization gives the geometry of the molecule.
6. Hybridized orbitals are usually involved only in σ bonds; π bonds involve the overlap of unhybridized orbitals.
7. Hybridization is not involved in isolated atoms, but only involved in covalent bond formation with other atoms.

However, it should be remembered that *hybridization is not a physical phenomenon*; it is merely a *mathematical operation* that combines the atomic orbitals in such a way that the new (hybrid) orbitals possess the geometric properties, etc., that are reasonably consistent with observations in a wide range (but not in all) of molecules. For example, the atomic orbitals of *s*, *p* and *d* types hybridize to give sp , sp^2 , sp^3 , sp^3d , sp^3d^2 type of hybridized atomic orbitals. The atomic orbitals from the same atom combine to produce hybrid orbitals which can overlap more effectively with orbitals from other atoms, thus producing strong bonds. Hence, the atomic (or hybrid) orbitals are thought to remain even when the atom is chemically bonded in a molecule.

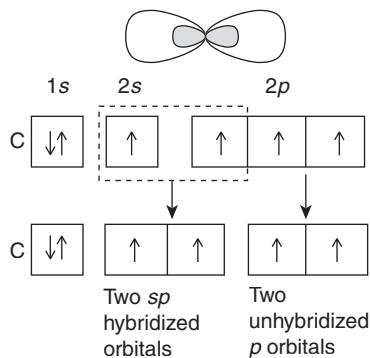
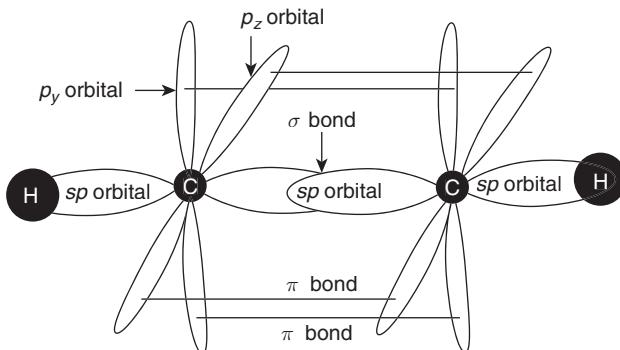
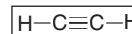
sp Hybridization

The hybridization of one *s* orbital and one *p* orbital on a central atom gives rise to two *sp* orbitals. The two hybridized *sp* orbitals, are in a linear arrangement, that is, 180° apart as shown in Figure 1.

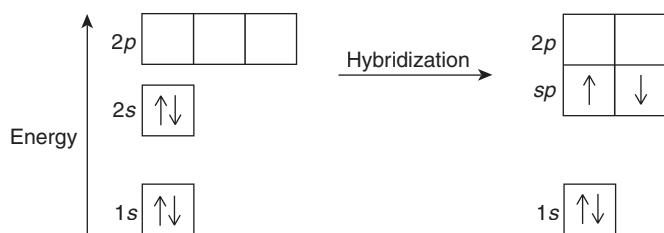
An example of *sp* hybridization is found in C_2H_2 (acetylene) and other alkynes with triple bonds. In this, the $2s$ orbital of each carbon atom mixes with only one of the three *p* orbitals, resulting in two *sp* orbitals while the other two *p* orbitals remain unchanged. The chemical bonding in acetylene then consists of the following:

1. Overlap between *sp*-*sp* hybridized orbital of the two carbon atoms forming a σ bond.
2. Lateral overlap of the two unhybridized *p* orbitals on one carbon atom with the respective *p* orbitals of the second carbon atom forming two π bonds.
3. Each carbon also forms a σ bond with a hydrogen by the overlap of its *sp* hybridized orbital with the *s* orbital of hydrogen: *s*-*sp* overlap at 180° .

The bonding in acetylene resulting from the overlap of orbitals is depicted in Figure 2.

Figure 1 *sp* hybridization.Figure 2 Bonding in $\text{CH}\equiv\text{CH}$.

Linear shape in molecules is basically due to *sp* type of hybridization. Another example of *sp* hybridization is BeH_2 molecule. The valence orbitals in Be, namely, $2s$, $2p$ undergo *sp* hybridization to form two hybridized *sp* orbitals. The *overlap* between the hydrogen $1s$ orbitals and the two *sp*-hybrid orbitals of the beryllium constitutes the two Be–H “bonds” in this molecule (Figure 3).

Figure 3 Bonding in BeH_2 .

sp^2 Hybridization

The hybridization of one s orbital and two p orbitals of a central atom gives rise to three sp^2 orbitals (Figure 4). The three sp^2 hybridized orbitals are trigonal and planar, 120° apart.

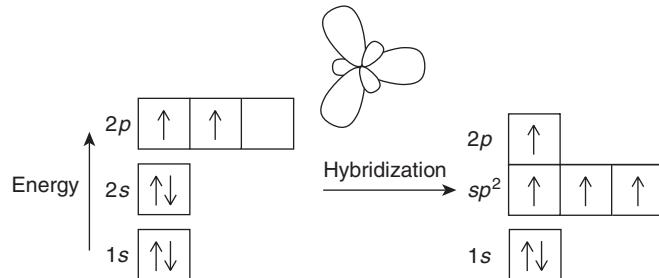


Figure 4 sp^2 hybridization of carbon in C_2H_4 .

For example, in ethene (C_2H_4), each carbon atom is sp^2 hybridized. Six sp^2 orbitals are generated (three from each carbon atom). One sp^2 orbital from each carbon atom overlaps with the other to form a σ bond between carbon atoms. Remaining two sp^2 orbitals of each carbon atom overlap with $1s$ orbitals of the two hydrogen atoms to produce four σ bonds. Unhybridized p_z orbital of each carbon atom forms a π bond by the parallel overlapping between two carbon atoms. Geometry of ethene molecule is trigonal in which bonds are 120° apart (Figure 5).

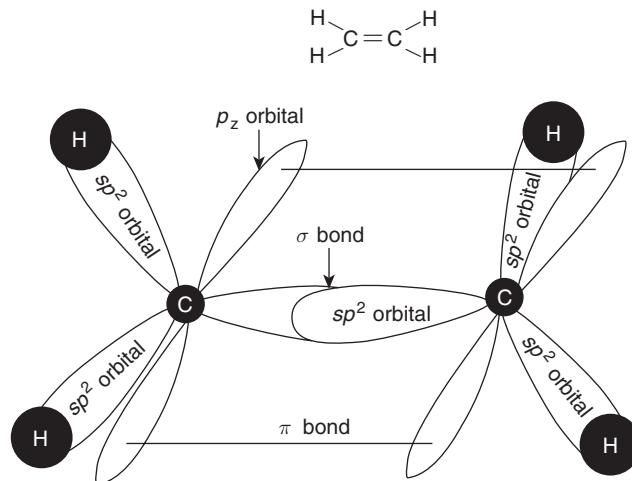
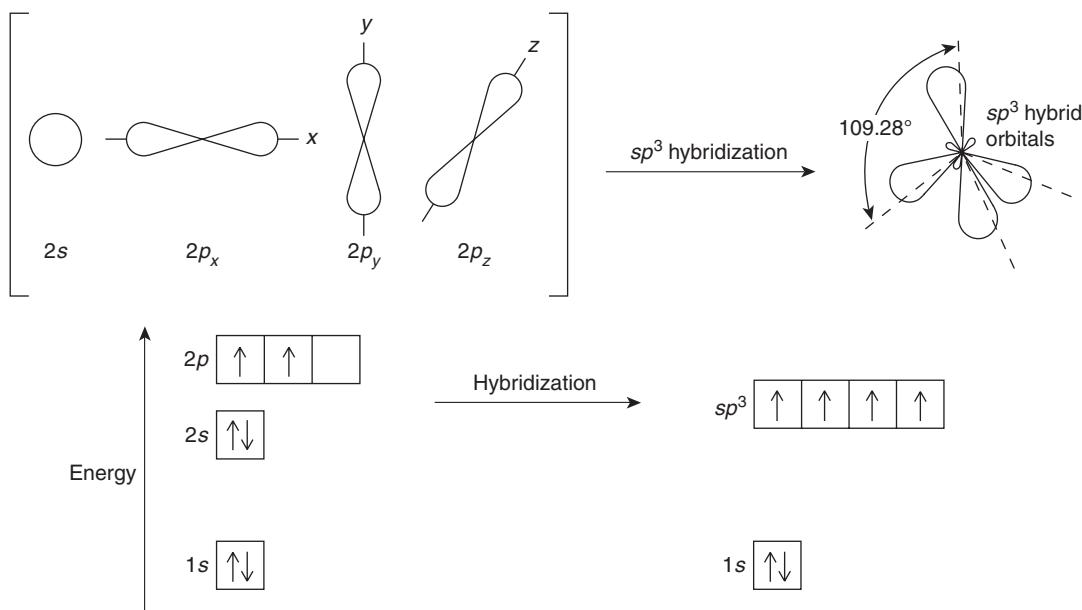


Figure 5 Bonding in $CH_2=CH_2$.

Other examples where sp^2 hybridization occurs are BF_3 , CO_3^{2-} , and NO_3^- .

sp^3 Hybridization

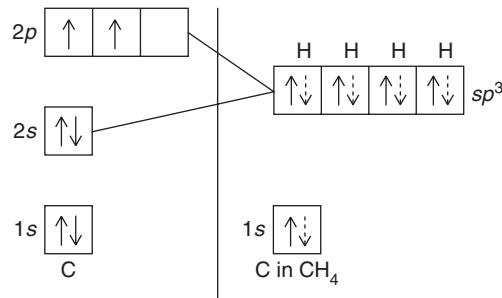
Mixing one s and all three p atomic orbitals produces a set of four equivalent sp^3 hybridized atomic orbitals. The four sp^3 hybrid orbitals having 75% p -character and 25% s -character point towards the

Figure 6 sp^3 hybridization.

vertices of a tetrahedron. Placement of the four orbitals in tetrahedral geometry provides the maximum separation between the electron pairs and minimizes electronic repulsion.

When sp^3 hybridized orbitals are used by the central atom in the formation of molecule, the molecule acquires the shape of a tetrahedron (Figure 6).

An important example of this bond type is methane, CH_4 . In the free carbon atom, there are two unpaired electrons in separate $2p$ orbitals. The single $2s$, and the three $2p$ orbitals of carbon mix into four sp^3 hybrid orbitals which are chemically and geometrically identical. The four sp^3 orbitals of carbon atom overlap with $1s$ orbitals of four hydrogen bonds to produce four σ bonds (Figure 7).

Figure 7 Bonding in CH_4 .

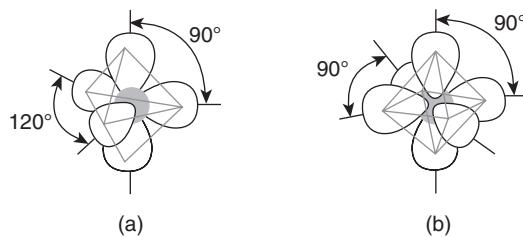


Figure 8 (a) Trigonal bipyramidal sp^3d hybridized orbitals; (b) octahedral sp^3d^2 hybridized orbitals.

Similarly, hybridization of one s , three p and one d atomic orbitals produce five sp^3d hybrid orbitals, which are trigonal bipyramidal in shape. Hybridization of one s , three p and two d atomic orbitals produces six sp^3d^2 hybridized orbitals which are octahedral-shaped (Figure 8).

For example, phosphorus in PCl_5 undergoes sp^3d hybridization and sulphur in SF_6 has sp^3d^2 hybridization (Figure 9).

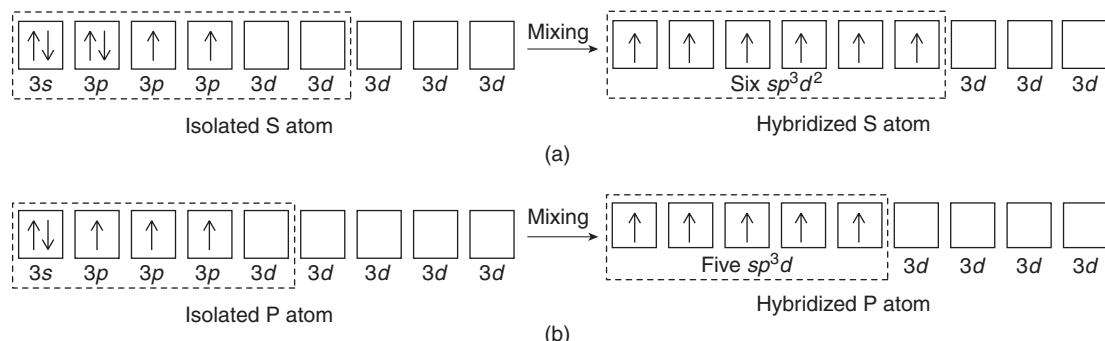


Figure 9 Hybridization of (a) sulphur atom in SF_6 and (b) phosphorus atom in PCl_5 .

Lone Pair in Hybrid Orbitals

In the ammonia molecule, the nitrogen atom ($1s^22s^22p^3$) has three unpaired p electrons, but by mixing the $2s$ and $3p$ orbitals, four sp^3 hybrid orbitals are obtained with five outer electrons. Three of the four sp^3 hybrid orbitals with one electron each form shared electron bonds with hydrogen, resulting in ammonia, NH_3 . The fourth of the sp^3 hybrid orbitals contains the two remaining outer shell electrons which form a non-bonding lone pair. In acidic solutions, these can coordinate with a hydrogen ion, forming the ammonium ion NH_4^+ . Although no bonds are formed by the lone pair in NH_3 , these electrons give rise to a charge cloud that takes up space just like any other orbital.

In the water molecule, the oxygen atom ($1s^22s^22p^4$) forms four sp^3 orbitals. Two of these are occupied by the two lone pairs on the oxygen atom, while the other two unpaired electrons are used for bonding (Figure 10).

The observed H—O—H bond angle in water (104.5°) and H—N—H bond angle in NH_3 (107.8°) are less than the tetrahedral angle (109.5°); because the non-bonding electrons tend to remain closer to the

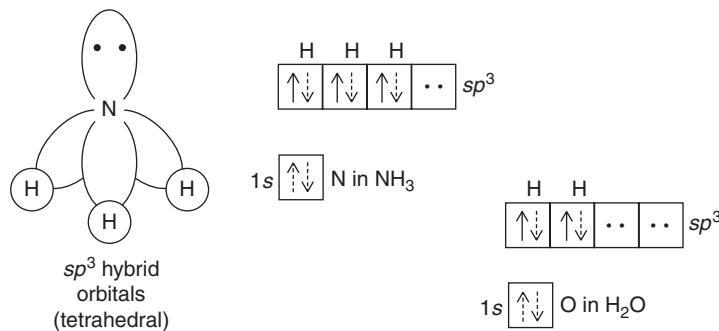


Figure 10 Hybridization in NH₃ and water.

central atom and exert greater repulsion on the other orbitals, thus pushing the bonding orbitals closer together.

Concept Check

- Who proposed the valence bond (VB) theory? What are the basic postulates of VB theory?
- Distinguish between σ and π bonds.
- What are the conditions to be satisfied by atomic orbitals to participate in hybridization?
- Explain the hybridization involved and predict the shape in the molecules: (a) XeF₂, (b) BCl₃ and (c) CCl₄.

1.6 Molecular Orbital Theory

Qualitative molecular orbital (MO) theory was introduced by Robert S. Mulliken and Friedrich Hund and a mathematical description was provided by Douglas Hartree and Vladimir Fock in 1930.

The molecular orbital theory proposes that all the atomic orbitals of the atoms involved in the covalent bond, combine to form new orbitals known as molecular orbitals which are associated with the molecule as a whole; while the valence bond theory considers only the valence electrons of atoms taking part in bonding and the inner atomic orbitals are left undisturbed. Two atomic orbitals of correct symmetry interact to form two molecular orbitals, while orbitals of incorrect symmetry do not overlap. The two molecular orbitals are formed by “addition” and “subtraction” of the wave function of the atomic orbitals. When the overlap occurs in the region where both the wave functions have the same sign, constructive interaction takes place and bonding molecular orbital is formed. If the overlap occurs in the region where the wave functions have opposite sign, destructive interaction takes place resulting in antibonding orbitals.

These molecular orbitals are quantized and assigned the symbols σ , π , δ , ϕ , ... analogous to the atomic orbitals s , p , d , f , When the interaction occurs along the line joining the two nuclei, the resulting molecular orbital is called σ . When the overlap occurs in the regions directly above and below the line joining the nuclei, π molecular orbitals are obtained. The δ molecular orbitals are formed when the interaction occurs in all the four regions, that is, above, below and on both sides of line connecting the nuclei. The electrons of the original atomic orbitals of the bonding atoms then fill the molecular orbitals. The molecular orbital theory is based on the following assumptions:

1. When two atoms approach each other, their atomic orbitals lose their identity and mutually overlap to form new orbitals called molecular orbitals.
 2. The molecular orbitals are polycentric and are associated with the nuclei of all the atoms constituting the molecule.
 3. Only atomic orbitals of about the same energy and same symmetry interact significantly.
 4. The total number of molecular orbitals produced is always equal to the total number of atomic orbitals contributed by the atoms that have combined.
 5. When two atomic orbitals overlap, they interact to form two molecular orbitals, in the following two ways:
 - When the atomic orbitals overlap in-phase, it leads to an increase in the intensity of the negative charge in the region of overlap; molecular orbital formed has lower potential energy than the separate atomic orbitals and is called a *bonding molecular orbital*.
 - When the atomic orbitals overlap out-of-phase, it leads to a decrease in the intensity of the negative charge between the nuclei and leads to higher potential energy; molecular orbital of this type is called *antibonding molecular orbitals*. Electrons in this type of molecular orbital destabilize the bond between atoms.
- The amount of stabilization of the bonding orbital equals the amount of destabilization of the antibonding orbital.
6. Electrons of the combining atoms are then assigned to these molecular orbitals. Each molecular orbital can accommodate a maximum of two electrons of successively higher energy according to the Pauli's exclusion principle and Hund's rule of maximum multiplicity.

Linear Combination of Atomic Orbitals

One common mathematical approximation to generate molecular orbitals for some small diatomic molecules is called the linear combination of atomic orbitals (LCAO) approach. Consider two atoms A and B which have atomic orbitals described by the wave functions ψ_A and ψ_B . When the electron clouds of these two atoms overlap as the atoms approach, the wave function for the molecule can be obtained by a linear combination of the atomic orbitals ψ_A and ψ_B .

The atomic orbitals ψ_A and ψ_B combine to give rise to a pair of molecular orbitals ψ_g and ψ_u . The function ψ_g corresponds to increased electron density in between the nuclei due to in-phase overlap and is therefore a bonding molecular orbital. [$\psi_g = \psi_A + \psi_B$]. It is lower in energy than the original atomic orbitals. Function ψ_u corresponds to out-of-phase overlap and hence corresponds to minimized electron density in between the nuclei. This is an antibonding molecular orbital which is higher in energy [$\psi_u = \psi_A - \psi_B$].

s – s Combinations of Orbitals

Suppose the atoms A and B are hydrogen atoms; then the wave functions $\psi_{(A)}$ and $\psi_{(B)}$ describe the 1s atomic orbitals on the two atoms. Two combinations of the wave functions $\psi_{(A)}$ and $\psi_{(B)}$ are possible (Figure 11):

1. Where the signs of the two wave functions are the same.
2. Where the signs of the two wave functions are different.

(If one of the wave functions $\psi_{(A)}$ is arbitrarily assigned a +ve sign, the other may be either +ve or -ve.) Wave functions which have the same sign may be regarded as waves that are in phase, which when combined add up to give a larger resultant wave. Similarly wave functions of different signs correspond

to waves that are completely out of phase and which cancel each other by destructive interference. (The signs + and – refer to signs of the wave functions, which determine their symmetry, and have nothing to do with electrical charges.) The two combinations are:

$$\psi_{(g)} = N\{\psi_{(A)} + \psi_{(B)}\}$$

and

$$\psi_{(u)} = N\{\psi_{(A)} + [-\psi_{(B)}]\} \equiv N\{\psi_{(A)} - \psi_{(B)}\}$$

The latter equation should be regarded as the summation of the wave functions and *not* as the mathematical difference between them.

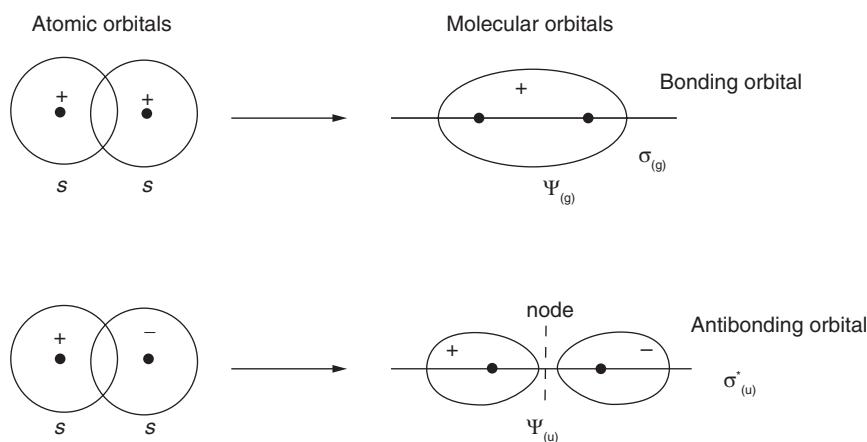


Figure 11 $s-s$ Combinations of atomic orbitals.

When a pair of atomic orbitals $\psi_{(A)}$ and $\psi_{(B)}$ combine, they give rise to a pair of molecular orbitals $\psi_{(g)}$ and $\psi_{(u)}$. The number of molecular orbitals produced must always be equal to the number of atomic orbitals involved. The function $\psi_{(g)}$ leads to increased electron density in between the nuclei, and is therefore a bonding molecular orbital. It is lower in energy than the original atomic orbitals. Conversely $\psi_{(u)}$ results in two lobes of opposite sign cancelling and hence giving zero electron density in between the nuclei. This is an antibonding molecular orbital which is higher in energy (Figure 12).

The molecular orbital wave functions are designated $\psi_{(g)}$ and $\psi_{(u)}$; g stands for *gerade* (even) and u for *ungerade* (odd). g and u refer to the symmetry of the orbital about its centre. If the sign of the wave function is unchanged when the orbital is reflected about its centre (i.e., x, y and z are replaced by $-x$, $-y$ and $-z$) the orbital is *gerade*. An alternative method for determining the symmetry of the molecular orbital is to rotate the orbital about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remains the same, the orbital is *gerade*, and if the sign changes, the orbital is *ungerade*.

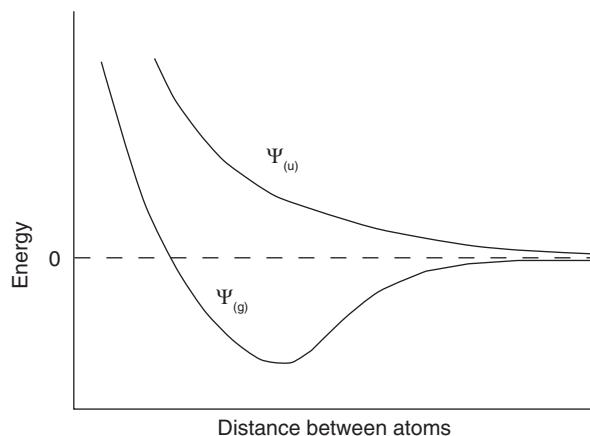


Figure 12 Energy of $\psi_{(g)}$ and $\psi_{(u)}$ molecular orbitals.

The energy of the bonding molecular orbital $\psi_{(g)}$ passes through a minimum (Figure 12) and the distance between the atoms at this point corresponds to the internuclear distance between the atoms when they form a bond. Consider the energy levels of the two $1s$ atomic orbitals, and of the bonding $\psi_{(g)}$ and antibonding $\psi_{(u)}$ orbitals (Figure 13).

The energy of the bonding molecular orbital is lower than that of the atomic orbital by an amount Δ . This is known as the *stabilization energy*.

Similarly, the energy of the antibonding molecular orbital is increased by Δ . Atomic orbitals may hold up to two electrons (provided that they have opposite spins) and the same applies to molecular orbitals. In the case of two hydrogen atoms combining, there are two electrons to be considered: one from the $1s$ orbital of atom A and one from the $1s$ orbital of atom B. When combined, these two electrons both occupy the bonding molecular orbital $\psi_{(g)}$. This results in a saving of energy of 2Δ , which corresponds to the bond energy: It is only because the system is stabilized in this way that a bond is formed.

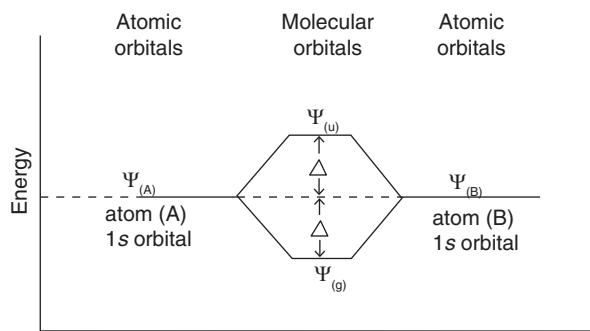


Figure 13 Energy levels of $s-s$ atomic and molecular orbitals.

The linear combination of atomic orbitals (LCAO) and their subtraction give rise to equal number of similar orbitals. Some of them are more stable, less energetic as compared to the atomic orbitals and are called **bonding orbitals**. Some of them are less stable, more energetic than atomic orbitals and are called **antibonding orbitals**. The electrons are accommodated in the resulting molecular orbitals following Aufbau principle, Hund's rule and Pauli's exclusion principle.

Molecular Levels and $\sigma-\sigma^*$ Electronic Transitions

No two molecular orbitals have all the symmetry properties same. When the atoms are in ground state, the electrons occupy the lowest possible energy level. On excitation, the promotion of an electron from bonding σ molecular orbital to antibonding σ^* molecular bond takes place and is known as $\sigma-\sigma^*$ transition. The electronic configuration of a σ bond in ground state configuration of σ molecular bond and in the excited state after $\sigma-\sigma^*$ transition is shown in Figure 14.

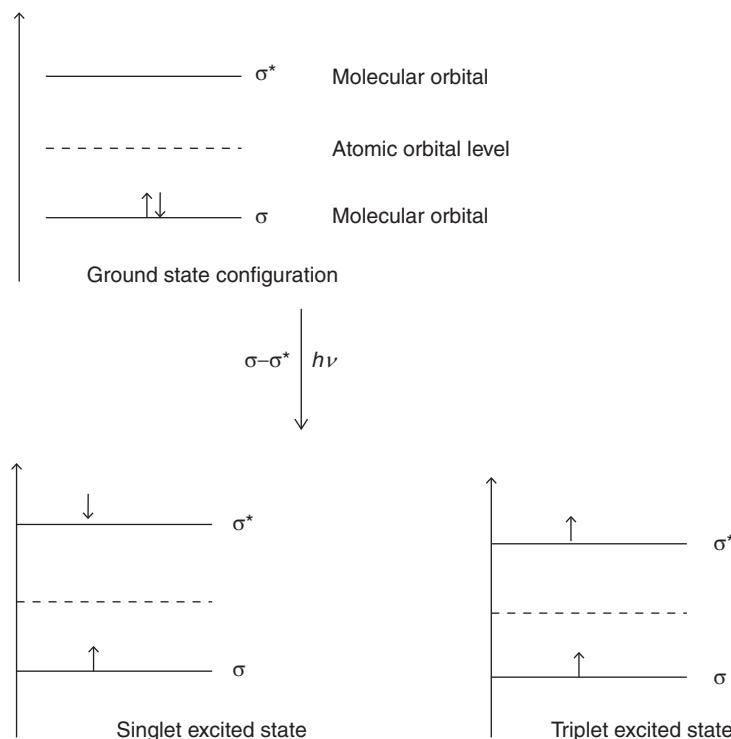


Figure 14 Electrons in the ground state of σ bond and in excited states after undergoing $\sigma-\sigma^*$ transition.

The $\sigma-\sigma^*$ transition in C–C single bond of ethane occurs in the normal UV region occurs at 154 nm of UV beam. It is invisible in the normal UV which generally starts at 200–400 nm range.

s – p Combination of Orbitals

An s orbital may combine with a p orbital provided that the lobes of the p orbital are pointing along the axis joining the nuclei. When the lobes which overlap have the same sign this results in a bonding

MO with an increased electron density between the nuclei. When the overlapping lobes have opposite signs this gives an antibonding MO with a reduced electron density in between the nuclei (Figure 15).

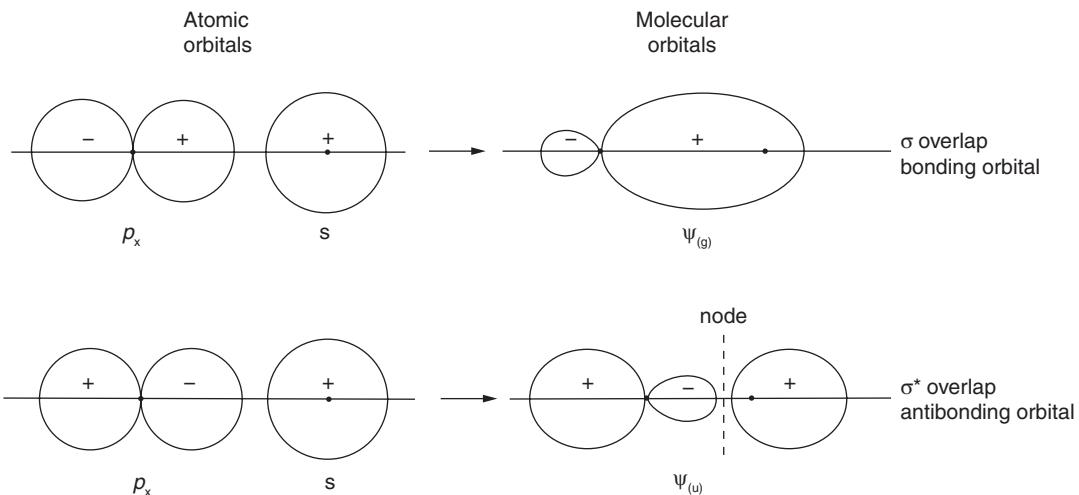


Figure 15 $s - p$ combination of atomic orbitals.

$p - p$ Combinations of Orbitals

Consider first the combination of two p orbitals which both have lobes pointing along the axis joining the nuclei. Both a bonding MO and an antibonding MO are produced (Figure 16).

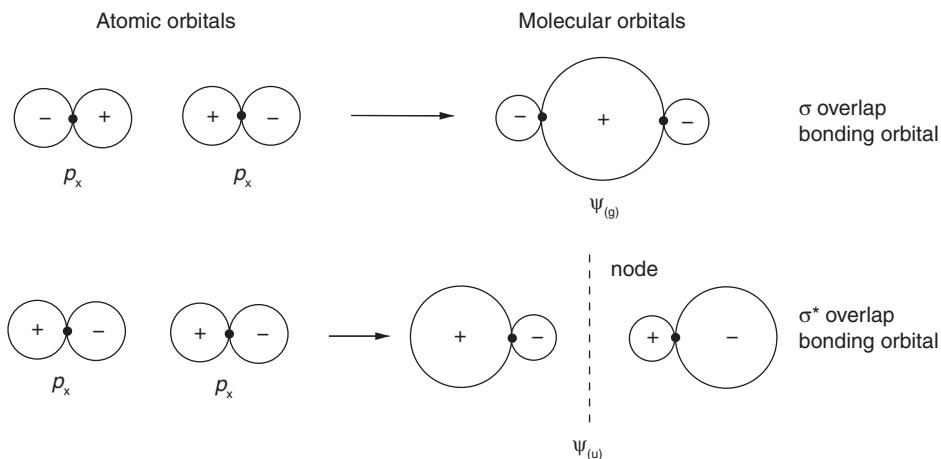


Figure 16 $p - p$ combination of atomic orbitals.

Next consider the combination of two p orbitals which both have lobes perpendicular to the axis joining the nuclei. Lateral overlap of orbitals will occur, resulting in π bonding and π^* antibonding MOs being produced (Figure 17).

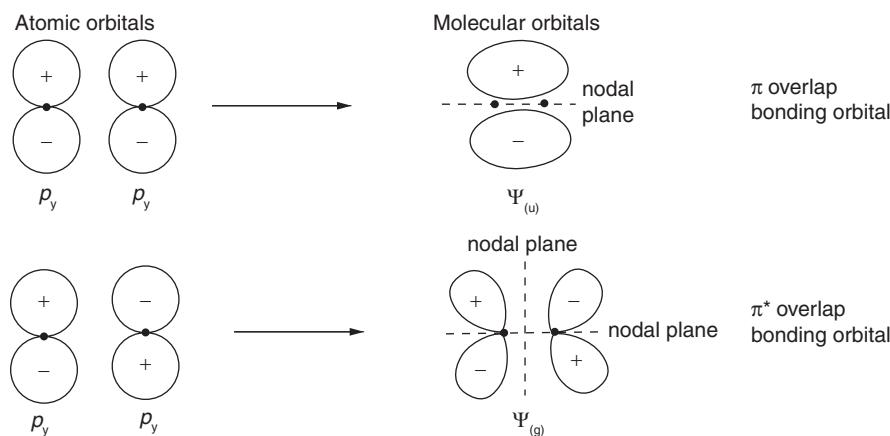


Figure 17 $p - p$ combinations giving π bonding.

There are three points of difference between these π molecular orbitals and the σ orbitals described previously:

1. For π overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei, whilst for σ overlap the lobes point along the line joining the two nuclei.
2. For π molecular orbitals, ψ is zero along the internuclear line and consequently the electron density ψ^2 is also zero. This is in contrast to σ orbitals.
3. The symmetry of π molecular orbitals is different from that shown by σ orbitals. If the bonding π MO is rotated about the internuclear line a change in the sign of the lobe occurs. The π bonding orbitals are therefore *ungerade*, whereas all σ bonding MOs are *gerade*. Conversely the antibonding π MO is *gerade* whilst all σ antibonding MOs are *ungerade*.

Pi bonding is important in many organic compounds such as ethene (where there is one σ bond and one π bond between the two carbon atoms), ethyne (one σ and two π), and benzene, and also in a number of inorganic compounds such as CO_2 and CN^- .

Molecular Levels and $\pi - \pi^*$ Electronic Transition

When the atoms are in ground state, the electrons occupy the lowest possible energy level. On excitation, the promotion of an electron from bonding π molecular orbital to antibonding π^* molecular bond takes place and is known as $\pi - \pi^*$ transition. The electronic configuration in ground state configuration of π molecular bond and in the excited state after $\pi - \pi^*$ transition is shown in Figure 18.

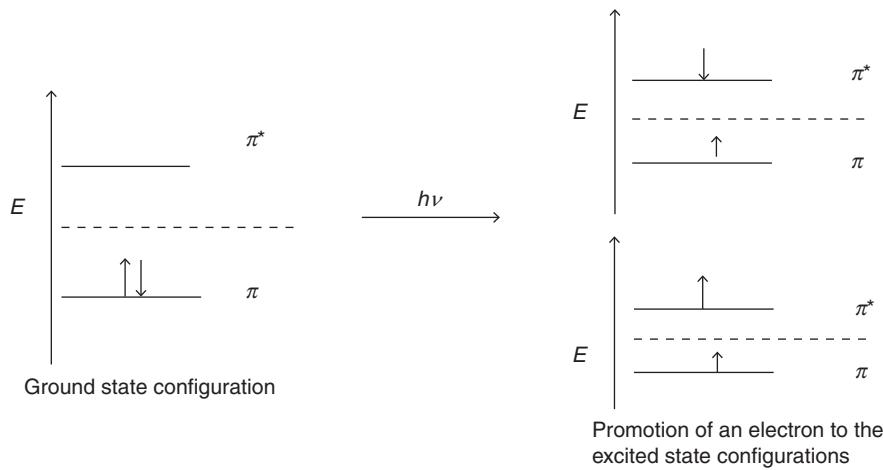


Figure 18 Electrons in the ground of π bond and in excited state after undergoing $\pi-\pi^*$ transition.

The $\pi-\pi^*$ transition in C=C bond of ethylene occurs at 180 nm and the $\pi-\pi^*$ transition in C=O bond for formaldehyde at 185 nm. Ethylene has both C–C σ bond and C–C π bond, so the two transitions for the electrons of the molecule in ground to excited state can be depicted as shown in Figure 19.

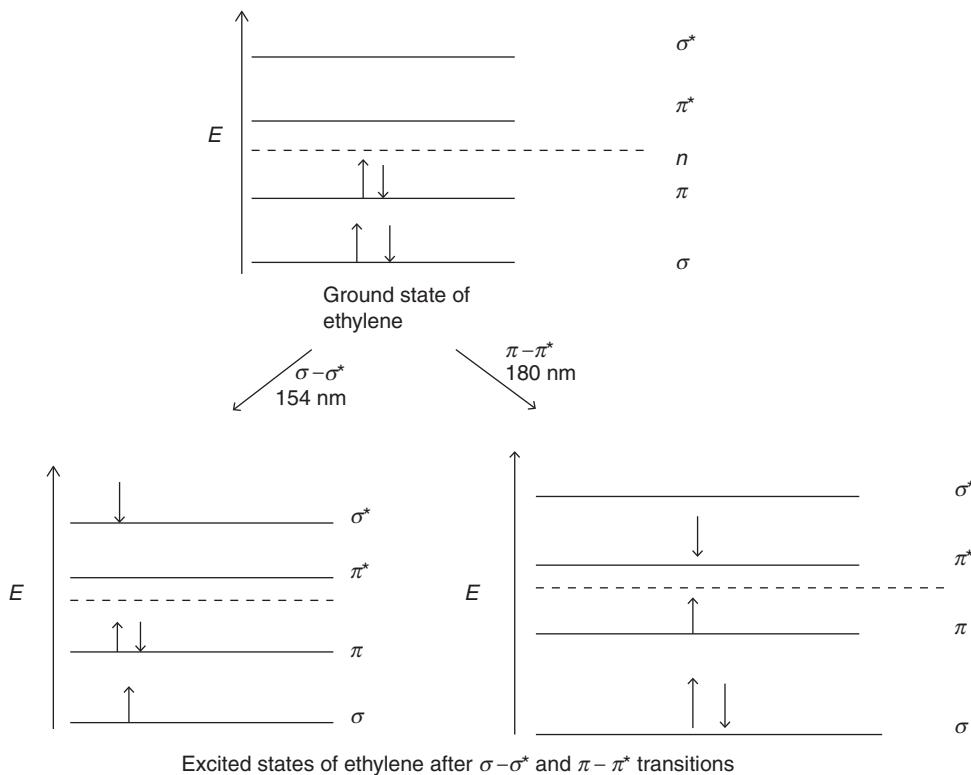


Figure 19 The ground state configuration for ethylene and the excited state after $\sigma-\sigma^*$ and $\pi-\pi^*$ transitions.

The molecular orbitals formed by the linear combinations of different atomic orbitals can thus be represented as shown in Table 1.

Table 1 Atomic and molecular orbitals

Atomic Orbitals	Molecular Orbitals
$1s_A + 1s_B$	$\sigma 1s$
$1s_A - 1s_B$	$\sigma^* 1s$
$2s_A + 2s_B$	$\sigma 2s$
$2s_A - 2s_B$	$\sigma^* 2s$
$2px_A + 2px_B$	$\sigma 2p_x$
$2px_A - 2px_B$	$\sigma^* 2p_x$
$2py_A + 2py_B$	$\pi 2p_y$
$2py_A - 2py_B$	$\pi^* 2p_y$
$2pz_A + 2pz_B$	$\pi 2p_z$
$2pz_A - 2pz_B$	$\pi^* 2p_z$

Symmetry Properties of Molecular Orbitals

We have learnt that the molecular orbital wave functions are designated as $\psi_{(g)}$ and $\psi_{(u)}$, where g stands for *gerade* (even) and u stands for *ungerade* (odd). Also, g and u refer to the symmetry of the orbital around its center.

- Center of symmetry:** If the sign of the wave function is unchanged when the orbital is reflected about its center (i.e., x, y and z are replaced by $-x$, $-y$ and $-z$) the orbital is gerade, that is, **center of symmetry** is present. In other words, if we draw a line from any point to the center and extend equal distance to the point at the opposite side and there is no change in the sign of the wave function of molecular orbital, it is gerade (g) and otherwise it is ungerade (u). Some lines of σ molecular orbitals are referred to as σ_g and σ^* as σ_u^* .
- σ or Mirror plane symmetry:** If a mirror is placed on the internuclear axis and the two resulting parts bear mirror image relationship, the molecular orbital is symmetric otherwise antisymmetric. π orbital is symmetric with respect to mirror plane symmetry and π^* molecular orbital is antisymmetric with respect to σ .
- C_2 symmetry:** If the rotation of the molecular axis by 180° ($360^\circ/2$) about this internuclear axis results in identical structure, it is symmetric otherwise antisymmetric. σ molecular orbitals possess C_2 symmetry and π molecular orbitals are antisymmetric with respect to C_2 .

The symmetry properties of different molecular orbitals are listed in Table 2.

Table 2 Symmetry elements for molecular orbitals

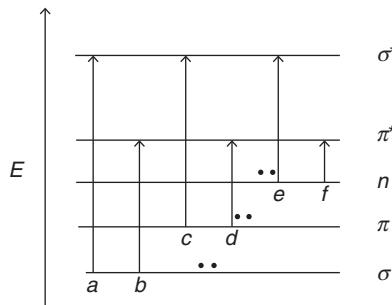
Molecular Orbital	Mirror Plane or σ Symmetry	C_2 Symmetry	Inversing Symmetry
σ	S	S	G
σ^*	A	S	U
π	S	A	U
π^*	A	A	G

Selection Rules for Transitions

We observe from Figure 19 that the transitions $\sigma - \pi^*$ and $\pi - \sigma^*$ do not take place. This can be explained on the basis of selection rules for electronic transition between two molecular orbitals. Electronic transitions between molecular orbitals of the same inversion symmetry is prohibited or forbidden, that is,

$$\begin{array}{ll} g \not\rightarrow g & u \not\rightarrow u \text{ forbidden} \\ g \rightarrow u & u \rightarrow g \text{ allowed} \end{array}$$

In a system with σ , π and n electrons (e.g., carbonyl compounds) six electronic transitions are possible. These are listed as follows and shown in Figure 20. Of the six possible transitions, only four types are allowed according to the selection rules.

**Figure 20** Electronic transitions in system with σ , π and n orbitals.

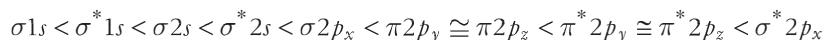
1. $a = \sigma - \sigma^*$ transition (highest energy transition)
2. $b = \sigma - \pi^*$ transition ($g \rightarrow u$, so forbidden)
3. $c = \pi - \sigma^*$ transition ($u \rightarrow u$, so forbidden)
4. $d = \pi - \pi^*$ transition (lower energy transition)
5. $e = n - \sigma^*$ transition (higher energy transition)
6. $f = n - \pi^*$ transition (lowest energy transition)

The distance (energy gap) is more between π^* and σ^* molecular orbitals as compared to distance (energy gap between n and π^* molecular orbitals. Therefore, energy of $n - \sigma^*$ transition is higher than that of $\pi - \pi^*$ transition. The energy required for the transitions is in the order:



Energy Levels and Filling of Molecular Orbitals

The order of the energy levels of these molecular orbitals is given as:



These molecular orbitals are then filled with the total number of electrons (not just the valence electrons) counted by taking the atomic number of both the atoms of the covalent bond. The electrons are filled from the lowest energy orbital in the order of increasing energy and orbitals of equal energy are half-filled with parallel spin before they begin to pair up. Molecular orbital theory also predicts the bond order and hence the qualitative bond strength between covalently bonded atoms, which is given by:

$$\text{Bond order} = \frac{1}{2}(N_b - N_a)$$

where N_b and N_a are the number of electrons in the bonding and antibonding molecular orbitals.

Furthermore, the MO theory has been very useful and successful in predicting the magnetic behavior of molecules. In filling up the molecular orbitals, if a molecule contains no unpaired electrons then it is diamagnetic and if molecules contain one or more unpaired electrons then it is paramagnetic.

Molecular Orbital Diagram

The diagram showing the relative energy levels of the combining atomic orbitals, the molecular orbitals formed from them and the order of filling up of the electrons is called the molecular orbital (MO) diagram. The orbitals of the individual combining atoms are written on either side of the diagram as horizontal lines at heights denoting their relative energies. The electrons in each atomic orbital are represented by arrows. The molecular orbitals of the molecule are represented in the middle of the diagram. Dashed lines connect the parent atomic orbitals with the molecular orbitals. For example the MO diagram for the simplest molecule, H_2 , is shown in Figure 21.

The two hydrogen atoms with one electron each in $1s$ atomic orbitals combine to form $\sigma 1s$ (bonding) $\sigma^* 1s$ (antibonding) molecular orbitals; the two electrons fill a single bonding $\sigma 1s$ molecular orbital. The configuration of the H_2 molecule is written as $\sigma 1s^2$. As H_2 molecule has one electron pair in its bonding orbital and none in its antibonding orbital, molecular orbital theory predicts that H_2 has a bond order of 1 $\lceil(1/2)(2 - 0) = 1\rceil$ and is diamagnetic as there are no unpaired electrons. Further applications of the molecular orbital theory to other simple diatomic molecules are discussed:

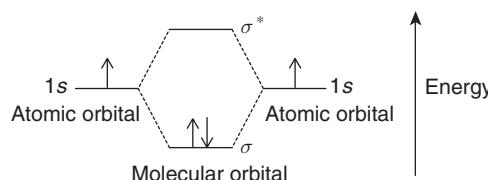
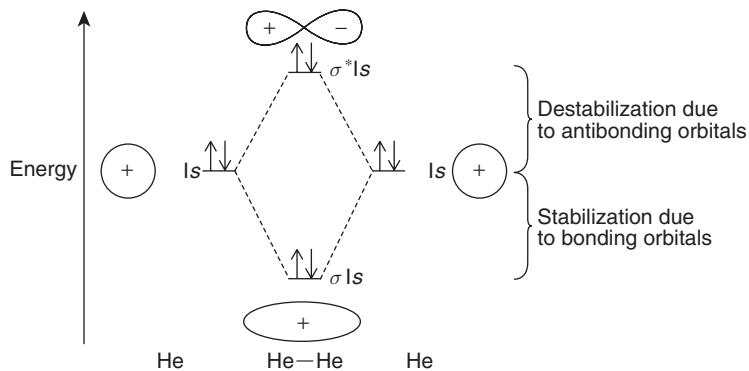


Figure 21 MO diagram of H_2 .

Homodiatomic Molecules

The possible MO diagram for He_2 molecule is shown in Figure 22.

Figure 22 MO diagram of He₂.

It can be seen from the MO diagram that the configuration of He₂ is ($\sigma 1s$)² ($\sigma^* 1s$)²; the amount of stabilization due to filling of two electrons in bonding orbital is equal to the amount of destabilization due to the two electrons in antibonding molecular orbital. Therefore, there is no net stabilization due to bonding so the He₂ molecule will not exist. The bond order calculation also shows that the bond order is zero [(1/2)(2 – 2) = 0] for the He₂ molecule. The MO theory thus gives exactly the same prediction for He₂ as is observed that helium is a noble gas and does not form covalent compounds.

Relative Energy Levels of Molecular Orbitals of Li₂ and N₂

The study of the energies of electrons in molecules revealed that the relative energy levels of molecular orbitals of Li₂ to N₂ are different from those of O₂ and F₂. The explanation for the difference comes from the consideration of mixing of atomic orbitals. Because the 2s and 2p atomic energy levels for Li to N are relatively close and have less than half-filled 2p orbitals, mixing occurs and causes the $\sigma^* 2s$ level to move down and the $\sigma 2p_x$ level to move up in energy. This process is called *sp* mixing. This effect causes the relative order of molecular orbitals to change, and a typical relative energy level diagram for Li₂, Be₂, B₂, C₂ and N₂ is shown in Figure 23.

Table 3 Electronic configuration and bond energy (kJ/mol) from Li₂ to F₂

Molecule	Electronic Configuration	Bond Energy (kJ/mol)
Li—Li	KK $\sigma 2s^2$	110
Be—Be	KK $\sigma 2s^2 \sigma^* 2s^2$	0 (does not exist)
B—B	KK $\sigma 2s^2 \sigma^* 2s^2 \pi 2p_y^1 \pi 2p_z^1$	290
C=C	KK $\sigma 2s^2 \sigma^* 2s^2 \pi 2p_y^2 \pi 2p_z^2$	602
N≡N	KK $\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2$	942
O=O	KK $\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^1 \pi^* 2p_z^1$	494
F—F	KK $\sigma 2s^2 \sigma^* 2s^2 \sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2 \pi^* 2p_y^2 \pi^* 2p_z^2$	155

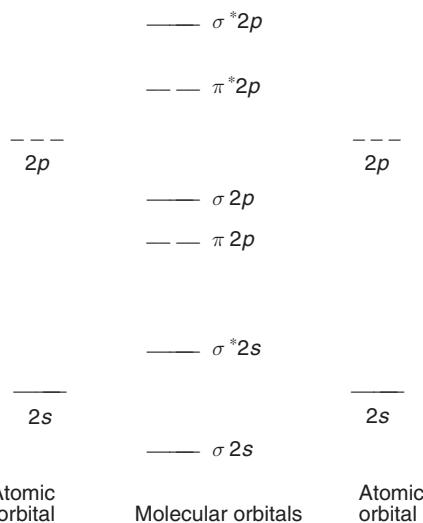


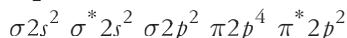
Figure 23 Relative energy levels of atomic and molecular orbitals in Li_2 to N_2 molecules.

The electronic configuration, the bond length and the bond energy of the molecules Li_2 to F_2 are given below in Table 3. KK in the electronic configuration represents the closed K shell structure ($\sigma 1s^2 \sigma^* 1s^2$). Note that B_2 and O_2 are paramagnetic due to the unpaired electrons in the molecular orbitals. Other molecules in this group are diamagnetic.

Relative Energy Levels of Molecular Orbitals of O_2 and F_2

The $2s$ and $2p$ energy levels of O and F are very far apart. The three $2p$ orbitals of each O (or F) atom can form one σ and two π bonding and their corresponding antibonding molecular orbitals. The interaction of the $2p$ orbitals for the σ bond is stronger, and the levels of σ and antibonding σ orbitals are farther apart than those of π and antibonding π orbitals. Thus, the typical relative energy level diagram of O_2 and F_2 has the following arrangement as shown in Figure 24.

The electronic configuration for O_2 is:



This electronic configuration indicates a bond order of 2, and the molecule can be represented by $\text{O}=\text{O}$. There is no net bonding from the $\sigma 2s$ orbitals, because the number of bonding electrons equals the number of antibonding electrons. The two electrons in $\pi^* 2p^2$ cancel two of the six bonding electrons ($\sigma 2p^2 \pi 2p^4$). Therefore, there are four total bonding electrons. The two electrons in the $\pi^* 2p^2$ orbitals have the same spin, and they are responsible for the paramagnetism of oxygen. The MO diagram (Figure 25) and some related properties of the molecules B_2 to F_2 (Table 4) are given as follows:

Heteronuclear Diatomic Molecules

The MO theory can also be extended to heteronuclear diatomic molecules, that is, molecules that consist of two dissimilar atoms, such as HF, CO, NO, etc. The atomic orbitals of the two different atoms involved in bonding are now at different energy levels; the atom with higher electronegativity

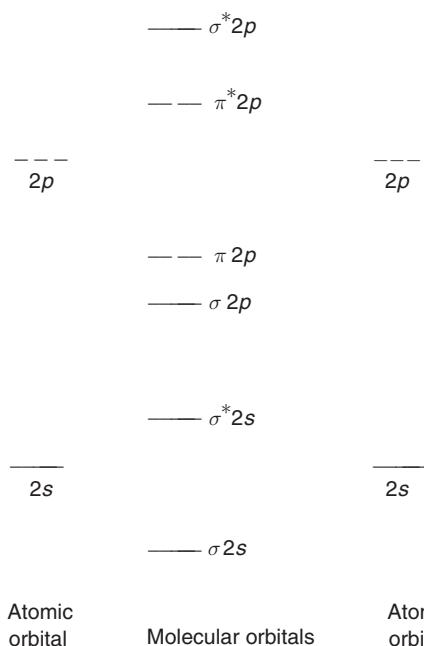


Figure 24 Relative energy levels of atomic and molecular orbitals in O_2 and F_2 molecules.

Table 4 Some properties of the molecules B_2 to F_2

Properties	B_2	C_2	N_2	O_2	F_2
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

will have its atomic orbitals at lower energy, making larger contribution to the bonding molecular orbital. The atomic orbital with the higher energy makes larger contribution to the antibonding molecular orbital. However, there is no interaction if the energy difference between orbitals is greater than 13 eV.

The electrons of the covalent bond in such molecules are no longer evenly shared between the two atoms, because it is energetically favorable for the electron pair to reside closer to one nucleus than to the other. This means that the chemical bond is polarized. For example, $H^{\delta+}-F^{\delta-}$ electron pair is located closer to the F nucleus than to the H nucleus.

	B_2	C_2	N_2	O_2	F_2
σ^*2p	—	—	—	σ^*2p	—
π^*2p	—	—	—	π^*2p	$\uparrow\uparrow$
$\sigma2p$	—	—	$\uparrow\downarrow$	$\pi2p$	$\uparrow\downarrow\downarrow\downarrow$
$\pi2p$	$\uparrow\uparrow$	$\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	$\sigma2p$	$\uparrow\downarrow$
σ^*2s	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	σ^*2s	$\uparrow\downarrow$
$\sigma2s$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\sigma2s$	$\uparrow\downarrow$

Figure 25 MO diagram of the molecules B_2 to F_2 .

The atomic orbitals in heteronuclear molecules combine together only if all the following conditions are satisfied:

1. They have the correct symmetry.
2. There is efficient overlap.
3. The orbitals are relatively close together in energy.

Heteronuclear diatomic molecules can have non-bonding orbitals, in addition to bonding and antibonding orbitals. Consider the following examples:

1. **HF molecule:** The atomic orbital energy levels are: hydrogen $1s$ (-13.61 eV), fluorine $2s$ (-40.17 eV) and $2p$ (-18.65 eV). In this case, there is no s -orbital interaction, because energy difference > 13 eV. The orbitals of $1s$ of hydrogen and $2p_x$ of fluorine can overlap to form a σ orbital due to compatible symmetry; while $1s$, $2p_y$ and $2p_z$ of fluorine have no net overlap and are non-bonding. The MO diagram is as shown in Figure 26.

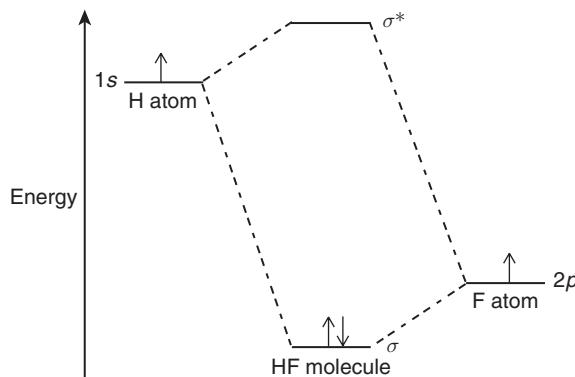


Figure 26 MO diagram of HF.

2. **Li–F molecule:** The electrons in the Li–F bond are quite close in energy to fluorine's $2p$ orbitals. The bonding molecular orbital is primarily obtained by the interaction $2s$ of lithium and $2p_x$ orbital of fluorine. The electrons in $2p_y$ and $2p_z$ orbitals on F that cannot bond with Li remain on

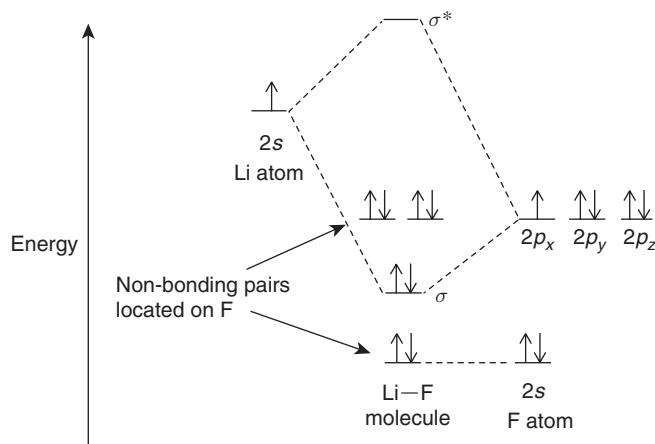


Figure 27 MO diagram of LiF.

F as lone pairs since fluorine is more electronegative than lithium. The electrons are more stable with lower energy, when they remain as lone pairs on fluorine rather than on lithium. So the MO diagram (Figure 27) predicts that the bond should be polarized towards fluorine.

The construction of correlation diagrams of other heteronuclear diatomic orbitals follows exactly the same principles as those employed for LiF. The more electronegative element's orbitals are placed lower on the correlation diagram than those of the more electropositive element.

3. **CO molecule:** The MO diagram (Figure 28) for the diatomic carbon monoxide (CO) shows that it is isoelectronic with nitrogen (N_2).

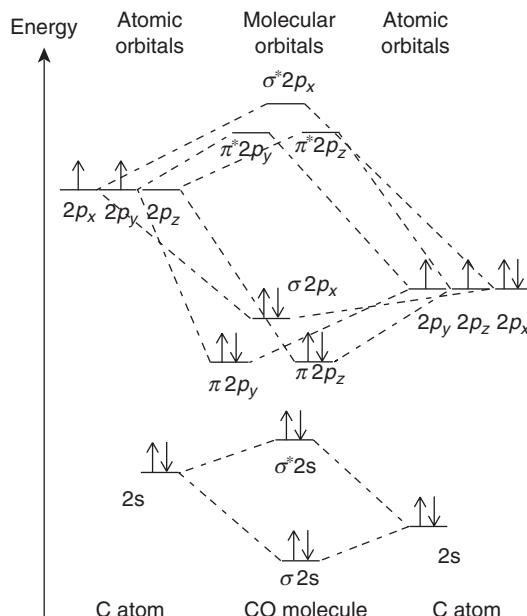


Figure 28 MO diagram of CO.

The heteronuclear diatomic ions such as cyanide ion, CN^- , and nitrosonium ion, NO^+ , are also isoelectronic with nitrogen, N_2 . The only difference in their MO diagrams lies in the relative energies of the orbitals.

Molecular Orbitals of Butadiene and Benzene

Molecular Orbitals of 1,3-Butadiene

1,3-Butadiene contains two double bonds that are conjugated. It is made up of $4sp^2$ hybridized carbon atoms, each contributing a p atomic orbital containing one electron. The central carbon atoms of 1,3-butadiene (Figure 29) are close enough for overlap to occur between the p orbitals of $\text{C}2$ and $\text{C}3$. This overlap is not as much as that between the orbitals of $\text{C}1$ and $\text{C}2$ (or those of $\text{C}3$ and $\text{C}4$). The $\text{C}2-\text{C}3$ orbital overlap, however, gives the central bond partial double-bond character and allows the four π electrons of 1,3-butadiene to be delocalized over all four atoms.

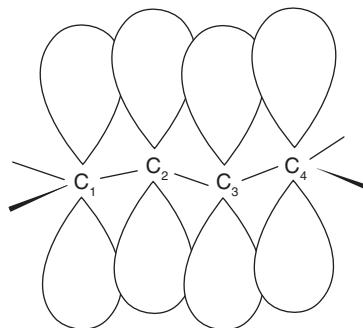


Figure 29 The p orbitals of 1,3-butadiene.

Figure 30 shows how the four p orbitals of 1,3-butadiene combine to form a set of four π molecular orbitals.

- Two of the π molecular orbitals of 1,3-butadiene are bonding molecular orbitals. In the ground state these orbitals hold the four π electrons with two spin-paired electrons in each.
- The other two π molecular orbitals are antibonding molecular orbitals. In the ground state these orbitals are unoccupied.
- An electron can be excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) when 1,3-butadiene absorbs light with a wavelength of 217 nm.
- The delocalized bonding that for 1,3-butadiene is characteristic of all conjugated polyenes.

Molecular Orbitals of Benzene

The fact that the bond angles of the carbon atoms in the benzene ring are all 120° strongly suggests that the carbon atoms are sp^2 hybridized. Based on this, if we can construct a planar six-membered ring from sp^2 carbon atoms, representations like those shown in Figures 31 (a) and 31 (b). In these models, each carbon is sp^2 hybridized and has a p orbital available for overlap with p orbitals of its neighboring carbons.

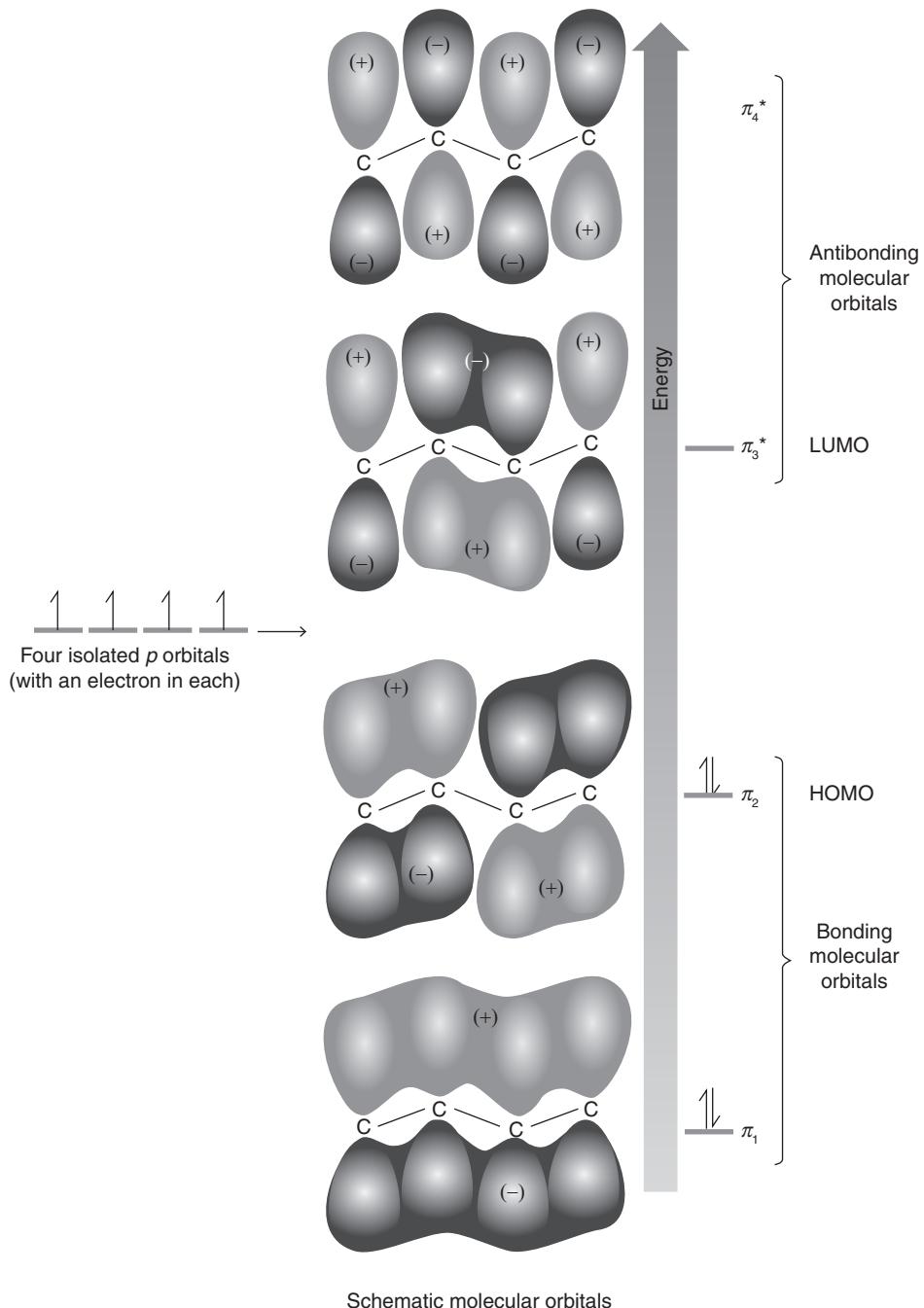


Figure 30 Formation of the π molecular orbitals of 1,3-butadiene from four isolated *p*-orbitals.

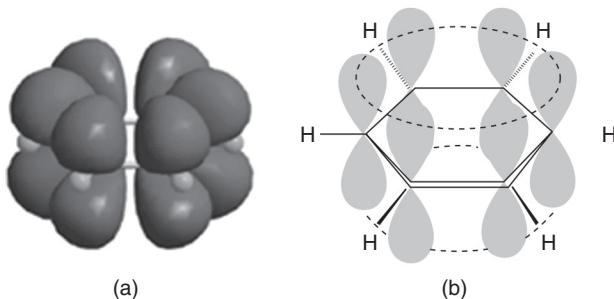


Figure 31 (a) Six sp^2 -hybridized carbon atoms joined in a ring (each carbon also bears a hydrogen atom). Each carbon has a p orbital with lobes above and below the plane of the ring. (b) A depiction of the p orbitals in (a). Overlap of the p orbitals around the ring results in a molecular orbital encompassing the top and bottom faces of the ring.

From the principles of quantum mechanics, we know that the number of molecular orbitals in a molecule is the same as the number of atomic orbitals from which they are derived, and each orbital can accommodate a maximum of two electrons if their spins are opposed.

If we consider only the p atomic orbitals contributed by the carbon atoms of benzene, there should be six π molecular orbitals. Three of the molecular orbitals have energies lower than that of an isolated p orbital; these are the bonding molecular orbitals. Three of the molecular orbitals have energies higher than that of an isolated p orbital; these are the antibonding molecular orbitals. These orbitals are shown in Figure 32.

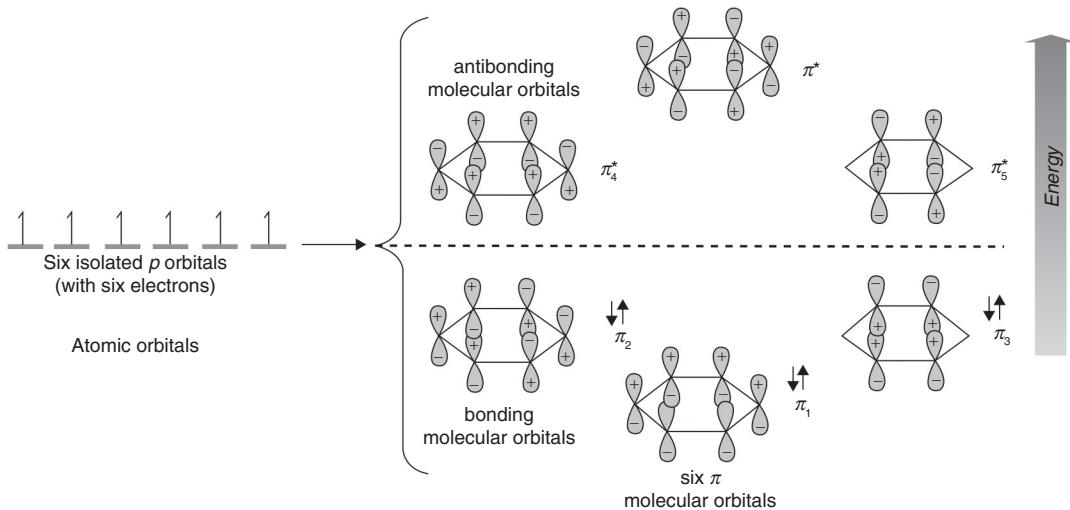


Figure 32 Six p atomic orbitals in benzene (one from each carbon atom) combine to form six π molecular orbitals.

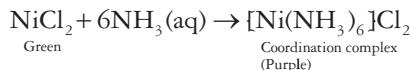
Concept Check

- What are the molecular orbitals obtained by the linear combination of the atomic orbitals $1s$, $2s$ and $2p$? Give their increasing order of energy.
- Give the molecular orbital configuration and the bond order in the molecules N_2 , F_2 , CN^- and O_2^- .
- How does molecular orbital theory account for magnetic properties of molecules?

1.7**Theories for Bonding in Coordination Compounds**

Coordination compounds are a special class of compounds in which the central metal atom or ion, is surrounded by oppositely charged ions or neutral molecules called ligands. They are also called complex compounds or simply complexes.

The properties of the complex compounds are completely different from the saturated moieties forming it. This can be exemplified by the fact that when aqueous NH_3 is added to a saturated solution of NiCl_2 , the color immediately changes from green to purple. The Ni^{2+} species almost disappear, and on evaporation, the solution yields violet crystals corresponding to the formula $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$. This newly generated species is called coordination complex and its properties are entirely different from the reactants forming it, that is, aqueous NH_3 and NiCl_2 in this case.



Four theories have been postulated for the formation of coordination compounds. These are:

1. Werner's coordination theory
2. Sidgwick theory
3. Valence bond theory
4. Crystal field theory

We will briefly discuss the first three and then crystal field theory in detail, along with formation of complexes with octahedral, tetrahedral and square planar complexes.

Werner's Coordination Theory

The first systematic study on physical, chemical, structural and behavioral aspects of coordination compounds was done by Swiss chemist, Alfred Werner in 1893. The main postulate of the theory is that the metal ion encapsulated inside the coordination complex exhibits two types of valencies: primary valency and secondary valency.

1. The *primary valency* is ionizable as well as non-directional. It corresponds to the *oxidation state* in the modern-day terminology. Normally, if a complex ion exhibits positive charge, the primary valency corresponds to the number of charges present on the complex ion and this charge is balanced by same number of negative ions. Thus, primary valency can also be defined by the number of anions neutralizing the charge on the complex ion.
2. The *secondary valency* is directional, non-ionizable and corresponds to *coordination number* in the modern-day terminology. It equals the total number of ligands coordinately bonded to the central metal ion inside the coordination sphere. Every metal ion has fixed number of secondary valencies, which are directed towards fixed positions in space around the central metal atom. This results in a definite geometry and stereochemistry of the complex.

Based on this theory, Werner deduced and explained the structure of various cobalt amines.

Sidgwick Coordination Theory

Werner's coordination theory was further modified by Sidgwick using the Lewis concept of electron pair bond. It was based on the observation that each molecule or ion that coordinates to the central metal atom or ion has at least one unshared electron pair available for bond formation. The *donor* atom (ligand) donates the electron pair, while the *acceptor* atom (central metal ion) accepts this electron pair. The bond formed $M \leftarrow L$ is coordinate, dative and semipolar, where M is the acceptor metal ion that accepts both the electrons from the donor group L.

Sidgwick also made an observation that this tendency to accept electrons by the metal ion from the ligand atom continues till the total number of electrons in the metal ion is equal to the atomic number of noble gas element found in the same period in which the metal is situated. This total number of electrons represents the effective atomic number (EAN) of the metal. By using this rule, it is possible to predict the number of ligands in the coordination compound as well as the products of their reactions.

Valence Bond Theory

This theory was developed by Pauling and gave valence bond treatment of bonding in complexes. The main postulates of the theory are as follows:

- For the coordination bond formation between central metal ion and the ligand, the central metal ion makes available a number of empty orbitals; and the number of these empty orbitals is equal to the coordination number of the metal ion. For example, if the coordination number is 6, the central metal ion will make available six empty orbitals and if it is 4, the metal ion will make available four empty orbitals.
- The atomic orbitals made available by the central metal ion will be a mixture of *s*, *p*, *d* orbitals, all of which are of different energies and orientation. All these orbitals hybridize to give orbitals that are equivalent in energy and symmetry, which then form bonds with the ligands. These equivalent orbitals result in some particular geometry of the complex such as tetrahedral, square planar, octahedral, etc. (Table 5).
- The *d*-orbitals involved in the hybridization can be inner *d*-orbital ($n - 1$) or the outer *d*-orbital (n). Accordingly, the complexes formed would be low-spin (inner orbital) and high-spin (outer orbital), respectively.
- Each ligand will have at least one lone pair of electrons. It can have more than one pair of electrons to donate but should have at least one.
- The coordinate bond is formed when there is an overlap between hybridized empty orbitals of the central metal ion and filled orbitals of the ligand. The greater the extent of overlap, the stronger will be the bonding and more stable will be the complex.

Table 5 Hybridization involved in complexes of different geometries

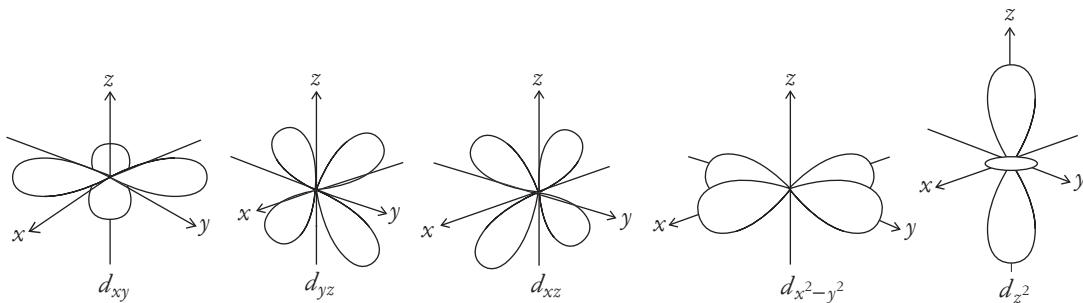
<i>Coordination Number</i>	<i>Hybridization Involved</i>	<i>Geometry</i>
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Square bipyramidal
6	sp^3d^2 , d^2sp^3	Octahedral

6. A complex is paramagnetic in nature if it contains unpaired electrons and is diamagnetic if the electrons are paired.
7. Presence of a strong ligand causes the electrons to pair up against the Hund's rule of maximum multiplicity.

The valence bond theory could successfully explain the magnetic properties and structure of a large number of coordination compounds.

1.8 Crystal Field Theory

Crystal field theory was originally developed for the study of optical properties of the crystalline solids. In this theory, the interaction between the ligand and the central metal ion is treated as a purely electrostatic interaction, as opposed to the valence bond theory where the interaction is treated as covalent in nature. This theory was propounded by H. Bethe and Van Vleck in the 1930s. According to this theory, the interaction between the central metal atom/ion and the ligand in the complex is purely electrostatic. It suggests that the metal ion is situated in an electric field produced by the ligands surrounding the ion. Neutral as well as negatively charged ligands can donate an electron pair to the metal ion and generate an electric field approximately equal to a set of negative point charges around the central metal/ion. Hence, this interaction of d -orbitals of the central metal ion with the ligands gives rise to crystal field. In a free atom, all the d -orbitals are degenerate, that is, have the same energy. In a complex, however, this degeneracy is destroyed and the orbitals split into two groups of orbitals e_g and t_{2g} having different energies. This effect which causes the splitting of degenerate d -orbitals is called *crystal field splitting or energy level splitting*.



This division of d -orbitals into two groups is based upon the orientation of their lobes with respect to coordinates:

1. The e_g set of orbitals comprises d_{z^2} and $d_{x^2 - y^2}$ orbitals which are axial orbitals, that is, have their lobes along the axes. The “ e ” in e_g indicates doubly degenerate set.
2. The t_{2g} set of orbitals comprises d_{xy} , d_{yz} and d_{zx} which are non-axial orbitals, that is, have their lobes lying between the axes. The “ t ” in t_{2g} indicates triply degenerate set.

Crystal Field Splitting in Octahedral Complexes

Octahedral complexes have coordination number 6. The metal ion placed at the center of the octahedron is surrounded by six ligands placed at the six corners of a regular octahedron. The splitting of d -orbitals in octahedral complexes is shown in Figure 33. The splitting is observed according to the fact that in case of octahedral complexes, the ligands approach along the axis.

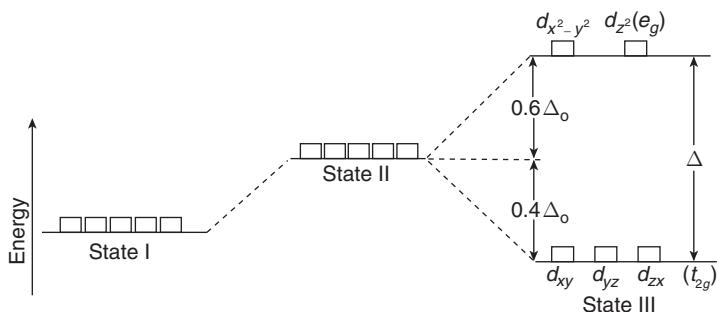


Figure 33 Splitting of d -orbitals in octahedral complexes.

From the figure:

State I: This represents the state of a free metal ion where all the five d -orbitals are degenerate.

State II: As the ligands approach the central metal atom/ion along the axis, the lone pair of electrons present on the ligands exerts a force of repulsion on the outer d electrons of the metal atom/ion. This repulsion increases the energy of the orbitals, thereby giving rise to five excited degenerate d -orbitals.

State III: As the lobes of the axial orbitals d_{z^2} and $d_{x^2 - y^2}$ are lying directly in the path of approaching ligands, this e_g set of orbitals will experience a greater force of repulsion and will be raised in energy as compared to the excited five d -orbitals degenerate set. On the other hand, the lobes of the d_{xy} , d_{yz} and d_{zx} orbitals lie between the axes and will thus experience comparatively less force of repulsion. So they possess lower energy as compared to the excited five d -orbitals degenerate set.

The difference in the energies of the two sets e_g and t_{2g} is called crystal field splitting energy (CFSE) and is represented by Δ . For octahedral complexes, it is represented by Δ_o . Its magnitude depends upon the field strength of both the metal ion and the ligand.

Crystal Field Splitting in Tetrahedral Complexes

Tetrahedral complexes have coordination number 4. The metal ion is at the center of the tetrahedron and the four ligands surrounding it are placed at the four corners of the tetrahedron. These four ligands approach the central metal ion in a different manner since now the ligands approach in between the axes. As shown in Figure 34, the ligands interact more with t_{2g} set of orbitals lying close to the axes of approaching ligands as compared to the e_g set of orbitals lying between the axes. This causes more repulsion and therefore increases in energy of t_{2g} set of orbitals as compared to the e_g set. Similar to octahedral complexes, here also crystal field splitting takes place but in reverse order (Figure 35).

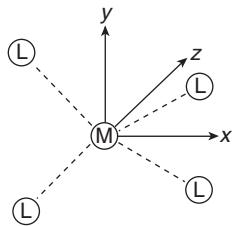


Figure 34 Approach of the four ligands in a tetrahedral field.

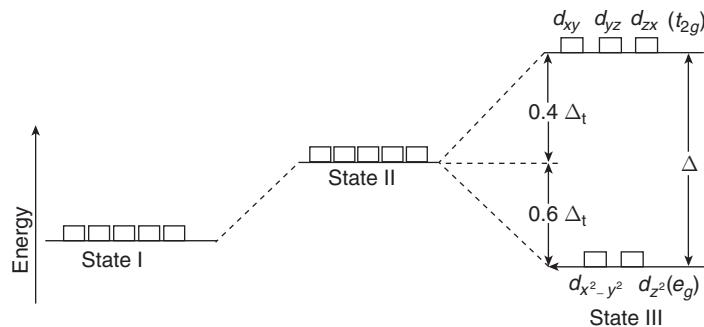


Figure 35 Splitting of d -orbitals in a tetrahedral complex.

In the case of tetrahedral complexes, crystal field splitting is denoted by Δ_t , where t indicates tetrahedral. Now, since the d -orbitals do not directly interact with the approaching ligands in the tetrahedral complexes, the extent of splitting is less than that of octahedral complexes. So,

$$\Delta_t < \Delta_o$$

$$\Delta_t = \frac{4}{9} \Delta_o$$

This lower value of Δ_t may also be due to the less number of surrounding ligands, which are only 4 in this case as compared to 6 in octahedral complexes.

Crystal Field Splitting in Square Planar Complexes

Square planar complexes have a coordination number 4. There are four ligands that are arranged in a square planar arrangement around the central metal ion as shown in Figure 36. Therefore, due to the orientation of the lobes of $d_{x^2-y^2}$, the ligands can exert the maximum influence on this orbital. The d_{xy} orbital lies in the same plane but its lobes are oriented in between the ligands, so it will also experience repulsion but to a lesser extent than $d_{x^2-y^2}$ orbital. Both these orbitals will have energy higher than the degenerate d orbitals, the increase being more in the former. Although the effect of ligands on the remaining orbitals will be comparatively less, it is not possible to predict this effect. However, their effect on d_{xz} and d_{yz} pair will be equal because of their similar orientations and so these remain degenerate.

The comparative crystal field splitting in octahedral, tetrahedral and square planar complexes is shown in Figure 37.

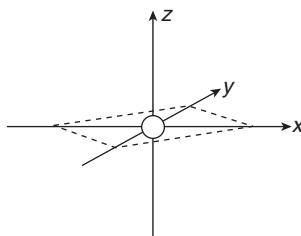


Figure 36 Square planar arrangement of four ligands around the central ion.

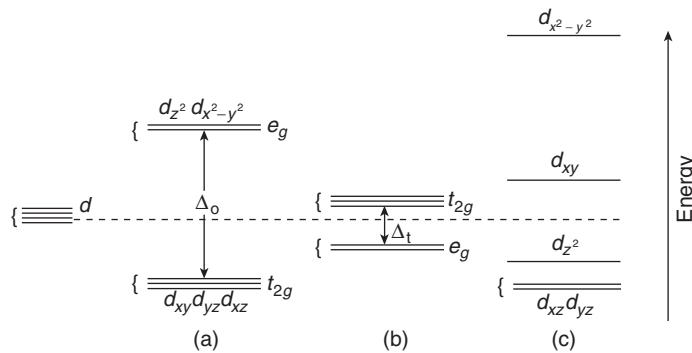
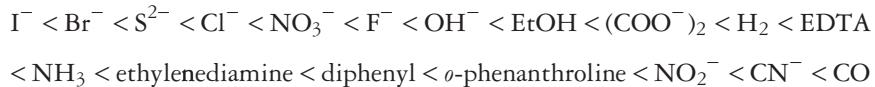


Figure 37 Crystal field splitting in (a) octahedral field, (b) tetrahedral field and (c) square planar field.

The various factors that influence the magnitude of crystal field splitting are as follows:

1. **Nature of ligand:** If it is easier for a ligand to approach metal atom and interact with it, then the extent of crystal field splitting is high. The ligands that cause only a small degree of crystal field splitting are called *weak field ligands*, whereas the ligands that cause a large degree of crystal field splitting are called *strong field ligands*. The strong field ligands give a higher value of Δ_o , and weak ones give a lower value. Some common ligands arranged in the increasing order of their splitting power are as follows:



This arrangement of ligands in the order of their abilities to split the d -orbital energies is called the *spectrochemical series*.

When the first, second and third electrons enter the d -orbital, they occupy the three t_{2g} (lower energy) orbitals one by one. However, when the fourth and the next electron enter the d -orbitals, the following two alternative options are available for the electron:

- The fourth and the next electron may pair up with the electrons in the t_{2g} orbitals (contrary to the Hund's rule of maximum multiplicity).
- The fourth and the next electron may enter the higher e_g orbitals in accordance with Hund's rule of maximum multiplicity.

The exact path chosen by the electron depends upon the strength of the ligand:

Case I: In the presence of a strong-field ligand such as CO, CN⁻, etc., the electrons pair up because Δ_o is large enough to force pairing by filling the lower energy t_{2g} d -orbitals. Thus, in the presence of a strong-field ligand, low-spin (diamagnetic) complexes are formed, for example, $[\text{Fe}(\text{CN})_6]^{4-}$.

Case II: In the presence of a weak-field ligand such as F⁻, H₂O, etc., since Δ_o is not large enough to force the pairing up of electrons, the next (fourth and fifth) electrons will enter the e_g orbitals. Thus, in the presence of a weak-field ligand, high-spin (paramagnetic) complexes are formed, for example, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.

2. **Oxidation state of the metal ion:** Higher the oxidation state of the metal ion, higher will be the splitting. The oxidation state defines the amount of the ionic charge on the central metal ion which

can interact with the ligand field. Thus, higher the ionic charge available for the interaction, higher will be the value of splitting.

3. **Transition series:** For metal ions that belong to the same group and that form similar kind of the complexes with the same oxidation state, it is observed that metal ions that belong to the $5d$ series have greater crystal field splitting value as compared to the metal ions of the $4d$ series. The crystal field splitting value of $3d$ series, further decreases by 30–40% as compared to the $4d$ series. The effect is basically attributed to the size and spatial arrangement of the orbitals under consideration. Thus, in transition series it can be seen that crystal field splitting follows the order:

$$5d > 4d > 3d$$

4. **Geometry of the complexes:** As already discussed, the value of the crystal field energy for octahedral complexes is almost double the value for tetrahedral complexes

$$\Delta_t = \frac{4}{9} \Delta_o$$

This can be attributed to the fact that the number of ligands in the octahedral field is 6 as compared to 4 in the case of tetrahedral complex. Also, in octahedral field the ligands approach in the line of the coordination axis as compared to tetrahedral field where ligands approach in between the axis.

Concept Check

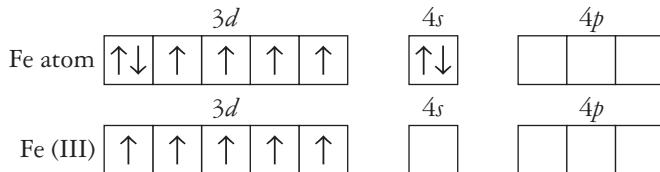
- Identify the primary and secondary valencies in the following complexes:
 $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$,
 $[\text{CoCl}_3(\text{NH}_3)_3]$
- Out of the primary and secondary valencies, which valency will determine the geometry and stereochemistry of the complex?
- What do you understand by the term effective atomic number (EAN) proposed by Sidgwick? What is the EAN of metal atom in the complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$?
- What is the hybridization of metal atom in the complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$?
- $\text{Ni}(\text{CO})_4$ is a diamagnetic complex, whereas NiCl_4 is paramagnetic. Explain.
- Both the complexes $\text{Ni}(\text{CO})_4$ and $[\text{Ni}(\text{CN})_4]^{2-}$ have coordination number 4; however, $\text{Ni}(\text{CO})_4$ is tetrahedral in shape while $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar. Explain the difference in geometry in terms of the difference in hybridization.
- According to crystal field theory, how do five degenerate d -orbitals split in the presence of ligands in octahedral complexes?
- Crystal field splitting in tetrahedral complexes (Δ_t) = $(4/9)\Delta_o$. Explain.
- How do weak and strong ligands differ in terms of crystal field splitting energy? Which among the following is the strongest ligand: Cl^- , NO_2^- , CN^- , CO ?
- How does crystal field splitting vary with oxidation state and size of metal ion?

1.9 Coordination Number and Geometry

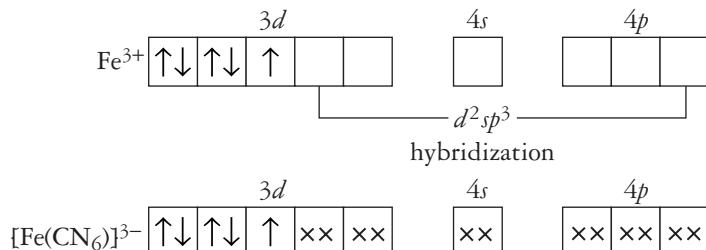
Complexes with Coordination Number 6

The bonding and structure of some complexes with coordination number 6 are discussed as follows:

1. $[\text{Fe}(\text{CN})_6]^{3-}$: Fe ($Z = 26$) is in +3 oxidation state in this complex. On formation of Fe(III) ion the electronic configuration changes from $3d^64s^2$ to $3d^54s^0$ as shown

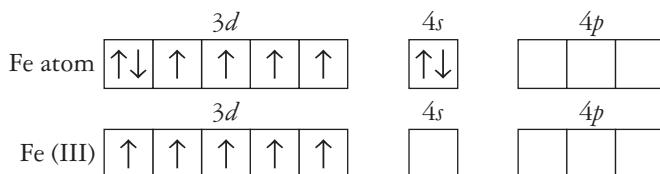


In presence of strong-field ligand CN^- , the electrons in Fe^{3+} pair up and leave two empty d -orbitals. The two empty d -orbitals along with $4s$ and three $4p$ orbitals hybridize to form six equivalent d^2sp^3 orbitals, directed towards the corners of an octahedron. The six pairs of electrons from six CN^- ligands occupy these orbitals to form the complex as shown

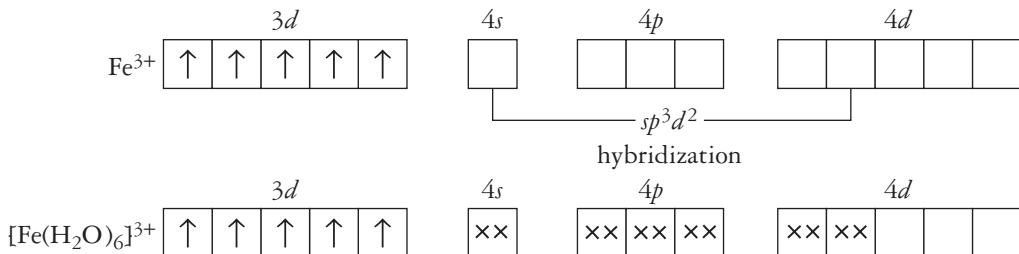


Due to the presence of one unpaired electron in the system the complex is weakly paramagnetic in nature.

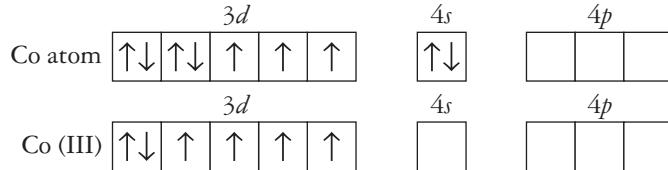
2. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$: In this complex, Fe is in +3 oxidation state. Formation of Fe(III) changes the electronic configuration from $3d^64s^2$ to $3d^54s^0$ as shown



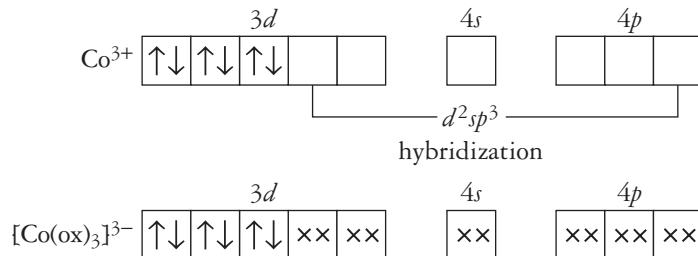
In presence of H_2O , which is a weak field ligand, there is no tendency on part of electrons to pair up. So empty $4s$, $4p$ (three) and $4d$ (two) orbitals hybridize to form six equivalent sp^3d^2 orbitals, directed towards corners of an octahedral. The six lone pair of electrons from the ligand H_2O occupy these orbitals to form the complex, which is highly paramagnetic due to presence of unpaired electrons.



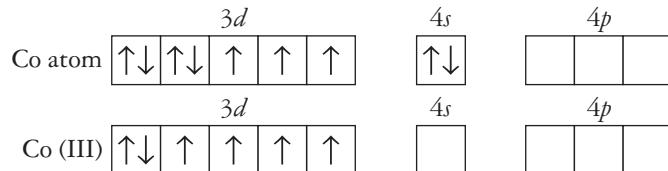
3. $[\text{Co}(\text{ox})_3]^{3-}$: In this complex, Co ($Z = 27$) is in the oxidation state +3. On formation of Co(III), the electronic configuration changes from $3d^74s^2$ (ground state) to $3d^64s^0$ as shown



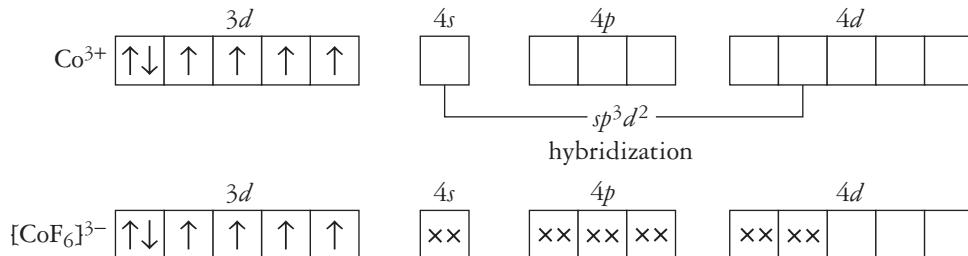
Oxalate is a strong-field ligand, so it causes electrons in $3d$ orbital to pair up. The two empty $3d$ orbitals, $4s$ and three $4p$ orbitals hybridize to form six equivalent d^2sp^3 orbitals. Six lone pairs from three oxalate ligands occupy these orbitals to form octahedral complex, which is diamagnetic due to the absence of any unpaired electron.



4. $[\text{CoF}_6]^{3-}$: In this complex cobalt is in oxidation state +3. On formation of Co(III), the electronic configuration changes from $3d^74s^2$ (in ground state) to $3d^64s^0$ as shown



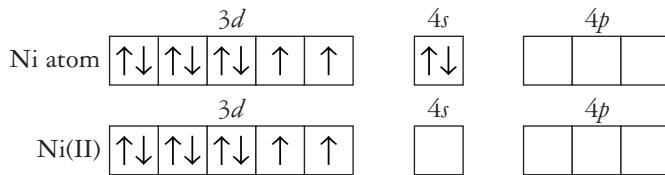
In presence of F^- , which is a weak-field ligand, the $3d$ electrons do not show any tendency to pair up. Therefore, $4s$, three $4p$ and two $4d$ orbitals hybridize to form six equivalent sp^3d^2 orbitals. The lone pair of electrons from six fluoride ligands occupy these orbitals to form an octahedral, paramagnetic complex.



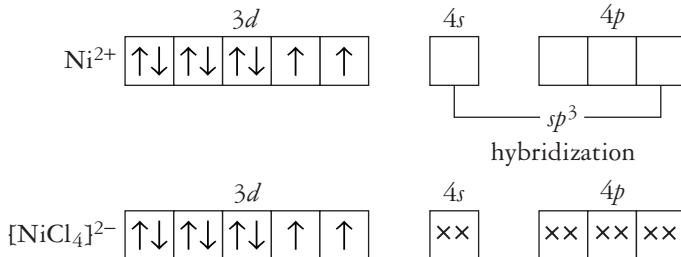
Complexes with Coordination Number 4

For coordination number 4 we can have two types of hybridization: sp^3 (tetrahedral geometry) and dsp^2 (square planar geometry). An example of tetrahedral geometry has already been discussed under the subsection "Valence Bond Theory". In this subsection, we will discuss both tetrahedral and square planar complexes.

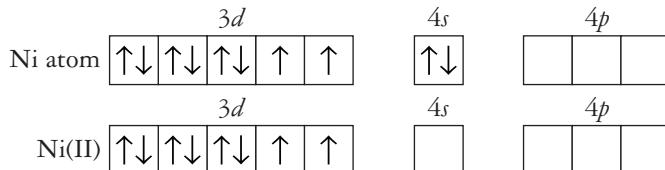
1. $[\text{NiCl}_4]^{2-}$: In this complex ion Ni ($Z = 28$) is in (+2) oxidation state. The configuration of Ni atom is $3d^84s^2$ which changes to $3d^84s^0$ on the formation of Ni(II).



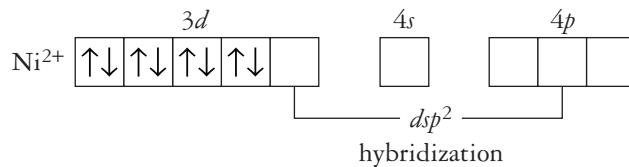
Since Cl^- is a weak-field ligand, it does not have the tendency to pair up the electrons in the $3d$ level. The empty $4s$ and $4p$ orbitals hybridize to form four equivalent sp^3 orbitals. The lone pair of electrons from four chloride ions occupy these hybridized orbitals giving rise to a tetrahedral and paramagnetic complex.



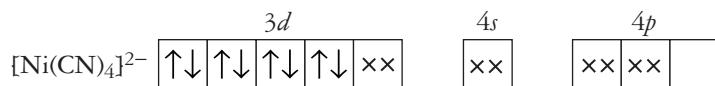
2. $[\text{Ni}(\text{CN})_4]^{2-}$: In this case again Ni is in (+2) oxidation state. The configuration of Ni atom is $3d^84s^2$ which changes to $3d^84s^0$ on the formation of Ni(II) with the loss of two electrons.



Since CN^- is a very strong-field ligand, it has the tendency to pair up electrons in the $3d$ level so as to set up space for its own electrons to be accommodated. Now, the configuration changes as shown



Thus, empty $3d$ orbitals, $4s$ and two $4p$ orbitals hybridize to form four equivalent dsp^2 orbitals. The four lone pairs from cyanide ligands occupy these orbitals to form square planar and diamagnetic complex.



Concept Check

- Comment on the nature of hybridization in the following complexes:
 $[\text{CoF}_6]^{3-}$, $[\text{FeCl}_4]^-$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$
- Explain the octahedral geometry and paramagnetic nature of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.
- Explain the tetrahedral geometry and diamagnetic nature of $[\text{Zn}(\text{NH}_3)_4]^{2+}$.

1.10 Metallic Bond

The theory of covalent bonding cannot be extended to explain the bonding mechanism in metals. This is because the individual atoms of a metal do not have enough valence electrons to share and form an octet. Thus, another theory was proposed to explain the force of attraction holding the atoms together in a piece of metal which is called the *metallic bond*. The metallic bond can account for most of the physical characteristics of metals such as strength, malleability (ability to be hammered into sheets), ductility (ability to be drawn into wires), luster and conductance of heat and electricity.

Theories of Metallic Bond

Various theories have been proposed to explain bonding in metals.

Electron Sea Model

In the case of metals, elements in which the valence electrons are not tightly bound to the nucleus, every atom achieves a more stable configuration by sharing the outer shell electrons with the various other atoms in the metal lattice. Quantum mechanically, atomic orbitals on all the atoms overlap to give a vast number of molecular orbitals which extend over the whole metal. Hence, the valence electrons become detached from their parent atom and move freely amongst all the atoms within the crystal. In other words, the electrons are said to be *delocalized*. The metal lattice is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons. This is described as “an array of positive ions in a sea of electrons” (Figure 38).

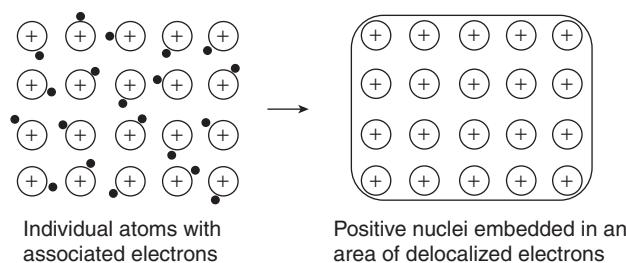


Figure 38 Electron sea model.

This theory of metallic bond successfully explains the observed physical characteristics of metals, such as strength, malleability, ductility, conduction of heat and electricity, and its metallic luster.

The strength of the metallic bond depends on the number of valence electrons contributed by the atoms to the delocalized electrons and the packing arrangement of the metal atom. More number of delocalized electrons and more closely packed atoms result in a stronger bond and a higher melting point. This explains why Group I metals have relatively low melting points compared to other metals. Since these metals have only one electron to contribute to the delocalized “sea” of electrons, are inefficiently packed and have large atomic radii, the delocalized electrons are farther away from the nucleus resulting in a weaker metallic bond.

The properties of the metals like malleability and ductility can be explained as the ability of the individual atoms to “slip” past one another, while being firmly held together by the electrostatic forces exerted by the electrons. As the electrons are delocalized over the positive ions and can move freely, the metals exhibit good electrical conductivity. Heat conduction by metals can also be explained on the same principle – the free electrons can transfer the energy at a faster rate than those which are covalently bonded having their electrons fixed in position.

Metals typically have a shiny, metallic luster because photons of light do not penetrate very far into the surface of a metal and are typically reflected, or bounced off from the metallic surface.

Band Theory or Molecular Orbital Theory

Molecular orbital theory may be extended to explain bonding in metals and is known as the band theory. Consider the example of a piece of sodium metal. Each sodium atom has single $3s$ valence electron. When two atoms are close together, the atomic orbitals will combine to form two molecular orbitals, 3σ and $3\sigma^*$. The two electrons will occupy the bonding molecular orbital, while the antibonding orbital will remain empty. Similarly for three sodium atoms, three molecular orbitals are formed – bonding, non-bonding and antibonding. When four sodium atoms combine, we get two 3σ orbitals and two $3\sigma^*$ orbitals. The quantum mechanical considerations do not permit these orbitals to be degenerate but they are closely placed, being almost similar in energy. The concept can be extended to n number of sodium atoms present in a piece of sodium metal. In this multi-atom system, the number of molecular orbital states will be equal to the number (n) of the atomic orbitals combining. Since the number of molecular orbitals is large, the spacing between them decreases to become almost negligible and we get a “band” of continuous energy levels (Figure 39). These molecular orbitals extend in all three dimensions over all the atoms in the metal piece.

The molecular orbital theory can explain most of the physical properties of metals. Since the energy levels are closely spaced, a very small amount of energy is required for the electrons to rise from filled orbitals to the unoccupied orbitals. The electrons have high degree of mobility and this explains the high electrical and thermal conductivity of metals. In presence of an electric field, the mobile electrons, which move in all directions in absence of a field, begin to move towards the anode causing the electric current to flow. Similarly when the metal is heated, the mobile electrons gain energy and move towards colder part of the metal, thus transferring heat. The metallic luster arises because of absorption of light of any wavelength by metal atoms on the surface and its re-emission. The electrons absorb light, move to higher energy level and then emit the same amount of light to come back to the ground state. The presence of a band of energy levels in metals offers infinite number of such possible transitions between energy levels.

The band theory can also successfully explain the classification of materials into conductors, insulators and semiconductors. This arises due to (results from) the difference in the gap between the filled/partially filled valence band and the unfilled conduction band (Figure 40).

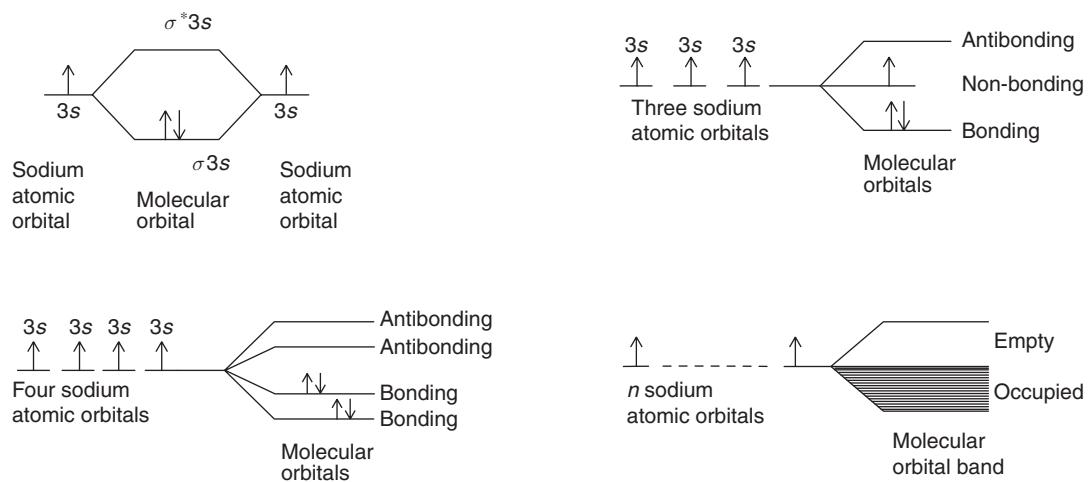
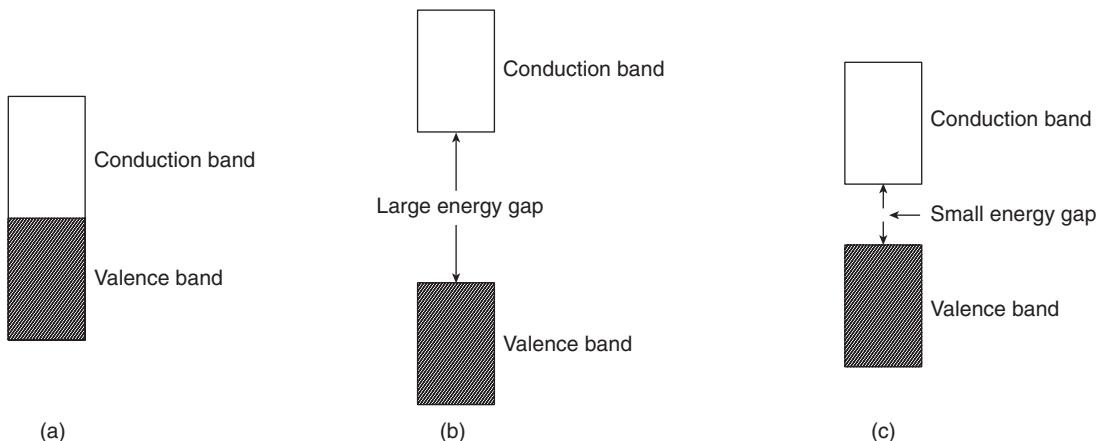
Figure 39 MO diagram for 2, 3, and n sodium atoms.

Figure 40 Valence and conduction band in (a) conductors, (b) insulators and (c) semiconductors.

1. In conductors, there is an overlap of valence and conduction bands; and the electrons from the valence band move effortlessly between the two bands. The electrons can thus move easily throughout the solid, making it a good conductor.
2. In insulators, the valence and conduction bands are widely separated and exist as distinct bands. The valence orbitals are filled so there is no movement of electrons possible, while the conduction band being empty, there are no electrons to move. Also, due to difference in the energy gap, a large amount of energy is required to promote the electrons from valence band to conduction band. So effectively there are no mobile charge carriers and hence insulators or non-metals do not conduct electricity.

3. In semiconductors, the valence and conduction bands are so placed that some amount of electrons can be excited to the upper vacant conduction band. Only a moderate amount of energy is required to promote electrons from filled valence band to empty conduction band. Semiconductors thus conduct electricity with some input of external energy. Also, since increase in temperature will increase the promotion of electrons to the conductance band, the conductivity of semiconductors increases with increase in temperature. Another way of increasing conductivity of semiconductors is through doping, which is discussed as follows:

Effect of Doping on Conductance

Silicon and germanium, each has four electrons in its outer orbital, forming perfect covalent bonds with four neighboring atoms and creating a fine crystal lattice. Their crystal lattices can be substituted with impurity atoms (dopants) which dramatically change their electrical properties. The unique properties of these substituted silicon and germanium crystals are used in semiconductors, which form the heart of microprocessors and integrated circuits in solid state electronics.

Intrinsically silicon and germanium conduct a small current. However, the addition of a small amount of dopant atoms into their regular crystal lattice produces dramatic change in their electrical properties, producing *n*-type and *p*-type semiconductors.

Impurity atoms with five valence electrons, like antimony, arsenic or phosphorus added to silicon or germanium, contribute extra electrons and greatly increase the conductivity, producing *n*-type semiconductors.

Impurity atoms with three valence electrons, like boron, aluminium or gallium creates deficiency of valence electrons, called *holes* and produces *p*-type semiconductors. A high degree of chemical purity and a perfect crystal structure are required during the process of manufacture of doped semiconductor materials, since defects in crystal structure greatly alter the semiconducting properties of the material. In fact, faults in the crystalline structure form the main cause of defective semiconductor devices. When semiconductor devices involve junctions between different semiconductor materials, lattice compatibility is an important consideration in their manufacture.

Concept Check

- What is the theory proposed to explain the bonding in metals?
- How does the theory for metallic bonding explain the following properties of metals: Luster, malleability and conductivity?

Key Terms

Electronic theory of valency	Covalent bond (single and multiple)	Electronegativity
Ionic (electrovalent) bond	Expanded octet	Coordinate (dative) bond
Ionization energy	Lewis electron dot formula	Classical mechanics
Electron affinity	Valence (outermost) shell	Quantum mechanics
Lattice energy	Polar and non-polar covalent bond	de Broglie's equation
Shared electron pair theory		Heisenberg's uncertainty principle

Schrodinger wave equation and function	Molecular orbital diagram	Effective atomic number
Valence bond theory	Linear combination of atomic orbitals	Werner's coordination theory
Hybridization	Sigma (σ) and pi (π) bonds	Sidgwick coordination theory
Geometry of molecules	Metallic bond	Valence bond theory
Molecular orbital theory	Coordination complex	Crystal field theory
Bonding and antibonding molecular orbitals	Coordination number	Primary valency
		Secondary valency

Objective-Type Questions

Multiple-Choice Questions

1. An electropositive element will combine with electronegative element to form
 - a. ionic bond.
 - b. covalent bond.
 - c. metallic bond.
 - d. hydrogen bond.
2. The amount of energy released when an electron is added to an isolated gaseous atom of an element is called
 - a. lattice energy.
 - b. electron affinity.
 - c. ionization energy.
 - d. none of the above.
3. Which one of the following pairs atoms is most likely to form an ionic bond?
 - a. Na and F
 - b. C and C
 - c. N and F
 - d. F and F
4. Which among the following will have highest polar (ionic) character?
 - a. LiF
 - b. K₂O
 - c. N₂
 - d. CCl₄
5. Which among the following will have highest melting point?
 - a. NaI
 - b. NaBr
 - c. NaCl
 - d. NaF
6. Covalent bonds are least likely to be formed in
 - a. between atoms of the same element.
 - b. between atoms of different elements on the right of the periodic table.
 - c. between elements with high ionization energies.
 - d. between an element in Group 1 and an element in Group 17.
7. Which among the following will have the shortest bond length?
 - a. C—C
 - b. C=C
 - c. C≡C
 - d. Same in all.
8. In which one of the following does the central atom possess an “octet” in its outer shell?
 - a. BH₃
 - b. SF₆
 - c. CH₄
 - d. PCl₅

9. Which of the following pairs do not form a coordinate covalent bond with each other?
- AlCl_3 and AlCl_3
 - H_2O and H
 - NH_3 and BF_3
 - CH_4 and AlCl_3
10. Which among the following will have highest repulsion?
- Bond pair–bond pair
 - Lone pair–lone pair
 - Bond pair–lone pair
 - Same in all
11. Which among the following will have the highest bond length?
- O_2^+
 - O_2
 - O_2^-
 - O_2^{2-}
12. Which among the following is paramagnetic?
- N_2
 - O_2
 - O_2^{2-}
 - H_2
13. Which among the following will have the highest bond order?
- N_2
 - N_2^+
 - N_2^-
 - N_2^{2-}
14. The bond order of O_2^+ molecular ion is
- 1.
 - 2.
 - 2.5.
 - 3.
15. Which of the following configurations corresponds to paramagnetic property?
- $\sigma 2s^2$
 - $\sigma 2p_x^2 \pi 2p_y^2 \pi 2p_z^2$
 - $\pi 2p_y^2$
 - $\pi^* 2p_y^1 \pi^* 2p_z^1$
16. Which of the following is true for energy of antibonding orbitals?
- a. It is greater than the energy of atomic orbitals.
- b. It is lower than energy of bonding orbitals.
- c. It is same as energy of bonding orbitals.
- d. It is lower than the energy of atomic orbitals.
17. Which one of the following is not true for metallic bonding?
- It gives rise to excellent electrical conductivity.
 - Electrons are free to move throughout the structure.
 - The strength of metallic bonds increases down a group.
 - The strength of metallic bonding affects the boiling point of metals.
18. Which one of the following does not exhibit intermolecular hydrogen bonding?
- HF
 - Liquid NH_3
 - $\text{C}_6\text{H}_5\text{OH}$
 - HI
19. Which one of the following is true for water?
- In ice, each water molecule is bonded to three others.
 - Water has a high boiling point due to intermolecular hydrogen bonding.
 - Water has a structure similar to that of diamond.
 - Water has a maximum density at 1°C .
20. Which of the following compounds will show hydrogen bonding?
- HI
 - NH_3
 - CH_4
 - NaH
21. Ethanol and dimethyl ether have same molecular formula $\text{C}_2\text{H}_6\text{O}$. However, the boiling point of ethanol is higher as compared to dimethyl ether because of
- resonance.
 - coordinate bonding.
 - hydrogen bonding.
 - ionic bonding.

22. The total number of electrons on the central atom including those gained by bonding is called
 a. coordination number.
 b. oxidation state.
 c. effective atomic number.
 d. none of the above.
23. The EAN of iron in $[\text{Fe}(\text{CN})_6]^{4-}$ is
 a. 34.
 b. 36.
 c. 37.
 d. 35.
24. A solution of potassium ferrocyanide would contain how many ions?
 a. 2
 b. 3
 c. 4
 d. 5
25. The coordination number of copper in tetraamminecopper(II) sulphate is
 a. 2.
 b. 3.
 c. 4.
 d. 6.
26. A complex with unpaired electron(s) in *d*-orbitals of the metal ion is a
 a. low-spin complex.
 b. high-spin complex.
 c. paramagnetic complex.
 d. diamagnetic complex.
27. Which of the following complexes is expected to be a paramagnetic complex?
 a. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 b. $[\text{Co}(\text{NH}_3)_6]^{3+}$
 c. $[\text{Ni}(\text{CO})_4]$
 d. $[\text{Ni}(\text{CN})_4]^{2-}$
28. $[\text{Ni}(\text{CN})_4]^{2-}$ is a square planar complex, Ni^{2+} in the complex is
 a. sp^3 hybridized.
 b. dsp^2 hybridized.
 c. sp^3d^2 hybridized.
 d. d^2sp^3 hybridized.

Fill in the Blanks

- The number of electrons lost or gained during the formation of an electrovalent bond is called _____ of the element.
- The energy required to remove the most loosely bound electron from an isolated gaseous element is called _____.
- An electronegative element combines with another electronegative element to form _____ bond.
- _____ bond is formed by the donation of electrons.
- Water molecule exhibits dipole moment due to _____ structure.
- Ethyl alcohol is completely miscible with water due to _____.
- Bond length of a molecule is _____ proportional to the bond order, whereas bond energy is _____ proportional to bond order.
- o*-nitrophenol is less acidic than *p*-nitrophenol due to presence of _____ hydrogen bonding.
- The most stable amongst the following O_2 , O_2^+ , O_2^- , O_2^{2-} is _____.
- The number of σ and π bonds in a molecule of ethene (C_2H_4) is _____ and _____, respectively.
- Low ionization energy and high electron affinity will favor the formation of _____ bond.
- The sulphur atom in SF_6 undergoes _____ hybridization and the molecule has _____ geometry.
- On the basis of VSEPR theory, XeF_4 will have _____ structure.
- The bond formed by end-to-end overlap of *s* or *p* orbitals is called _____ bond and

- that formed by lateral overlap of *p* orbitals is called _____ bond.
15. The carbon atom in C_2H_6 is _____ hybridized.
 16. Ligands remove the degeneracy of _____ of the metal ion.
 17. In the presence of ligands, *d*-orbitals of central metal ion exhibiting an octahedral geometry split into lower energy state _____ and higher energy state _____.
 18. The coordination compounds with minimum pairing of electrons are called _____.
 19. When all the electrons in *d*-orbitals of the metal are paired, the complex is _____.

Review Questions

Short-Answer Questions

1. What is electronic theory of valency? What are its limitations?
2. What is an ionic bond? What are the factors governing its formation?
3. Define lattice energy. What are factors that determine the magnitude of lattice energy?
4. Why do alkaline earth metals form positive ions less readily than alkali metals?
5. Which of the following compounds will have higher lattice energy?
 - a. NaCl and $CaCl_2$
 - b. NaCl and NaI
6. Why do Group 16 elements form negative ions less readily than Group 17 elements?
7. Explain why
 - a. sodium chloride conducts electricity in fused state or in aqueous solution but not in solid state.
 - b. ionic compounds have high boiling and melting points.
 - c. ionic compounds are brittle.
8. Explain why ionic compounds are soluble in water and polar solvents.
9. What is meant by electronegativity of an atom? What does it predict about the nature of bonding in a molecule?
10. How does Lewis theory of covalent bonding explain the bonds existing in O_2 , CO_3^{2-} , C_2H_4 and BCl_3 ? Explain using electron-dot formula.
11. Covalent compounds can exhibit geometric isomerism while ionic compounds do not – how is this justified?
12. Reactions involving ionic compounds are generally faster than those of covalent compounds. Justify.
13. Explain the bonding present in the following compounds. Mention what is specially common in these: (a) HNO_3 and (b) H_2SO_3 .
14. How does partial ionic character develop in covalent compounds?
15. What is the difference between covalent and coordination bonds?
16. Explain with example, the role of lone pair of electrons in determining the shape of the molecules.
17. What does ψ in the solution to Schrodinger's wave equation signify?
18. State (a) de Broglie's postulate and (b) Heisenberg uncertainty principle. What are their implications?

19. State the postulates of valence bond theory explaining the formation of strong covalent bonds.
20. Predict the shape of the following molecules using VSEPR theory: (a) BF_3 and (b) H_2O .
21. What is hybridization? What are the properties of hybrid orbitals?
22. What are the basic postulates of molecular orbital theory in explaining the bonding between atoms?
23. What are bonding and antibonding molecular orbitals?
24. What is meant by bond order? Calculate the bond order of He_2^+ , O_2 , N_2^- .
25. Describe how molecular orbital theory is helpful in predicting bond order and hence the bond strength of the bonds between atoms.
26. Explain why N_2 has greater dissociation energy than N_2^+ while O_2 has lower dissociation energy than O_2^+ .
27. Phosphorus can form both PCl_3 and PCl_5 while nitrogen can form only NCl_3 . Explain.
28. $[\text{Ni}(\text{CN}_4)]^{2-}$ is a square planar complex. Discuss the hybridization of the complex.
29. What do crystal field stabilization energy and pairing energy mean?
30. What is the effect of the nature of ligand on the stability of the complex?
31. Most metals are found to have a regular compact crystalline structure. Explain why?
32. What is the free electron (electron sea) theory of metallic bonding? How does it account for metallic luster?
33. Explain conductors and insulators on the basis of band theory.

Long-Answer Questions

1. What is an ionic bond? What are the essential conditions for formation of ionic bonds? Explain the formation of ionic bond in MgO .
2. Describe the physical and chemical properties of ionic compounds and explain how it augments the theory of ionic bonding.
3. Describe the characteristic properties of covalent compounds.
4. What are the salient features of valence bond theory?
5. What are the salient features of VSEPR theory? Discuss the geometry of the following using VSEPR theory: (a) NH_3 and (b) PCl_5 .
6. a. Discuss the shapes of NH_3 and H_2O molecules on the basis of VSEPR theory.
b. What are the shapes of PCl_5 , NH_3 , BCl_3 , SF_6 .
7. a. What is hybridization?
b. What are sp^2 and sp^3 hybridizations. Explain with examples.
8. What are the important features of molecular orbital theory? Draw the energy level diagram for molecular orbitals.
9. What are the essential difference between valence bond and molecular orbital theory?
10. What do you understand by LCAO method? What are conditions necessary for combination of atomic orbitals?
11. Explain the formation of following on basis of molecular orbital theory: (a) F_2 and (b) HF .
12. a. Draw the molecular orbital diagram for O_2 molecule.
b. Write the electronic configuration, calculate the bond order and predict the magnetic behavior of: O_2 , O_2^+ , O_2^- , O_2^{2-} .

13. a. Draw the molecular orbital diagram for NO molecule.
b. Write the electronic configuration, calculate the bond order and predict the magnetic behavior of NO, NO^+ , NO^- .
14. With the help of molecular orbital diagram, explain why hydrogen forms diatomic molecule while helium remains monoatomic.
15. How and why are the molecular orbital diagrams of nitrogen (N_2) and oxygen (O_2) molecules different? What are the implications?
16. Discuss the concept of primary and secondary valencies in coordination complexes as postulated by Werner's coordination theory.
17. How does the formation of a coordination compound take place according to valence bond theory? What are the limitations of the theory?
18. Using valence bond theory explain why $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is outer orbital complex and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is inner orbital complex.
19. What are the salient features of crystal field theory?
20. Explain the crystal field splitting of d -orbitals by the ligands in octahedral complexes with coordination number six.
21. Both $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{CoF}_6]^{3-}$ are octahedral complexes. Use crystal field theory to predict the magnetic nature of the two complexes.
22. Apply crystal field theory to explain why:
 - a. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is colored and $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colorless.
 - b. $[\text{Co}(\text{NH}_3)_6]^{3+}$ is orange yellow in color and $[\text{CoF}_6]^{3-}$ is blue in color.
23. What is the band theory for metallic bonding? How does it explain the categorization of metals into conductors, insulators and semiconductors?
24. Discuss the electron sea model (free electron theory) for metallic bonding. How does it account for: (a) thermal conductivity and (b) metallic luster.
25. What is metallic bond? Explain it on the basis of molecular orbital theory.

Answers

Multiple-Choice Questions

1. (a)
2. (b)
3. (a)
4. (a)
5. (d)
6. (d)
7. (c)
8. (c)
9. (d)
10. (b)
11. (d)
12. (b)
13. (a)
14. (c)

15. (d) 3. covalent
16. (a) 4. Coordination
17. (c) 5. angular
18. (d) 6. hydrogen bonding
19. (b) 7. inversely, directly
20. (b) 8. intramolecular
21. (c) 9. O_2^+
22. (c) 10. five, one
23. (b) 11. electrovalent
24. (d) 12. sp^3d^2 , octahedral
25. (c) 13. Octahedral
26. (c) 14. σ, π
27. (a) 15. sp^3
28. (b) 16. d -orbitals
 17. t_{2g}, e_g
 18. high spin complexes
 19. diamagnetic

Fill in the Blanks

1. electrovalency
2. ionization energy



2

Water and Its Treatment

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Sources of water and impurities found in natural water.
- Hardness of water and types of hardness.
- Degree of hardness and its units.
- Methods for determination of hardness of water.
- Alkalinity – types and method for estimation.
- Analysis of water for impurities:
 - ▶ Determination of chlorides by argentometric method.
 - ▶ Determination of fluoride by SPADNS method.
 - ▶ Determination of nitrate by phenol disulphonic method.
- ▶ Determination of sulphate by gravimetric method.
- Disadvantages of use of hard water for domestic and industrial purposes.
- Characteristics of potable water and treatment of water for domestic use.
- Desalination of brackish water by flash evaporation, electrodialysis and reverse osmosis.
- Characteristics for boiler feed water.
- Techniques of softening water: Internal and external treatments.
- Sewage treatment.
- Recycling wastewater and rainwater harvesting

Water, which is unique to the Earth, covers almost 75% of the Earth's surface. It is the only known substance that can naturally exist as a gas, liquid and solid within a relatively small range of air temperatures and pressures found on the Earth's surface.

In many ways, water is a miracle liquid. It is essential for all living things on this planet, and it is often referred to as a universal solvent because many substances dissolve in it. This property of water as a solvent makes its pollution inevitable.

2.1 Sources of Water

The Earth has around 1.39 billion km³ of water. Out of this, 96.5% is held in the oceans, seas and bays in the form of saline water. The remaining exist in the form of freshwater held as groundwater, snow, glaciers and rivers. Their distribution is as follows: 1.74% is present in permanent snow, icecaps and glaciers; 1.7% is held in groundwater; and minute percentages are stored in soil moisture, ground ice, lakes, rivers, swamp water, biological water and the atmosphere.

Concept Check

- How is water distributed on the Earth?
- What is the difference between freshwater and saline water?

2.2 Impurities in Water

Natural water carries with it a host of impurities in dissolved, suspended and colloidal forms. These impurities need to be removed to make water amenable for domestic and potable as well as industrial purposes.

The following types of impurities are commonly found in natural waters:

1. **Biological impurities:** These include organisms such as bacteria, protozoans, viruses, etc., which cause diseases such as cholera, typhoid, dysentery, botulism, meningitis, polio, cold and hepatitis. Apart from causing diseases, these impurities also impart color, odor and turbidity to water. Water can be disinfected by chlorination and boiling.
2. **Suspended impurities:** These include organic matter such as leaves, branches, twigs, animals and a host of decaying or dead waste. Organic matter imparts color, odor to water and alters its taste. Water has to undergo screening, filtration, sedimentation and disinfection for the removal of organic matter.

Inorganic suspended impurities may also be present in water, which include sediments, clay and sand. They impart turbidity and need to be coagulated and filtered.

3. **Colloidal impurities:** These are solid impurities which may be present in water in the finely divided and suspended state. Such impurities are not easy to settle and impart color and turbidity to water. Inorganic impurities like iron and aluminium hydroxides may be removed by coagulation and filtration. Organic suspended impurities like oil globules, animal matter, humic acids, etc., require specific chemical treatments.
4. **Dissolved impurities:** These include dissolved gases and dissolved inorganic salts. Organic impurities are generally not water soluble and do not exist in the dissolved state. Dissolved gases like ammonia and hydrogen sulphide impart a bad odor to water. Dissolved oxygen, nitrogen oxides and carbon dioxide lead to boiler corrosion. These gases can be removed by deaeration and using specific chemical treatments. Dissolved inorganic salts like bicarbonates, chlorides and sulphates of calcium and magnesium impart hardness to water. Water may also be rendered alkaline due to salts of sodium and potassium. These impurities can be removed by using ion exchange, lime-soda treatment and reverse osmosis.

Concept Check

- What are the different types of impurities present in natural water?
 - Discuss the biological impurities present in natural water and their effects.
-

2.3 Hardness of Water

After the discovery of soap, it was found that water from different sources reacted differently with soap. Rain water, for example, formed soft and creamy lather with soap, while water from a bore well formed a sticky curd-like residue that did not lather well and the water was difficult to clean with. Naturally, the former water came to be known as "soft water" and the latter as "hard water".

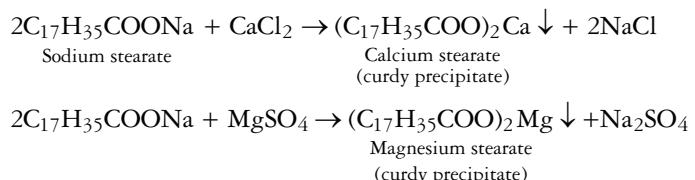
Formation of Hard Water

Water is often called the universal solvent, and as part of that definition, water picks up minerals as it travels many miles over rocks and through soil making its way to water treatment facilities. Those

minerals, mostly calcium and magnesium, are dissolved and held in solution. These cannot be removed by physical processes such as filtration and sedimentation.

To understand why hard water gives out a curd-like precipitate with water, we must first understand what is soap and how it reacts with water. Soap is a sodium salt of a fatty acid. The sodium end of a soap molecule is attracted to water, while the fatty acid end is soluble in fats and oils. Soap allows the mixing of two immiscible phases, oil (or fats) and water. The fatty end mixes with dirt (oil), and the ionic sodium end is attracted to water. This gives rise to emulsified dirt.

However, the fatty acid part of soap in the presence of calcium and magnesium ions in hard water, quickly replaces the sodium ions forming calcium and/or magnesium salts of fatty acids. Neither calcium, nor magnesium are strongly attracted to water and so they precipitate out as soap curd.

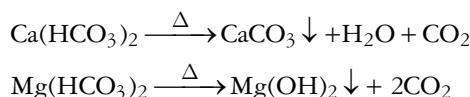


Thus, hard water is water that contains an appreciable quantity of dissolved minerals like calcium and magnesium and does not form lather with soap. In other words, hardness of water is the soap-consuming capacity of water. It can also be defined as the capacity of precipitation of soaps or as a characteristic property of water that prevents the lathering of soap.

Types of Hardness

Hardness is classified into temporary hardness and permanent hardness.

1. **Temporary hardness:** This hardness results in water that contains bicarbonates of calcium and magnesium. It can be removed by boiling. The bicarbonates decompose on boiling giving rise to carbonates and hydroxides which are insoluble and deposit at the bottom of the vessel.



This hardness is also known as carbonate or alkaline hardness.

2. **Permanent hardness:** This hardness is due to presence of chlorides and sulphates of calcium and magnesium in water. Thus, it can be caused mainly by the presence of salts such as MgCl_2 , MgSO_4 , CaCl_2 and CaSO_4 and also salts of heavier elements such as iron and aluminium. This type of hardness cannot be removed by boiling but can be removed by the addition of softening agents (see Section 2.4).

Degree of Hardness

The degree of hardness is defined as the number of parts by weight of calcium carbonate hardness per particular number of parts of water, depending upon the unit employed. Though the hardness does not always arise due to presence of CaCO_3 in water, it is a standard practice to express it in terms of equivalents of CaCO_3 . The reasons for use of CaCO_3 as standard are as follows:

1. Its molecular weight is exactly hundred, which makes calculations convenient.
2. It is the most insoluble salt that can be precipitated out of water.

Mathematically, degree of hardness can be expressed as:

$$\begin{aligned}\text{Equivalent of CaCO}_3 &= \frac{\left[\begin{array}{l} \text{Strength of substance} \\ \text{producing hardness (mg/l)} \end{array} \right] \times \left[\begin{array}{l} \text{Chemical equivalent} \\ \text{of CaCO}_3 \end{array} \right] \times 2}{\left[\begin{array}{l} \text{Chemical equivalent of} \\ \text{hardness producing substance} \end{array} \right] \times 2} \\ &= \frac{\left[\begin{array}{l} \text{Strength of substance} \\ \text{producing hardness (mg/l)} \end{array} \right] \times 100}{\left[\begin{array}{l} \text{Chemical equivalent of} \\ \text{hardness producing substance} \end{array} \right] \times 2}\end{aligned}$$

Units of Hardness

The various units used to express hardness of water are as follows:

- Parts per million (ppm):** It is the number of equivalent parts of CaCO_3 present per million (10^6) parts of water by weight.
- Milligrams per liter:** It is the number of mg of CaCO_3 dissolved in 1 l of water. We know that 1 l of water weighs 1 kg = $1000 \times 1000 = 10^6$ mg.

$$\begin{aligned}\text{So, } 1 \text{ mg/l} &= 1 \text{ mg of CaCO}_3 \text{ per } 10^6 \text{ mg of water} \\ &= 1 \text{ part of CaCO}_3 \text{ per } 10^6 \text{ parts of water} \\ &= 1 \text{ ppm}\end{aligned}$$

- Degree Clarke (${}^\circ\text{Cl}$):** It is the number of equivalent parts of CaCO_3 present per 70,000 parts of water or 1 gallon of water.
- Degree French (${}^\circ\text{Fr}$):** It is the number of equivalent parts of CaCO_3 present per 10^5 parts of water.

These various units of hardness are related as:

$$1 \text{ ppm} = 1 \text{ mg/l} = 0.1 {}^\circ\text{Fr} = 0.07 {}^\circ\text{Cl}$$

Problem 1

Calculate the temporary hardness, permanent magnesium hardness, total permanent hardness and total hardness in terms of calcium carbonate equivalents in a water sample containing following dissolved salts per liter: Calcium bicarbonate (12.2 mg), magnesium bicarbonate (8.2 mg), magnesium sulphate (5.6 mg), magnesium chloride (6.2 mg), calcium sulphate (10.3 mg) and sodium sulphate (7.5 mg). Given that atomic weight of Mg = 24 amu, Ca = 40 amu, S = 32 amu, O = 16 amu, Cl = 35.5 amu and C = 12 amu.

Solution

We know that

$$\begin{aligned}\text{Hardness of substance in terms of CaCO}_3 &= \text{Strength of substance in mg/l} \\ &\quad \times \frac{\text{Chemical equivalent of CaCO}_3}{\text{Chemical equivalent of substance}}\end{aligned}$$

So, the hardness of different salts in terms of calcium carbonate equivalent is:

- $\text{Ca}(\text{HCO}_3)_2$: $12.2 \text{ mg/l of } \text{Ca}(\text{HCO}_3)_2 = 12.2 \times \frac{100}{162} = 7.53 \text{ mg/l of } \text{CaCO}_3$
- $\text{Mg}(\text{HCO}_3)_2$: $8.2 \text{ mg/l of } \text{Mg}(\text{HCO}_3)_2 = 8.2 \times \frac{100}{146} = 5.61 \text{ mg/l of } \text{CaCO}_3$
- MgSO_4 : $5.6 \text{ mg/l of } \text{MgSO}_4 = 5.6 \times \frac{100}{120} = 4.67 \text{ mg/l of } \text{CaCO}_3$
- MgCl_2 : $6.2 \text{ mg/l of } \text{MgCl}_2 = 6.2 \times \frac{100}{95} = 6.52 \text{ mg/l of } \text{CaCO}_3$
- CaSO_4 : $10.3 \text{ mg/l of } \text{CaSO}_4 = 10.3 \times \frac{100}{136} = 7.57 \text{ mg/l of } \text{CaCO}_3$

Sodium sulphate does not contribute to the hardness of water. Therefore, using the above values, we get

- Temporary hardness is caused by bicarbonates of calcium and magnesium $= 7.53 + 5.61 = 13.14 \text{ mg/l}$.
- Permanent magnesium hardness is due to magnesium chloride and magnesium sulphate $= 4.67 + 6.52 = 11.19 \text{ mg/l}$.
- Total permanent hardness is permanent magnesium hardness + permanent calcium hardness (due to CaSO_4) $= 11.19 + 7.57 = 18.76 \text{ mg/l}$.
- Total hardness = temporary hardness + permanent hardness $= 13.14 + 18.76 = 31.9 \text{ mg/l}$.

Problem 2

A water sample contains $200 \text{ mg of } \text{CaSO}_4 \text{ per liter}$. Calculate the hardness in terms of CaCO_3 equivalent in mg/l , ppm , ${}^\circ\text{Cl}$ and ${}^\circ\text{Fr}$.

Solution

Now,

$$\begin{aligned}\text{Hardness in terms of } \text{CaCO}_3 \text{ equivalent} &= \text{Strength of } \text{CaSO}_4 \times \left[\frac{\text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of } \text{CaSO}_4} \right] \\ &= 200 \times \frac{100}{136} = 147.05 \text{ mg/l}\end{aligned}$$

As $1 \text{ mg/l} = 1 \text{ ppm}$, therefore, hardness $= 147.05 \text{ ppm}$.

As $1 \text{ mg/l} = 0.1 {}^\circ\text{Fr}$, therefore, hardness $= 147.05 \times 0.1 = 14.70 {}^\circ\text{Fr}$.

As $1 \text{ mg/l} = 0.07 {}^\circ\text{Cl}$, therefore, hardness $= 147.05 \times 0.07 = 10.29 {}^\circ\text{Cl}$.

Problem 3

- How many grams of MgCl_2 dissolved in water will give hardness of 76 ppm ?
- A water sample (500 ml) has a hardness equivalent for 50 ml of 0.1 N CaSO_4 . What is the hardness in ppm ?

Solution

- Hardness of MgCl_2 is

$$\text{Hardness of MgCl}_2 = \text{Strength of MgCl}_2 \times \left[\frac{\text{Chemical equivalent of CaCO}_3}{\text{Chemical equivalent of MgCl}_2} \right]$$

$$76 = \text{Strength of MgCl}_2 \times \frac{100}{95}$$

Therefore,

$$\text{Strength of MgCl}_2 = \frac{76 \times 95}{100} = 72.2 \text{ ppm or } 72.2 \text{ mg/l}$$

(b) Hardness in ppm is calculated as follows:

$$\text{Normality} = \text{Number of gram equivalents/liter}$$

$$\text{or} \quad \text{Number of gram equivalents} = \text{Normality} \times \frac{\text{Volume of CaSO}_4}{1000 \text{ ml}} \\ = 0.1 \times \frac{50}{1000} = 5 \times 10^{-3}$$

Also,

$$\text{Number of gram equivalents} = \frac{\text{Weight in grams}}{\text{Equivalent weight}}$$

Therefore,

$$\text{Weight in grams in 500 ml of water} = \text{Number of gram equivalent} \times \text{Equivalent weight of CaSO}_4 \\ = 5 \times 10^{-3} \times \text{equivalent weight of CaSO}_4$$

or

$$\text{Weight in grams in 1000 ml of water} = 2 \times 5 \times 10^{-3} \times \text{equivalent weight CaSO}_4 \\ = 10^{-2} \times \text{equivalent weight CaSO}_4$$

Therefore, the hardness due to CaSO_4 is calculated as

$$\text{Hardness due to CaSO}_4 = \text{Strength of CaSO}_4 \times \left[\frac{\text{Chemical equivalent of CaCO}_3}{\text{Chemical equivalent of CaSO}_4} \right] \\ = 10^{-2} \times \text{equivalent weight of CaSO}_4 \times \frac{50}{\text{Equivalent weight of CaSO}_4} \\ = 50 \times 10^{-2} \text{ g/l} = 500 \text{ mg/l} = 500 \text{ ppm}$$

Problem 4

A sample of water on analysis was found to contain

$$\text{Ca(HCO}_3)_2 = 16.2 \text{ mg/l}; \text{CaSO}_4 = 6.8 \text{ mg/l}; \text{MgSO}_4 = 3.6 \text{ mg/l}$$

Calculate the permanent and temporary hardness in $^{\circ}\text{Cl}$.

Solution

The hardness due to $\text{Ca}(\text{HCO}_3)_2$, CaSO_4 and MgSO_4 is

$$\text{Hardness due to } \text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ ppm} \times \frac{100}{162} = 10 \text{ ppm}$$

$$\text{Hardness due to } \text{CaSO}_4 = 6.8 \times \frac{100}{136} = 5 \text{ ppm}$$

$$\text{Hardness due to } \text{MgSO}_4 = 3.6 \times \frac{100}{120} = 3 \text{ ppm}$$

Permanent hardness due to MgSO_4 and $\text{CaSO}_4 = 5 + 3 = 8 \text{ ppm}$.

Temporary hardness due to $\text{Ca}(\text{HCO}_3)_2 = 10 \text{ ppm}$.

Hardness in terms of ${}^{\circ}\text{Cl}$ is calculated as follows:

As 1 ppm = $0.07 {}^{\circ}\text{Cl}$, therefore,

Temporary hardness = $10 \times 0.07 = 0.7 {}^{\circ}\text{Cl}$.

Permanent hardness = $8 \times 0.07 = 0.56 {}^{\circ}\text{Cl}$.

Concept Check

- Define hardness of water.
- What is soap? How does soap react with hard water and soft water?
- Explain the cleansing action of soap.
- Illustrate with reactions the formation of a “curdy white precipitate” formed when bore well water is used for bathing.
- How is the total hardness of water calculated?
- Define temporary hardness. How can it be removed?
- What is permanent hardness? How is it different from temporary hardness?
- What are the different units used to express hardness of water?
- What is the relationship between different units of hardness?

2.4 Determination of Hardness of Water

The hardness of water may be determined by a semi-quantitative method – the soap solution method or a more reliable quantitative method – complexometric titration with EDTA.

Soap Solution Method***Principle***

The soap solution method for determination of hardness is based on the principle that when soap solution is added to hard water, it will not produce lather until all the hardness-causing ions have been precipitated out.

The permanent and temporary hardness of water can be estimated using this method. Total hardness can be determined by titrating an aliquot of hard water against standard soap solution. Then a similar aliquot is boiled to remove the temporary hardness and the resulting liquid is titrated against the standard soap solution for permanent hardness. The difference between the two readings will indicate temporary hardness.

Procedure

A standard soap solution is prepared by dissolving 100 g of sodium stearate in 800 cm³ of alcohol and the resultant solution is diluted to 1 l with distilled water.

Standard hard water (1 g CaCO₃/l) is prepared by dissolving 1.0 g dry CaCO₃ in minimum amount of 1:1 HCl. Resultant solution is evaporated to dryness and the residue is dissolved in distilled water and diluted to 1 l.

The following four estimations are carried out using these standard solutions:

- Lather factor of distilled water:** For this, 50 cm³ of distilled water is titrated against soap solution till lather persists for 2 min after shaking and standing (V_1 cm³).
- Standardization of soap solution:** For this, 50 cm³ of standard hard water is titrated against soap solution till lather persists for 2 min after shaking and standing (V_2 cm³).
- Total hardness of unknown hard water sample:** For this, 50 cm³ of unknown hard water is titrated against soap solution till lather persists for 2 min after shaking and standing (V_3 cm³).
- Permanent hardness in unknown hard water sample:** For this, 250 cm³ of hard water is boiled till it evaporates to one-third of its original volume. It is then filtered and precipitated, and the filter paper washed with distilled water. Filtrate along with washings are transferred to a 250 cm³ standard volumetric flask and diluted to 250 cm³ with distilled water. Then, 50 cm³ of the above sample is titrated against soap solution till lather persists for 2 min after shaking and standing. (V_4 cm³).

Calculations

The following have been determined from the above procedure.

50 cm³ of distilled water required V_1 cm³ of soap solution.

50 cm³ of standard hard water required V_2 cm³ of soap solution.

50 cm³ of unknown hard water required V_3 cm³ of soap solution.

50 cm³ of boiled hard water required V_4 cm³ of soap solution.

Using these, we can calculate the total hardness of water as follows:

50 cm³ of standard hard water = $(V_2 - V_1)$ cm³ soap solution

or 50 mg CaCO₃ = $(V_2 - V_1)$ cm³ soap solution

or 1 cm³ soap solution = $50/(V_2 - V_1)$ mg CaCO₃.

50 cm³ of unknown hard water = $(V_3 - V_1)$ cm³ soap solution

or, 50 cm³ unknown hard water = $(V_3 - V_1) \times 50/(V_2 - V_1)$ mg CaCO₃.

Thus, 50 cm³ of unknown hard water contains $50 \times (V_3 - V_1)/(V_2 - V_1)$ mg CaCO₃

or 1000 cm³ of unknown hard water contains $1000 \times (V_3 - V_1)/(V_2 - V_1)$ mg CaCO₃ hardness.

Thus,

$$\text{Total hardness} = 1000 \times \frac{V_3 - V_1}{V_2 - V_1} \text{ mg/l}$$

Using this value of total hardness, the temporary and permanent hardness can be calculated as follows:

50 cm³ of boiled water = $(V_4 - V_1)$ cm³ soap solution

or 50 cm³ boiled water = $\frac{(V_4 - V_1) \times 50}{(V_2 - V_1)}$ mg CaCO₃

Thus, 50 cm³ of boiled water contains $\frac{50 \times (V_4 - V_1)}{(V_2 - V_1)}$ mg CaCO₃

and 1000 cm³ of boiled water contains $1000 \times \frac{(V_4 - V_1)}{(V_2 - V_1)}$ mg CaCO₃ hardness.

Thus, permanent hardness = $1000 \times (V_4 - V_1)/(V_2 - V_1)$ mg/l.

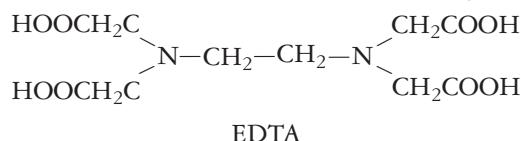
Hence, temporary hardness = total hardness – permanent hardness

$$= 1000 \times \frac{V_3 - V_4}{V_2 - V_1} \text{ mg/l}$$

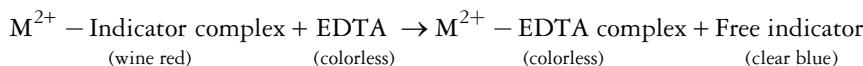
Complexometric Titration Method using EDTA

Principle

Hardness of water is mainly due to the presence of calcium and magnesium salts in it. Total hardness is the sum of temporary hardness (due to bicarbonates of calcium and magnesium) and permanent hardness (due to chlorides, sulphates, etc., of calcium and magnesium). Ethylenediamine tetraacetic acid (EDTA) is a reagent, which reacts with metal ions like Ca^{2+} , Mg^{2+} forming complex compounds. Therefore, this reagent can be used to determine the concentration of hardness-causing substances.



The completion of the reaction (end point of the titration) is identified using Eriochrome black-T (EBT) indicator. This is an organic dye, blue in color. It also forms relatively less stable complexes with bivalent metal ions of Ca, Mg, etc., which are wine red in color. Therefore, on addition of the indicator to hard water, it first reacts with free metal ions to give a wine red color. When EDTA is added, it attacks the metal–indicator complex and sets the indicator free. The reaction can be represented as



So, at the end point a change from wine red to blue color is observed. Since the reaction involves the liberation of H^+ ions and the indicator is sensitive to the concentration of H^+ ions (pH) of the solution, a constant pH of around 10 has to be maintained. For this purpose, ammonia–ammonium chloride buffer is used.

Procedure

A standard solution of EDTA is prepared by dissolving a known amount of EDTA (4–6 g) in 100–150 ml of deionized water and 4 ml NaOH and then making up the volume in a 250 ml volumetric flask.

About 25 ml of the given sample of hard water is taken in a clean conical flask and 3 ml of NH_3- NH_4Cl buffer followed by 5–6 drops of EBT indicator is added to it. This solution is titrated against standard EDTA solution to get concordance values (V ml).

Calculations

The strength of the EDTA solution may be calculated as:

Weight of EDTA dissolved in 250 ml of water = _____ g

Weight of EDTA dissolved per liter = _____ g \times 4

$$\text{Molarity of EDTA solution} = \frac{\text{_____ g} \times 4}{372.4} = \alpha \text{ M (say)}$$

We know that 1000 ml of 1 M EDTA \equiv 100 g of CaCO_3 . So,

$$V \text{ ml of a M EDTA} = \frac{100 \times V \times \alpha}{1000} \text{ g of } \text{CaCO}_3 = y \text{ g of } \text{CaCO}_3$$

25 ml of hard water contains y g of CaCO_3

Therefore, 10^6 ml of hard water sample contain

$$\frac{y \times 10^6}{25} \text{ g of } \text{CaCO}_3 = \frac{y}{25} \text{ ppm}$$

So, total hardness of water = ____ ppm.

Permanent hardness of water can be determined by titrating the water sample against standard EDTA solution after removal of temporary hardness by boiling the water sample. The difference between total and permanent hardness gives the temporary hardness.

Problem 5

A 100 ml sample of water required 13.5 ml of 0.02 M EDTA solution for titration using Eriochrome black-T as indicator. Another 100 ml of water from the same source was boiled and precipitate removed by filtration. The filtrate required 6 ml of 0.02 M EDTA for titration. Calculate the total hardness, permanent hardness and carbonate hardness of water sample.

Solution

From the stoichiometric reaction:

$$1000 \text{ ml of 1 M EDTA} = 100 \text{ g of } \text{CaCO}_3$$

$$1 \text{ ml of 1 M EDTA} = 100 \text{ mg of } \text{CaCO}_3$$

$$\text{Using } M_1 V_1 = M_2 V_2$$

$$13.5 \text{ ml of 0.02 M EDTA} = 0.27 \text{ ml of 1 M EDTA.}$$

Therefore,

$$0.2 \text{ ml of 1 M EDTA} = 100 \times 0.27 = 27 \text{ mg of } \text{CaCO}_3 \text{ in 100 ml water.}$$

$$\text{Total hardness} = 270 \text{ mg/l of } \text{CaCO}_3.$$

Similarly, in titration after boiling the water:

$$6 \text{ ml of 0.02 M EDTA} = 0.12 \text{ ml of 1 M EDTA.}$$

Therefore,

$$0.12 \text{ ml of EDTA} = 100 \times 0.12 = 12 \text{ mg of } \text{CaCO}_3 \text{ per 100 ml of water.}$$

$$\text{Permanent hardness} = 120 \text{ mg/l of } \text{CaCO}_3.$$

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 270 - 120 = 150 \text{ mg/l.}$$

Problem 6

One gram of CaCO_3 was dissolved in dilute HCl and the solution diluted to 1 l. Then 100 ml of this solution required 90 ml of EDTA solution. Also, 100 ml of water sample contain 36 ml of same EDTA solution. The water sample (100 ml) on boiling was titrated against 18 ml of EDTA solution. Calculate the total and permanent hardness.

Solution

The standard solution contains 1 g/l of CaCO_3 . Therefore, 100 ml of solution contains 100 mg CaCO_3 . Now, 90 ml of EDTA is required for 100 ml of CaCO_3 solution. So,

$$90 \text{ ml EDTA} = 100 \text{ mg } \text{CaCO}_3$$

or

$$1 \text{ ml EDTA} = \frac{100}{90} \text{ mg } \text{CaCO}_3$$

(a) In 100 ml of water sample:

36 ml of EDTA is required for 100 ml of water sample, so

$$1 \text{ ml EDTA is required for } \frac{100}{90} \text{ mg CaCO}_3$$

$$36 \text{ ml is required for } \frac{100}{90} \times 36 \text{ mg of CaCO}_3 = 40 \text{ mg of CaCO}_3$$

Therefore, 100 ml of water sample contain 40 mg of CaCO_3 ,

or 1000 ml of water sample contain 400 mg of CaCO_3 .

Hence, the total hardness of water is 400 mg/l.

(b) In 100 ml of water sample after boiling:

18 ml of EDTA is required for 100 ml of water sample

$$1 \text{ ml of EDTA is required for } \frac{100}{90} \text{ mg CaCO}_3$$

Therefore,

$$\frac{100}{90} \times 18 \text{ mg CaCO}_3 = 20 \text{ mg CaCO}_3$$

Now, 100 ml of water sample after boiling contain 200 mg CaCO_3 . Thus permanent hardness of water sample is 200 mg/l.

Problem 7

Calculate the hardness of water sample, 10 ml of which required 20 ml EDTA. Given that 20 ml of CaCl_2 solution whose strength is equivalent to 1.5 g of CaCO_3 per liter required 30 ml EDTA solution.

Solution

A CaCl_2 solution with strength equivalent to 1.5 g of CaCO_3 per liter, implies that:

$$\begin{aligned} 1000 \text{ ml CaCl}_2 \text{ solution} &= 1.5 \text{ g of CaCO}_3 \text{ equivalent hardness} \\ &= 1500 \text{ mg of CaCO}_3 \text{ equivalent hardness} \end{aligned}$$

Therefore,

$$1 \text{ ml CaCl}_2 \text{ solution contains} = 1.5 \text{ mg CaCO}_3 \text{ equivalent hardness}$$

Given that:

30 ml EDTA solution required for 20 ml of CaCl_2 solution

30 ml EDTA solution is required for $20 \times 1.5 \text{ mg of CaCO}_3 = 30 \text{ mg of CaCO}_3$

1 ml EDTA solution is required for $30/30 = 1 \text{ mg of CaCO}_3$

10 ml of hard water sample requires = $20 \text{ ml EDTA} = 20 \times 1 \text{ mg of CaCO}_3$

Therefore, 1 l of hard water sample requires = 2000 mg of CaCO_3 .

Hardness of water sample is 2000 mg/l or 2000 ppm.

Concept Check

- What is a complexometric titration?
- Write the formula of EDTA.
- What is the change of color observed during the complexometric determination of hardness of water with EDTA? Write reactions to support your answer.
- Which indicator is used in the above titration? What role does it play?
- Explain the procedure of preparing standard EDTA solution. Why is the EDTA solution called standard?
- What is the purpose of adding a buffer to the sample solution? Which buffer is used for this experiment?
- How is the molarity of EDTA calculated?

2.5 Disadvantages of Hard Water

Water is used extensively in industry and for domestic purposes. The quality of water required for both purposes differs, but the presence of hardness in water has many disadvantages both in industrial and domestic uses.

Domestic Purposes

Presence of hardness affects the domestic uses of water described as follows:

1. **Laundering:** Laundering clothes in hard water results in the formation of a white precipitate that sticks to the clothes, making them harsh and scratchy. As a result of this, fabric softeners have to be used which shortens the life of clothes.
2. **Bathing:** As explained earlier, soap does not form a soft lather with hard water. Since lather is not formed the dirt does not get trapped in soap bubbles, but remains on the skin and is difficult to remove. Thus, the cleansing effect of soap does not work with hard water. The curdy precipitate also sticks to the hair and makes it greasy and lifeless.
3. **Dishwashing:** The cleansing action of soaps is reduced even further when it comes in contact with hot hard water, as it releases more minerals on contact. Thus, the dishes, instead of getting washed become more spotted and this reduces the quality of the crockery over a few washes.

Industrial Purposes

In industry, water is used mainly to generate steam for cooling and sometimes directly as solvent. The disadvantages of hard water used for industrial purposes are described as follows:

1. **Sugar industry:** Water used in the sugar industry must be free from bacteria, sulphates, nitrates and carbonates, which, if present, do not allow sugar to crystallize properly and the stability of sugar is affected.
2. **Concrete industry:** Water free of chloride and sulphate ions is mandatory for the concrete industry, as the presence of these ions compromises the hardenability of concrete.
3. **Pharmaceutical industry:** Water used in the pharmaceutical industry needs to be extra pure and free from hazardous ions and microorganisms.
4. **Textile industry:** Water is extensively used in the textile industry. Clothes are subjected to extensive washing, rinsing, dyeing and bleaching actions. As such the water needs to be soft, free from hardness-causing cations, which if present would result in excessive and unnecessary use of

water for washing purpose. The texture of clothes would also get affected if hard water is used. The water should also be free from iron and manganese salts, which cause staining.

5. **Dyeing industry:** The presence of cations in water used for dyeing can result in a change in color from what is desired. Hence, water for the dyeing industry needs to be free from color-altering cations.
6. **Water boilers and pipes:** Hard water contains dissolved salts of calcium and magnesium. When this water comes in contact with heating appliances, these salts precipitate out and form limescale deposits on the appliances. Due to these scales, there is wastage of energy for heating purposes (upto 25%), and the appliances may also fail after regular usage. Furthermore, pipes carrying hard water often get clogged with the limescale deposits, and thus have to be replaced after only a few years.

Concept Check

- Enumerate the disadvantages of hard water used for domestic purpose. How can they be overcome?
- What are the disadvantages of hard water when used in different industries?

2.6 Alkalinity of Water

Alkalinity can be defined as the ability of water to neutralize acids. Alkalinity of water is due to the presence of carbonates, bicarbonates and hydroxides of sodium, potassium, magnesium and calcium present alone or in combination. However, hydroxide and bicarbonates cannot exist together as they react to form carbonate ions.

Naturally occurring alkalinity in water functions as the Earth's natural buffering system. Even when small amounts of strong acids, in the form of acid rain, get added to natural water, the water resists the change in pH. The acid converts carbonates to bicarbonates and converts bicarbonates to carbon dioxide, with both reactions resulting in very little change in pH of water.

Theoretically, a pH of 7.0 represents a neutral system, with a higher pH being alkaline and lower pH being acidic. However, in water chemistry, the neutral pH is not achieved as some alkalinity is present, even at a pH of 5.

Types of Alkalinity

1. **Carbon dioxide alkalinity:** At a pH of 4.2–4.5 or lower, all alkalinity is in the form of carbon dioxide.
2. **Carbon dioxide and bicarbonate alkalinity:** Carbon dioxide and bicarbonate are in a balance between the pH range of 4.2–4.5 at the low end and 8.2–8.4 at the high end. At a pH of 8.2–8.4, there is no carbon dioxide and all alkalinity is in form of bicarbonate.
3. **Bicarbonate and carbonate alkalinity:** Bicarbonate and carbonate are in a balance between the pH range of 8.2–8.4 at the low end and 9.6 at the high end. At a pH of 9.6, there is no carbon dioxide or bicarbonate, and all alkalinity is in form of carbonate.
4. **Hydroxyl alkalinity:** As the pH increases above 9.6, hydroxyl alkalinity starts to occur. Most naturally occurring water sources have pH between 6 and 8.4, so the presence of hydroxides is the result of manmade activity.

Significance of Alkalinity of Water

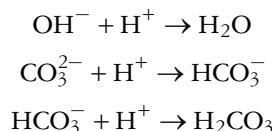
Alkaline compounds such as bicarbonates, carbonates, and hydroxides lower the acidity of the water by combining with the H⁺ ions to form new compounds. Thus, it imparts an acid-neutralizing capacity to water, without which any acid added to it would cause an immediate change in the pH. By measuring the alkalinity of water, one can assess the water sample's ability to neutralize acidic pollution from rainfall or wastewater. The alkalinity in water is influenced by rocks and soils, salts, plant processes, and industrial wastewater discharges. The amount of alkalinity in water determines its suitability for irrigation processes or wastewater treatment processes. It is usually measured in terms of equivalents of calcium carbonate (CaCO₃).

Estimation of Alkalinity

The estimation of alkalinity due to the presence of different ions can be carried out by titration of water with a standard acid solution in the presence of appropriate indicators, that is, phenolphthalein and methyl orange. Volume of acid used up to phenolphthalein end point corresponds to the complete neutralization of hydroxide ions and half-neutralization of carbonate ions (up to the formation of bicarbonate ions) and is known as P-alkalinity. The volume of acid used up to methyl orange point corresponds to the complete neutralization of hydroxide, carbonate and bicarbonate ions and is known as total or M-alkalinity.

Principle

The volume of acid used can be used to determine the strength of various ions which can be determined using volume of acid.



The M-alkalinity measurement is based on a sulphuric acid titration using methyl orange as indicator that changes from yellow at a pH of 4.5 to orange at a pH of 4.4 at the end point.

The P-alkalinity measurement is based on a sulphuric acid titration using phenolphthalein indicator that changes from pink at a pH of 8.3 to colorless at a pH of 8.2 at the end point.

Procedure

About 100 ml of water sample is taken in a conical flask and 2–3 drops of phenolphthalein indicator are added to it. Titration is carried out against standard sulphuric acid solution till the disappearance of pink color. The titre value (V₁ ml) is noted. Then 2–3 drops of methyl orange indicator are added to the same solution and titrated further with acid solution till the orange color develops. The titre value is noted (V₂).

Calculations

Volume of water sample = 100 ml.

Strength of acid = x N.

Volume of acid used for P-alkalinity = V₁.

Volume of acid for M-alkalinity = V₁ + V₂.

$$\text{P-alkalinity in terms of CaCO}_3 \text{ equivalents} = \frac{V_1 \times x \times 50}{100} \text{ g/l} = \frac{V_1 \times x \times 50 \times 10^6}{10^5} \text{ ppm}$$

$$\text{M-alkalinity in terms of } \text{CaCO}_3 \text{ equivalents} = \frac{(V_1 + V_2) \times x \times 50 \times 10^6}{10^5} \text{ ppm}$$

The interpretation of the results is summarized in Table 1:

Table 1 Interpretation of alkalinity values

Alkalinity	OH^-	CO_3^{2-}	HCO_3^-
$P = 0$	0	0	M
$P = (1/2)M$	0	$2P$	0
$P < (1/2)M$	0	$2P$	$M - 2P$
$P > (1/2)M$	$2P - M$	$2(M - P)$	0
$P = M$	P	0	0

Problem 8

A 100 ml water sample required 25 ml of 0.05 N sulphuric acid for phenolphthalein end point and another 10 ml for methyl orange end point. Determine the nature and amount of alkalinity present in water.

Solution

Given that

Volume of water sample = 100 ml.

Volume of sulphuric acid for phenolphthalein end point = 25 ml.

Normality of sulphuric acid = 0.05 N.

Using $N_1 V_1 = N_2 V_2$, normality of phenolphthalein alkalinity is:

$$N_1 = \frac{0.05 \times 25}{100}$$

Phenolphthalein alkalinity in terms of CaCO_3 equivalent is

$$\text{P-alkalinity} = \frac{0.05 \times 25}{100} \times 50 \text{ g/l} = 0.625 \text{ g/l} = 625 \text{ mg/l} = 625 \text{ ppm}$$

Volume of sulphuric acid consumed for methyl orange end point = $25 + 10 = 35$ ml.

Using $N_1 V_1 = N_2 V_2$, normality of methyl orange alkalinity is:

$$N_1 = \frac{35 \times 0.05}{100}$$

Methyl orange alkalinity in terms of CaCO_3 equivalents is

$$\text{M-alkalinity} = \frac{35 \times 0.05}{100} \times 50 \text{ g/l} = 0.875 \text{ g/l} = 875 \text{ mg/l} = 875 \text{ ppm}$$

Since P-alkalinity $>$ M-alkalinity/2, alkalinity is due to both OH^- and carbonate ions.

Alkalinity due to carbonate ions = $2(\text{M-alkalinity} - \text{P-alkalinity}) = 2(875 - 625) = 500$ ppm.

Alkalinity due to hydroxyl ions = $2(\text{P-alkalinity}) - \text{M-alkalinity} = 375$ ppm.

Problem 9

A water sample is not alkaline to phenolphthalein. However, 100 ml of the water sample reached the end point of titration using methyl orange as indicator with 36.5 ml of 0.02 N HCl. What are the types and amounts of alkalinity present in water?

Solution

The water is not alkaline to phenolphthalein implies that hydroxyl and carbonate ions are both absent. The alkalinity of water is due to bicarbonate ions which is measured using methyl orange as indicator.

For measurement of bicarbonate alkalinity, it is given that:

$$\text{Volume of water sample} = 100 \text{ ml.}$$

$$\text{Volume of HCl for methyl orange end point} = 36.5 \text{ ml.}$$

$$\text{Normality of HCl} = 0.02 \text{ N.}$$

Using $N_1 V_1 = N_2 V_2$, normality of methyl orange alkalinity is

$$N_{\text{methyl orange}} = \frac{0.02 \times 36.5}{100}$$

Methyl orange alkalinity in terms of CaCO_3 equivalent is

$$\frac{0.02 \times 36.5}{100} \times 50 = 0.365 \text{ g/l} = 365 \text{ mg/l} = 365 \text{ ppm}$$

Problem 10

The carbonate alkalinity of a water sample was found to be 75 ppm CaCO_3 equivalent. After carrying out lime treatment, the alkalinity of water was found to increase to 300 ppm CaCO_3 equivalent. Calculate the excess amount of Ca(OH)_2 present in water after lime treatment. Express in terms of mg/l of Ca(OH)_2 .

Solution

Total alkalinity (A_t) = Alkalinity (hydroxide) (A_h) + Alkalinity (carbonate) (A_c)

Given that $A_t = 300$ ppm and $A_c = 75$ ppm. Therefore,

$$A_h = A_t - A_c = 300 - 75 = 225 \text{ ppm } \text{CaCO}_3 \text{ equivalent}$$

Since alkalinity due to hydroxide ions will arise from the presence of excess Ca(OH)_2 in water, so

$$\begin{aligned} \text{Excessive amount of } \text{Ca(OH)}_2 &= 225 \text{ ppm } \text{CaCO}_3 \text{ equivalent} \\ &= 225 \text{ mg/l of } \text{CaCO}_3 \\ &= \frac{225 \times 74}{100} \text{ mg/l of } \text{CaCO}_3 \\ &= 166.5 \text{ mg/l of } \text{Ca(OH)}_2 \end{aligned}$$

Problem 11

Amounts of 400 mg NaOH and 256 mg Na_2CO_3 are dissolved in 5 l of distilled water. Determine the alkalinity due to carbonate and hydroxide ions. Express in terms of mg/l.

Solution

Given that

5 l of water contain 400 mg NaOH.

1 l of water contains $400/5 = 80$ mg NaOH.

Therefore, strength of NaOH = 80 mg/l.

Alkalinity due to OH is

$$\frac{80}{\text{Equivalent weight of NaOH}} = \frac{80}{40} = 2 \text{ mg equiv./l}$$

5 l of water contains 256 mg Na_2CO_3 .

1 l of water contains $256/5 = 51.2$ mg/l.

Therefore, the strength of $\text{Na}_2\text{CO}_3 = 51.2$ mg/l.

Alkalinity due to Na_2CO_3 is

$$\frac{51.2}{\text{Equivalent weight of } \text{Na}_2\text{CO}_3} = \frac{51.2}{53} = 0.966 \text{ mg equiv./l}$$

Concept Check

- Define alkalinity of water.
- What are the different types of alkalinity?
- How is alkalinity of water determined using indicator method?

2.7 Analysis of Water

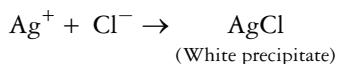
Apart from the hardness causing ions, water has a lot of other ions mixed in it, for example, chlorides, sulphates, phosphates, nitrates, fluorides, iron, etc., which add to the impurity of water. In order to check the purity of water, a range of experiments are carried out, a few of which are described in detail in the following subsections.

Determination of Chlorides by Argentometric Method

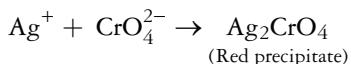
Chlorides occur widely in water and wastewaters and are usually associated with Na^+ ion. Although chlorides are not harmful, concentration beyond 250 mg/l imparts a peculiar taste to water rendering it unacceptable for drinking purpose.

Principle

Chloride ion is determined by titration of the water sample with standard AgNO_3 in a neutral to slightly alkaline condition. Chloride ions react with silver ions and form a white precipitate.



Once all the chloride ions are used up, the silver ions react with the chromate ion from potassium chromate to form a red colored silver chromate precipitate.



End point of the titration is the appearance of a red colored persistent precipitate.

Procedure

Standard sodium chloride (0.0141 M) is prepared by dissolving 824.0 mg NaCl (dried at 140°C) in H₂O and making up to 1000 ml.

Standard silver nitrate titrant (0.0141 M) is prepared by dissolving 2.395 g AgNO₃ in H₂O and making up to 1000 ml. Standardize against 0.0141 M NaCl.

To 25 ml of water sample in a graduated cylinder, add 5 drops of chromate indicator solution and titrate with silver nitrate solution until a pinkish or reddish tinge persists in the yellow solution.

Calculations

Normality of silver nitrate solution = N₁.

Volume of silver nitrate used = V₁.

$$\text{Normality of chloride in water sample} = \frac{N_1 V_1}{100}$$

$$\text{Amount of chlorine} = \frac{N_1 V_1}{100} \times 35.5 \text{ g/l} = \frac{N_1 \times V_1 \times 50 \times 10^6}{10^5} \text{ ppm equivalents of CaCO}_3$$

Determination of Fluoride by SPADNS Method

Fluoride ions have dual significance in water supplies. While excess of fluoride causes disfiguration of teeth, a concentration less than 0.8 mg/l causes dental cavities. The optimum concentration to be maintained is 0.8–1.0 mg/l.

Principle

Under the acidic conditions, fluorides react with zirconium SPADNS [Sodium 2-(*p*-sulphophenylazo)-1,8-dihydroxy-3,6-naphthalene disulphonate] solution and color of SPADNS reagent gets bleached. Bleaching is a function of fluoride ions and is directly proportional to the concentration of fluoride ions.

Procedure

The reagent is prepared by dissolving 958 mg of SPADNS in distilled water and diluting it to 500 ml in a flask. Then in a separate flask, 133 mg of zirconyl chloride octahydrate (ZrCl₂·8H₂O) is dissolved in 25 ml distilled water, to which 350 ml of concentrated HCl is added and the solution is diluted to 500 ml with distilled water. Equal volumes of SPADNS solution and zirconyl acid solutions are mixed.

Stock solution of fluoride is prepared by dissolving 0.221 g of anhydrous sodium fluoride in water and then making up the volume to 1 l. The solution is diluted to get a standard solution of 10 mg/l of fluoride. Then 1 ml, 2 ml, 3 ml, 4 ml, 5 ml and 6 ml of this solution is pipetted out into six 50 ml standard flasks.

To each of the six flasks, 10 ml of zirconyl-SPADNS reagent and 1 drop of NaAsO_2 (to remove residual chlorine) are added. The solutions are diluted up to the mark and mixed well.

The absorbances of the solutions are measured at 570 nm against a blank reagent and a calibration curve is drawn by plotting absorbance against concentrations using colorimeter.

For determination of fluoride in water sample, suitable aliquots are taken, 10 ml of zirconyl-SPADNS reagent is added and absorbance is measured. Using the calibration curve, the concentration of fluoride can be calculated.

Determination of Nitrate by Phenol Disulphonic Method

High nitrate levels may be found in water close to agricultural land where fertilizers may be extensively used. High levels of nitrate in water can cause methemoglobinemia or blue baby syndrome, diuresis and hemorrhaging of spleen. The maximum contaminant level (MCL) in drinking water as nitrate (NO_3^-) is 45 mg/l, whereas the MCL as nitrate-nitrogen is 10 mg/l.

Principle

Nitrate reacts with phenoldisulphonic acid (PDA) to produce a nitro derivative, which in alkaline solution develops a yellow color. The development of yellow color is attributed to rearrangement in the structure of the nitro derivative. The development of color in the solution follows Beer's law and is proportional to the concentration of NO_3^- present in the sample. The concentration of NO_3^- is determined using a colorimeter or spectrophotometer. A standard calibration curve is prepared by measuring the absorbance of a series of standard solutions of PDA and plotting them against concentration.

Procedure

The standard PDA solution is prepared by dissolving 12.5 g in 75 ml of concentrated sulphuric acid, making up the volume to 150 ml and then heating in a water bath for 2 h. A calibration curve is plotted by using suitable aliquots of standard nitrate (KNO_3) solution in 5–500 mg NO_3^- range. Then 5 ml, 10 ml, 15 ml, 20 ml and 25 ml of standard KNO_3 solutions are taken in 5 separate beakers and evaporated to dryness on a hot plate. To each of them, 2 ml of PDA is added and the residue is dissolved. Then, 10 ml of concentrated NH_3 (to develop color) is added and diluted to 100 ml standard volumetric flasks. The contents were mixed well and the solutions from each of the standard flasks are transferred to a cuvette. The absorbance is measured at 410 nm wavelength filter using colorimeter.

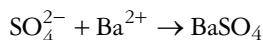
The nitrate content of water sample is determined by taking 25 ml of the given water sample in a beaker and evaporated to dryness on a hot plate. Then 2 ml of PDA is added into the beaker and the residue is dissolved. Following this, 10 ml of concentrated NH_3 is added (to develop color) and the solution is diluted to 100 ml standard volumetric flask. Contents were mixed well and the solution from the standard flask is transferred to a cuvette. The absorbance is measured at 410 nm wavelength filter using a colorimeter. The concentration of NO_3^- in the water sample is determined using the calibration curve.

Determination of Sulphate by Gravimetric Method

The presence of sulphates in drinking water can give it a noticeable taste. The maximum permitted level for sulphate that does not affect the taste of water appreciably is less than or equal to 500 mg/l.

Principle

The sulphate ions in a sample are precipitated by the addition of barium chloride solution to water sample acidified with hydrochloric acid and kept near the boiling point.



In highly alkaline water maintained near the boiling temperature, BaCO_3 may get precipitated and to eliminate this, the sample is acidified. To precipitate sulphate ions as completely as possible, excess barium chloride is used. The precipitate of BaSO_4 is highly insoluble and hence there is considerable tendency for most of the precipitate to form in colloidal condition, which cannot be removed by ordinary filtration procedures. To facilitate the conversion of colloidal form to crystalline form, the samples at temperatures near the boiling point for a few hours are digested.

The precipitate is filtered, washed, dried and weighed as BaSO_4 . This gravimetric method gives the most accurate results and is the recommended procedure for sulphate concentrations above 10 mg/ml.

Procedure

The reagent used is 5% barium chloride solution. About 200 ml of water sample is transferred into a beaker. Two drops of methyl red indicator are added to it. Concentrated HCl is added to it drop by drop till the color changes to pink after which two drops are added in excess. The solution is heated to nearly boiling and the volume is reduced to 50 ml. Hot barium chloride solution is added to it, with stirring until the formation of white precipitate is complete after which two drops are added in excess. The precipitate (BaSO_4) is digested for about 2 h (or until the precipitate settles down). It is filtered quantitatively by ashless filter paper and washed several times with distilled water until the washings are free from chloride ions. The precipitate along with filter paper is ignited in a previously weighed Gooch crucible at 800–900°C till all traces of filter paper are burnt. The crucible is cooled in a desiccator and weighed. Let the amount of BaSO_4 precipitated be W g.

Calculations

We know that, 233.4 g of BaSO_4 contains 96.06 g of sulphate.

Therefore, W g of BaSO_4 contains $\frac{96.06 \times W}{233.4}$ g of sulphate.

That is, 200 ml of water sample contain $\frac{96.06 \times W}{233.4}$ g of sulphate.

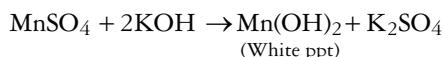
Therefore, 1000 ml of water sample contain

$$\frac{96.06 \times W \times 1000}{233.4 \times 200} \text{ g of sulphate}$$

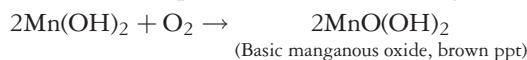
Determination of Dissolved Oxygen by Winkler's Method

Principle

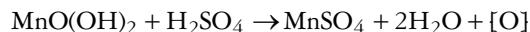
In this method, the water sample is taken and divalent manganese solution along with alkaline potassium iodide solution is added to it.



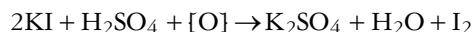
The dissolved oxygen present in water sample oxidizes divalent manganese to tetravalent manganese.



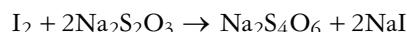
This basic manganic oxide formed acts as an oxygen carrier to enable the dissolved oxygen in molecular form to take part in the reaction. Upon acidification, the tetravalent manganese reverts to divalent state with the liberation of nascent oxygen.



This nascent oxygen oxidizes KI to I₂.



The liberated iodine is titrated against standard sodium thiosulphate solution using starch indicator.



Procedure

In a clean glass stoppered bottle, add 300 ml of water sample. Then 3 ml of manganous sulphate and 3 ml of alkaline potassium iodide solution are added.

Stopper the bottle and shake well to allow the precipitate to settle down. Add 1 ml of concentrated sulphuric acid slowly and mix well until the precipitate dissolves completely. Pipette out 100 ml of this solution into a clean conical flask and slowly titrate against standard sodium thiosulphate solution using 2 ml of starch indicator towards the end point. The value of dissolved oxygen in water can be calculated using volume of sodium thiosulphate solution used.

Calculations

$$\text{Normality} \times \text{Volume of oxygen solution} = \text{Normality} \times \text{Volume of Na}_2\text{S}_2\text{O}_3$$

Therefore,

$$\text{Normality of oxygen solution} = (\text{Normality} \times \text{Volume of Na}_2\text{S}_2\text{O}_3) / \text{Volume of oxygen solution}$$

$$= \frac{N \times V}{100} = \alpha N$$

Hence, weight of dissolved oxygen per liter is

$$\text{Normality} \times \text{Equivalent weight of oxygen} = \alpha \times 8.0 \times 1000 = \text{mg/l.}$$

Concept Check

- What is the argentometric method? Justify the name.
- What is the role of potassium dichromate in the argentometric method?
- Fluorides have a dual significance in water. Explain the statement.
- How is the colorimetric estimation of fluorine by SPADNS method performed?
- How is the nitrate ion determined by the phenol disulphonic acid method?
- How is the sulphate ion determined using gravimetry?
- How is the amount of dissolved oxygen in water determined by Winkler's method?

2.8 Water Quality Parameters

The raw or treated water is analyzed by testing their physical, chemical and bacteriological characteristics as described in the following subsections.

Physical Characteristics

The physical characteristics on which water quality depends are listed as follows:

1. **Turbidity:** A large amount of suspended solids present in water make it turbid. The turbidity depends upon fineness and concentration of particles present in water. Turbidity is measured by applying Nephelometry, in which level of light scattered by the particles at right angles to the incident light beam is measured. This scattered light level is proportional to the particle concentration in the sample. The unit of expression is *Nephelometric Turbidity Unit* (NTU). The Indian Standard value for drinking water is 10–25 NTU.
2. **Color:** The dissolved organic matter from decaying vegetation or some inorganic materials may impart color to the water. It can be measured by comparing the color of water sample with other standard glass tubes containing solutions of different standard color intensities. The standard unit of color is that which is produced by one milligram of platinum cobalt dissolved in one liter of distilled water. The Indian Standard value for treated water is 5–25 cobalt units.
3. **Taste and odor:** Most organic and some inorganic chemicals, originating from municipal or industrial wastes, contribute taste and odor to the water. These can be expressed in terms of odor intensity or threshold values.
4. **Temperature:** The increase in temperature decreases palatability because at elevated temperatures, carbon dioxide and some other volatile gases are expelled. The ideal temperature of water for drinking purposes is 5–12°C.

Chemical Characteristics

The chemical characteristics on which water quality depends are listed as follows:

1. **pH:** The concentration of hydrogen ions is commonly expressed in terms of the pH scale. Low pH corresponds to high hydrogen ion concentration and vice versa. A substance that when added to water increases the concentration of hydrogen ions (lowers the pH) is called an acid. A substance that reduces the concentration of hydrogen ions (raises the pH) is called a base. It is expressed on a scale ranging from 0 to 14, which is the common logarithm of the reciprocal of the hydrogen ion concentration. The recommended pH range for treated drinking waters is 6.5–8.5.
2. **Acidity:** The acidity of water is a measure of its capacity to neutralize bases. It may be caused by the presence of uncombined carbon dioxide, mineral acids and salts of strong acids and weak bases in water. It is expressed as mg/l in terms of calcium carbonate. It is important to measure acidity of water as presence of carbon dioxide causes corrosion in public water supply systems.
3. **Alkalinity:** The alkalinity of water is a measure of its capacity to neutralize acids. It is expressed as mg/l in terms of calcium carbonate. The various forms of alkalinity are (a) hydroxide alkalinity, (b) carbonate alkalinity, (c) hydroxide plus carbonate alkalinity, (d) carbonate plus bicarbonate alkalinity and (e) bicarbonate alkalinity. The measure of alkalinity is useful mainly in water softening and boiler feed water processes. It has been discussed in greater detail in Section 2.5.
4. **Hardness:** It is a characteristic property of water that prevents lathering of soap. It is caused by the presence of bicarbonates, sulphates, chlorides of calcium and magnesium. Hardness of water and its estimation has been discussed in detail in Sections 2.3 and 2.4.
5. **Chlorides:** Chloride ions may be present in combination with one or more of the cations of calcium, magnesium, iron and sodium. These chlorides have high solubility in water. Chlorides are not harmful but their concentration beyond 250 mg/l imparts a peculiar taste to water as discussed in Section 2.7.

6. **Sulphates:** These occur in water due to leaching from sulphate mineral and oxidation of sulphides. Sulphates are associated generally with calcium, magnesium and sodium ions. Sulphate in drinking water causes a laxative effect and leads to scale formation in boilers. It also causes odor and corrosion problems under aerobic conditions. Desirable limit for drinking water is 200 mg/l which may be extended up to 400 mg/l.
7. **Iron:** Iron dissolves in water to form ferrous bicarbonate under favorable conditions. Ferrous bicarbonate formed is oxidized into ferric hydroxide, which precipitates out. Under anaerobic conditions, ferric ion is reduced to soluble ferrous ion. Iron can impart bad taste to the water, cause discoloration in clothes and incrustations in water pipelines. Indian Standard value for drinking water is 0.3 to 1.0 mg/l.
8. **Solids:** Total solids is a measure of the matter that remains as residue after evaporation of the sample and its subsequent drying at a defined temperature (103–105°C). It consists of volatile (organic) and non-volatile (inorganic or fixed) solids. Further, solids are divided into suspended and dissolved solids. Suspended solids that settle by gravity are called settle-able solids, while others are called non-settle-able solids. Indian Standard's acceptable limit for total solids is 500 mg/l and tolerable limit is 2000 mg/l of dissolved limits.
9. **Nitrates:** Nitrates in surface waters occur by the leaching of fertilizers from soil during surface run-off and also nitrification of organic matter. Indian Standard value of nitrates is 45 mg/l. Concentrations above this limit are mainly harmful for young children. Excessive amounts can cause blue baby syndrome or methemoglobinemia which results in decreased oxygen carrying capacity of haemoglobin, which can even be fatal.
10. **Fluoride:** It forms fluoride compounds that prevent tooth decay and promote the development of a healthy bone structure. The concentration of fluoride is maintained upto 1 ppm in drinking water by addition of soluble fluoride ions. The enamel of the teeth is made harder by the fluoride ions. These convert hydroxyapatite $[3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2]$ to much harder fluorapatite $[3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2]$. The optimum concentration of fluorides to reduce dental caries (cavities) is from about 1 ppm to just less than 5 ppm. Levels greater than 1.5 ppm do not significantly decrease tooth decay, but increase the occurrence of discoloration of teeth. Concentrations of 4–6 ppm reduce the prevalence of osteoporosis, a disease characterized by the loss of bone mass; and toxic effects are noticed between 6 ppm and 7 ppm.
11. **Lead:** It is a heavy metal and gets mixed with water when water is transported through lead pipes. The children are more at risk. Lead causes brain damage, behavior problems, nerve disorders and digestive problems. It can also damage kidneys, liver and reproductive system. The permissible limit for lead is 50 ppb.
12. **Other metals:** The maximum permissible limit for other metals is aluminium, 0.03 ppm; manganese, 0.1 ppm; zinc, 5 ppm; copper, 0.05 ppm and cadmium, 0.005 ppm.

Bacterial Contamination

The methods to estimate the quality of water on the basis of presence of bacteria are:

1. **Standard plate count test:** In this test, the bacteria are made to grow as colonies, by inoculating a known volume of sample onto a solidifiable nutrient medium (Nutrient Agar), which is poured in a Petri dish. After incubating (35°C) for a specified period (24 hours), the colonies of bacteria are counted. The bacterial density is expressed as number of colonies per 100 ml of sample.

2. **Most probable number:** It is the number representing the likely bacterial density of water sample.
3. **Membrane filter technique:** In this test, a known volume of water sample is filtered through a membrane with opening less than 0.5 microns. The bacteria present in the sample will be retained upon the filter paper. The filter paper is then placed on a suitable nutrient medium and incubated for 24 hours at 35°C. Visible colonies are noticed after the incubation period which can then be counted. Each colony represents one bacterium of the original sample. The bacterial count is then expressed as number of colonies per 100 ml of sample.

2.9 Municipal Water

Water for domestic purposes is sourced from rivers and lakes. As such, it has a host of dissolved and colloidal impurities apart from debris like leaves, sticks and trash. To make this water fit for domestic consumption, free from contaminants, pathogenic impurities, color, odor and good in taste, is the most challenging task for the municipal agencies. The water should be of appropriate hardness with requisite amount of dissolved calcium and magnesium salts. Both very hard and very soft waters are not good for industrial purposes. This water is taken up for purification in water treatment plants. Different treatments are given to the water in order to bring it to the purity level needed for domestic consumption.

Specifications for Drinking or Potable Water

Drinking or potable water is fit for human consumption. The common specifications or standards prescribed and recommended for drinking water are as follows:

1. It should be colorless and odorless.
2. It should be good in taste.
3. It should not be hot.
4. Its turbidity should be less than 10 ppm.
5. It should be free from objectionable dissolved gases like H₂S.
6. It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts.
7. Its alkalinity should not be high. Its pH should be in the range of 7.0–8.5.
8. It should be reasonably soft, total hardness should be less than 500 ppm.
9. It should be free from disease producing organisms.
10. Chloride, fluoride and sulphate contents should be less than 250 ppm, 1.5 ppm and 250 ppm, respectively.

The specifications for drinking water in India have been set by Bureau of Indian Standards and are given in Table 2.

Table 2 Indian standard for drinking water

S. No.	Substance or Characteristic	Requirement (Desirable Limit)	Undesirable Effect Outside the Desirable Limit	Permissible Limit in the Absence of Alternate Source
1	Colour, Hazen units, Max	5	Above 5, consumer Acceptance decreases	25
2	Odour	Agreeable	—	Agreeable

(Continued)

Table 2 Continued

S. No.	Substance or Characteristic	Requirement (Desirable Limit)	Undesirable Effect Outside the Desirable Limit	Permissible Limit in the Absence of Alternate Source
3	Taste	Agreeable	—	Agreeable
4	Turbidity, NTU, Max	5	Above 5, consumer acceptance decreases	10
5	Dissolved solids mg/l, Max	500	Beyond this, palatability decreases and may cause gastrointestinal irritation	2000
6	pH value	6.5 to 8.5	Beyond this range, the water will affect the mucous membrane and/or water supply system	No relaxation
7	Total hardness (as CaCO ₃) mg/l, Max	300	Encrustation in water supply structure and adverse effects on domestic use	600
1	Copper (as Cu) mg/l, Max	0.05	Astringent taste, discoloration and corrosion of pipes, fitting and utensils will be caused beyond this limit	1.5
2	Iron (as Fe) mg/l, Max	0.3	Beyond this limit, taste/appearance are affected, there is adverse effect on domestic uses and water supply structures, and promotes iron bacteria	1.0
3	Manganese (as Mn) mg/l, Max	0.1	Beyond this limit, taste/appearance are affected, there is adverse effect on domestic uses and water supply structures	0.3

(Continued)

Table 2 Continued

S. No.	Substance or Characteristic	Requirement (Desirable Limit)	Undesirable Effect Outside the Desirable Limit	Permissible Limit in the Absence of Alternate Source
4	Nitrate (as NO_3) mg/l, Max	45	Beyond this, methaemoglobinemia takes place/may be indicative of pollution	No relaxation
5	Fluoride (as F) mg/l, Max	1.0	Fluoride may be kept as low as possible. High fluoride may cause fluorosis	1.5
6	Zinc (as Zn) mg/l, Max	5	Beyond this limit, it can cause astringent taste and an opalescence in water	15
7	Aluminium (as Al) mg/l, Max	0.03	Cumulative effect is reported to cause dementia	0.2
8	Chlorides (as Cl) mg/l, Max	250	Beyond this limit, taste, corrosion and palatability are affected	1000
9	Selenium (as Se) mg/l, Max	0.01	Beyond this, the water becomes toxic	No relaxation
10	Sulphate (as SO_4) mg/l, Max	200	Beyond this, it causes gastrointestinal irritation when magnesium or sodium are present	400
11	Alkalinity as Calcium carbonate mg/l, Max	200	Beyond this limit, taste becomes unpleasant	600
12	Calcium (as Ca) mg/l, Max	75	Encrustation in water supply structure and adverse effects on domestic use	200
13	Magnesium (as Mg) mg/l, Max	30	Encrustation in water supply structure and adverse effects on domestic use	100

(Continued)

Table 2 Continued

S. No.	Substance or Characteristic	Requirement (Desirable Limit)	Undesirable Effect Outside the Desirable Limit	Permissible Limit in the Absence of Alternate Source
14	Residual, free chlorine, mg/l, Min	0.2	—	1
15	Phenolic compounds (as C ₆ H ₅ OH) mg/l, Max	0.001	Beyond this, it may cause objectionable taste and odour	0.002
16	Mineral oil, mg/l, Max	0.01	Beyond this limit, undesirable taste and odour after chlorination take place	0.03
17	Anionic detergents (as MBAS) mg/l, Max	0.2	Beyond this limit, it can cause a light froth in water	1.0
18	Boron (as B) mg/l, max	0.3	—	1.5
19	Barium (as Ba) mg/l, Max	0.7	May lead to cardiovascular problem	No relaxation
20	Molybdenum (as Mo) mg/l, Max	0.07	Beyond this, it may cause osteoporosis/bone disorders	No relaxation
21	Sulphide (as H ₂ S) mg/l, Max	0.05	Beyond this, it may cause objectionable taste and odour	No relaxation

Source: Drinking Water Specification, Indian Standard, Second Revision of IS 10500

2.10 Treatment of Water for Domestic Purposes

Municipalities have to supply portable water. Rivers, lakes and wells are the most common sources of water used by them. Natural water from these sources do not conform to all required specifications of drinking water. Hence, to make these waters portable, treatment has to be given.

Pretreatment

1. Water is pumped from the river or lake and taken to holding tanks. It is stored in these reservoirs for a period of a few days to a few months to allow the sediments to settle and for natural purification to take place.
2. Large pieces of debris like leaves, twigs, branches, plastic bags, etc., are removed by screening.
3. Evaporation of water stored in these basins is minimized and growth of algae prevented by addition of copper sulphate.

It is important that the pH of water be maintained to as close to the neutral pH as possible. If water is slightly acidic, sodium hydroxide, lime or soda ash can be added to increase the pH. If required, acids like HCl or H_2SO_4 can be used to bring down the pH of alkaline waters. The stored water undergoes various purification processes before it becomes fit for human consumption.

Removal of Suspended Impurities

Actual treatment methods adopted depend upon the exact nature of impurities present in raw water. The processes to be employed for removing them are briefly discussed as follows:

1. **Screening:** It is a process of removing floating materials such as wood pieces, leaves, etc. from water. Raw water is passed through screens having holes, when the floating matter is retained by them and water is allowed to pass.
2. **Sedimentation:** It is the process of removing suspended impurities by allowing the water to stand undistributed in big tanks for 2–8 hours. Most of the particles settle down at the bottom of the tank due to gravitational force, and they are removed. The clear supernatant water is then drawn out from the tank. This process removes only 70–75% of suspended matter.
3. **Sedimentation with coagulation:** Finely divided silica, clay and organic matter do not settle down easily, and hence, cannot be removed by mere sedimentation. Most of these are in colloidal form and carry negative charge. Thus, they do not coalesce due to mutual repulsions. For their removal, coagulation is required. In this process, coagulants like $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$ or sodium aluminates ($NaAlO_2$) are added to water which hydrolyzes to form a gelatinous precipitate of $Al(OH)_3$. This insoluble, flocculent precipitate descends through the water, absorbs and entangles very fine suspended impurities forming bigger flocks, which settle down easily. Moreover, coagulants like alum provide Al^{3+} ions, which neutralize the negatively charged colloidal particles when they come closer and combine to form bigger particles. Due to the force of gravity, these bigger particles settle down.
4. **Filtration:** For further purification of water and for removing microorganisms, odor, color, taste and fine suspended particles, filtration is done. The process of filtration consists of percolating water through beds of fine sand, coarse sand and other granular material. There are different types of filters such as gravity filter, slow sand filter, rapid sand filter and pressure filters; the rate of flow of water also increasing in that order.
5. **Removal of microorganisms:** Even after filtration, water still contains a small percentage of disease-producing (pathogenic) bacteria which must be removed or destroyed if the water has to be used for drinking or municipal purposes. The process of destroying/killing the pathogenic bacteria, other microorganisms, etc. from the water to make it safe for use is known as disinfection. It does not ensure total destruction of all harmful microorganisms. On the other hand, sterilization means complete destruction of all harmful microorganisms. It is done by boiling the water for a period of time. Sterilization is a costly process and is used only by individuals particularly during the outbreak of epidemic in the region. This method cannot be employed in municipal water works, as it kills the bacteria only at the time of boiling but does not provide any protection against future contamination.

Method of Disinfection of Water

The characteristics of a disinfectant are as follows:

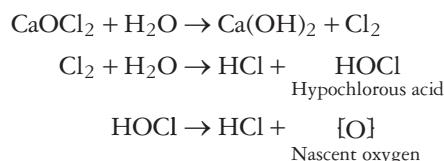
1. It should kill the disease-producing microorganisms quickly at room temperature.
2. It should be inexpensive.
3. It should not be toxic to human.

4. It should provide protection against any contamination in water during conveyance or storage.

The various methods of disinfecting water are as follows:

By Adding Bleaching Powder

The chemical reaction of bleaching powder in water is as follows:



It was earlier believed that nascent oxygen (thus liberated) destroys the pathogens by oxidation. In fact, enzymes in the cells of organisms get deactivated by their chemical reaction with hypochlorous acid. As enzymes are essential for the metabolic process of the microorganisms, so their inactivation results in the death of microorganisms.

The drawbacks of using bleaching powder are as follows:

- Excess of bleaching powder imparts bad taste and smell to treated water. Thus, only calculated quantity of it should be used.
- It is not stable, so it deteriorates due to its continuous decomposition during storage.
- It introduces calcium in water, and thus increases hardness.

By Chlorination

Chlorine is the most commonly used disinfectant in water treatment. It can be employed directly as gas or in the form of concentrated solution in water. It produces hypochlorous acid, which is a powerful germicide. Apparatus used for disinfection by chlorine is known as chlorinator (see Figure 1).

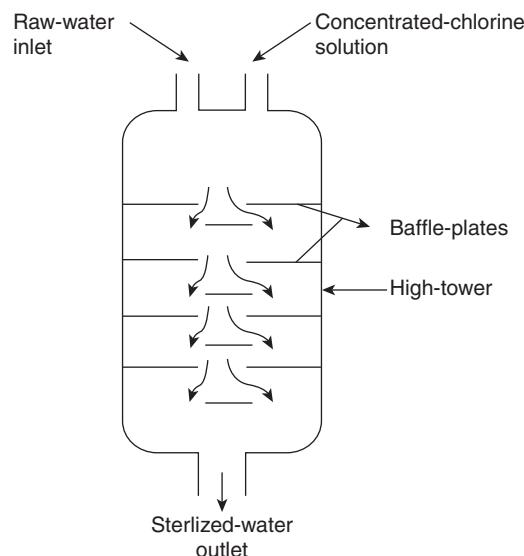


Figure 1 Schematic diagram of chlorinator.

It is a large tower that contains number of baffle plates. From its top, raw water and chlorine solution are introduced. These get thoroughly mixed during their passage through the tower. For filtered water, about 0.3–0.5 ppm of Cl_2 is sufficient. Disinfected water is taken out from the outlet at the bottom of chlorinator. The treated water should not contain more than 0.1–0.2 ppm of free chlorine.

The advantages of using chlorine as disinfectant are as follows:

1. The use of chlorine is more effective and economical.
2. It is stable, requires small space for storage and does not deteriorate on keeping.
3. It can be used at high as well as low temperatures.
4. It does not introduce any impurity in treated water.

The disadvantages of using chlorine as disinfectant are as follows:

1. If excess of chlorine is added, it produces bad taste and disagreeable odor. (As a result of chlorination of phenols, leading to the formation of chlorophenols, water acquires a peculiar odor.)
2. Excess of chlorine produces irritation on mucus membrane.
3. It is not effective at higher pH values.

Breakpoint Chlorination

Breakpoint chlorination means the chlorination of water to such an extent that living organism as well as other organic impurities in water is destroyed. It involves addition of sufficient amount of chlorine to oxidize organic matter, reducing substances and free ammonia in raw water, leaving behind mainly free chlorine which possesses disinfecting action against pathogenic bacteria. It is also known as free-residual chlorination. A typical relationship between the amount of chlorine added to water and the experimentally determined free residual chlorine is shown in Figure 2.

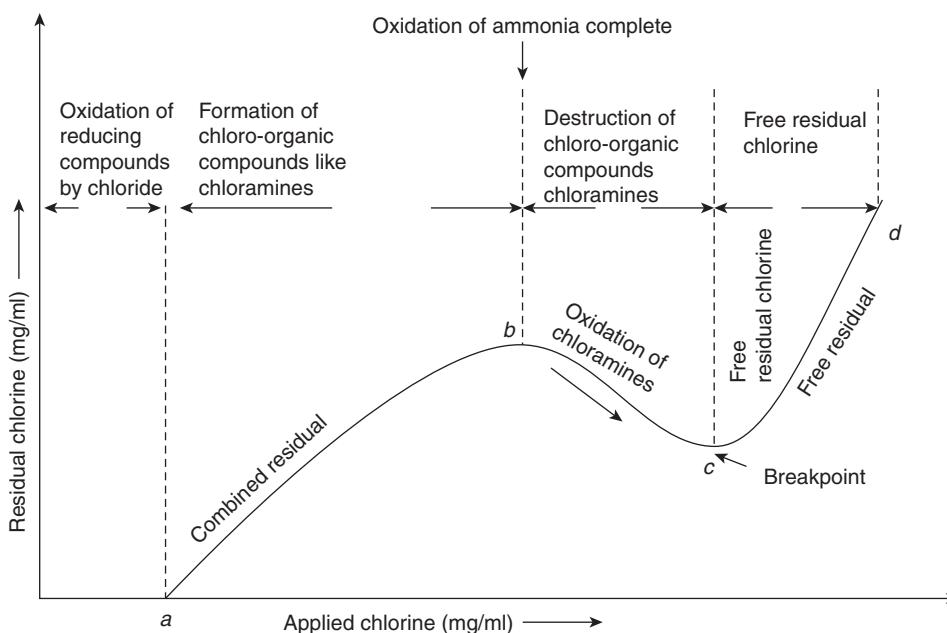


Figure 2 Experimental determination of free residual chlorine.

Initially, for lower doses of Cl_2 , there is no free residual chlorine since all the added chlorine gets consumed for doing complete oxidation of reducing substances present in water. As the amount of chlorine dosage is increased, amount of residual chlorine (experimentally determined) also shows steady increase. This stage corresponds to the formation of chloro-organic compounds without oxidizing them.

At still higher dose of applied chlorine, oxidation of organic compounds and microorganisms sets in; consequently, the amount of free residual chlorine also decreases. When the oxidative destruction is complete it reaches minima. After minima, the added chlorine is not used in any reaction. Thus, the residual chlorine keeps increasing in direct proportion to added chlorine.

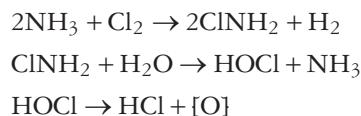
Hence, for effectively killing the microorganisms, sufficient chlorine (corresponding to minima in the curve) has to be added. Addition of chlorine in such dosage is known as breakpoint or residual chlorination.

The advantages of breakpoint chlorination are as follows:

1. It ensures complete destruction of organic compounds which impart color, bad odor and unpleasant taste to water.
2. It completely destroys all the disease producing bacteria.
3. It prevents the growth of any weeds in water.

By using Chloramines (ClNH_2)

Chloramines have better bactericidal action than chlorine.



As it is more stable and does not produce any irritating odor, it is obtained by mixing chlorine and ammonia in 2:1 ratio.

Disinfection by Ozone (O_3)

Ozone is made by passing silent electric discharge through cold and dry oxygen and is highly unstable, as it liberates nascent oxygen after breakdown



In fact, ozone is an excellent and harmless disinfectant since it produces nascent oxygen which is a powerful oxidizing agent. It oxidizes the organic matter present in water and also kills the bacteria.

Other Methods

Ultraviolet light is used as a disinfectant, especially for the swimming pool water. As no chemicals are used, this process is quite safe for human skin. Potassium Permanganate (KMnO_4) is a very useful disinfectant especially for water of wells.

Desalination of Brackish Water

The removal of dissolved minerals (including salts) from seawater or brackish water to produce potable water is called *desalination*. This technique is employed to tide over water shortages caused due to scarcity of water in the arid regions and depletion of water due to excessive human usage. The level of salinity of water can be expressed in terms of total dissolved solids, or TDS concentration. Freshwater has a TDS concentration of below 500 mg/l. On the other hand, seawater has a TDS concentration of around 35,000 mg/l and brackish water has a TDS concentration of around 1000–10000 mg/l. Using

desalination techniques, water can be separated into two streams: a brine stream with a TDS concentration much higher than feed water and a freshwater stream having a TDS concentration much lesser than the feed water.

There are many techniques which can be used for treatment of saline water. Distillation is one of the best techniques, but is cost prohibitive. The other effective treatments are as follows:

Reverse Osmosis

Osmosis describes the movement of solvent between two solutions having different concentrations separated by a semi-permeable membrane. The solvent moves from the solution of lower concentration to that of higher concentration until both the solutions acquire the same concentration.

In reverse osmosis, the direction of normal osmotic flow of water across the membrane is reversed by applying pressure to the compartment with high concentration. Then, the solvent flows from the compartment containing a higher concentration of the solute to that having a lower concentration and this results in concentration of the solute in one and dilution in the other. In case of saline water, reverse osmosis causes water in a salt solution to move through a semi-permeable membrane to the freshwater side (Figure 3).

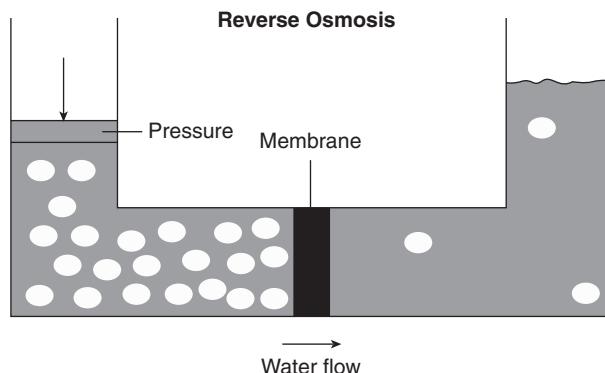


Figure 3 Schematic representation of desalination by reverse osmosis.

Electrodialysis

Electrodialysis uses semi-permeable and ion-selective membranes, which as the name suggests, are very selective towards cations and anions that are allowed to pass through them. For example, if they allow the cations to pass through them, then they will block the passage of anions and vice versa. Salts present in saline water dissociate into positively and negatively charged ions and passed through electrodialysis system. The electrodialysis system is made of a number of cell pairs with electrodes on the outside. The anion and cation exchange membranes are placed in the cells. Water to be treated passes simultaneously in parallel paths through all of the cells, resulting in water and concentrated ion solution (Figure 4). In this manner, water can be purified and the ion concentrate recovered.

Flash Distillation

Flash evaporation is an efficient technique used in the desalination of brackish water or seawater. In multi-stage flash distillation technique, the water is heated and then routed into a reduced-pressure flash evaporation stage where some of the water flashes into steam (Figure 5). This steam is subsequently condensed into salt-free water. The residual salty liquid from that first stage is introduced into a second

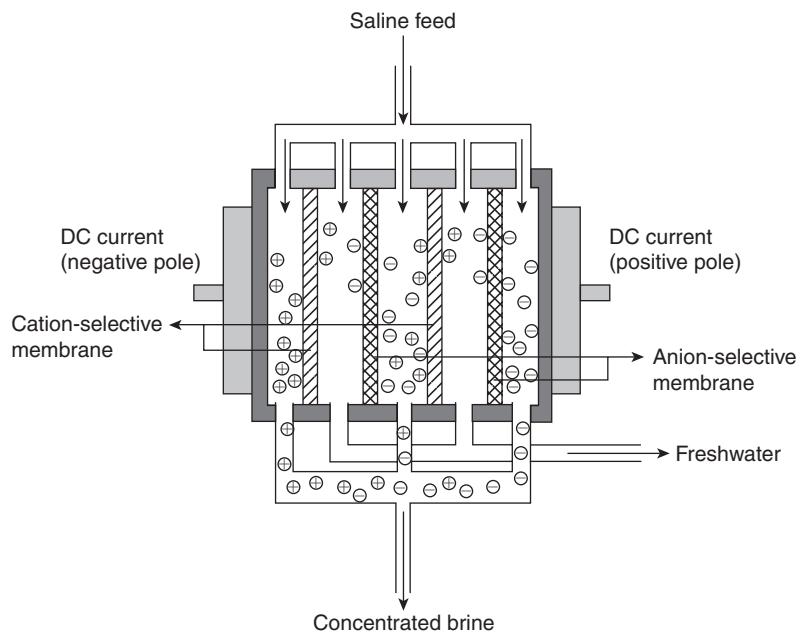


Figure 4 Schematic representation of desalination by electrodialysis.

flash evaporation stage at a pressure lower than that in the first stage. More water is flashed into steam that is also subsequently condensed into more salt-free water. Typically, such plants run through 24 or more sequential stages of flash evaporation.

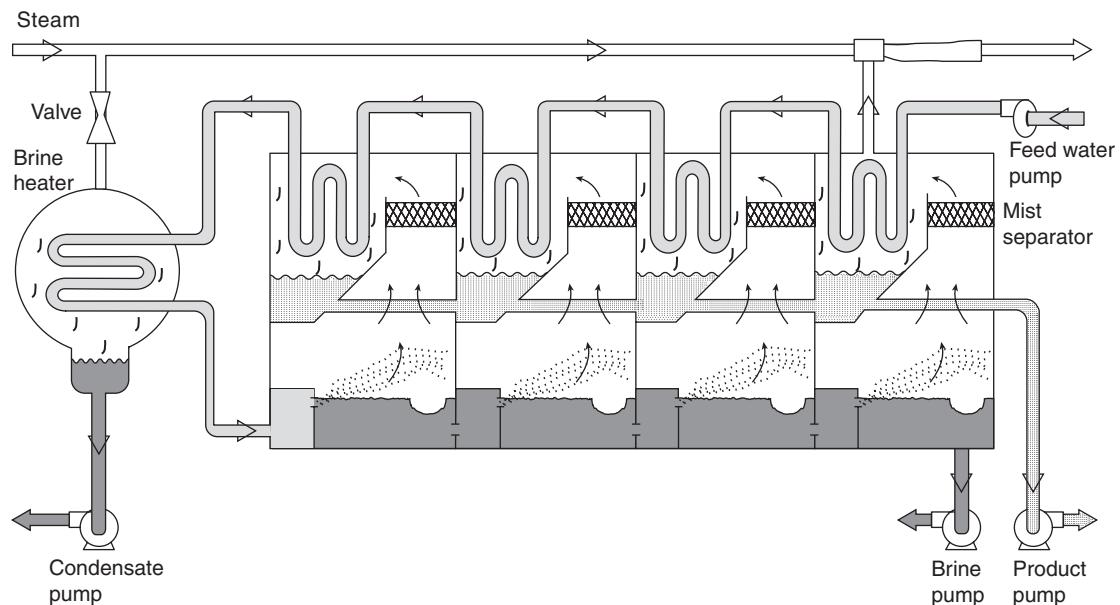


Figure 5 Schematic representation of desalination by multi-stage flash distillation.

Concept Check

- Where is the water for domestic purpose sourced from? What are the major steps involved in its purification?
- What is flocculation? Name a few flocculating agents.
- How is water disinfected by chlorination?
- What is ozonation? How does it compare with chlorination?
- What is the difference between freshwater, brackish water and seawater?
- How is desalination of water carried out by electrodialysis?
- What is the principle involved in desalination of water by reverse osmosis?

2.11 Boiler Feed Water

Water absorbs a large amount of heat for a given rise in temperature and expands extensively as it evaporates to form steam at atmospheric pressure. The steam is capable of carrying large quantities of heat. These unique properties of water make it an ideal raw material for heating and power-generating processes.

A boiler is a closed vessel in which water under pressure is transformed into steam by the application of heat. The water used in boilers is called boiler feed water. The steam so generated should be pure and uncontaminated and may be used for diverse purposes such as power generation, space heating, process heating, sterilization, drying, etc.

Characteristics of Boiler Feed Water

All natural waters contain varying amounts of dissolved and suspended matter and dissolved gases and these impurities cause boiler problems. So, careful consideration must be given to the quality of the water used for generating steam. The composition of boiler feed water must be such that the impurities in it can be concentrated a reasonable number of times inside the boiler, without exceeding the tolerance limits of the particular boiler design. If the feed water does not meet these requirements it must be pretreated to remove impurities. The impurities need not be completely removed in all cases, but brought down to tolerable limits. A number of chemical treatments of water inside or outside the boiler can effectively and economically counteract the impurities.

The boiler feed water purity depends both on quantity of impurities and nature of impurities: Certain impurities such as hardness, dissolved gases, iron, copper, silica, etc., greatly affect the boiler feed water quality while some dissolved salts are not of much consequence. The characteristic requirements of boiler feed water show wide variations which are determined by the quantity of feed water to be used, the design of the boiler and its operating parameters. A low-pressure fire-tube boiler can usually tolerate high levels of hardness with suitable treatment, whereas most of the impurities must be removed from water used in some modern, high-pressure boilers.

The amount of impurities permitted in boiler feed water have been standardized by different organizations. The pressures at which the boilers operate are an important consideration in these recommendations. For pressures up to 100 bar, the boiler feed water should have the following characteristics:

1. Dissolved oxygen below 0.02 mg/l.
2. Total hardness below 0.5 ppm.
3. Total iron below 0.03 mg/l, copper 0.01 mg/l and silica 5 mg/l.
4. Caustic alkalinity (P-alkalinity) below 0.5 ppm and soda alkalinity (M-alkalinity) below 1 ppm.

Specifications of Boiler Feed Water

We have seen that presence of hardness in boiler feed water leads to a number of problems. The water to be used as boiler feed thus needs to be meet some stringent quality parameters to avoid these troubles. The specifications are derived on the basis of working pressure of the boiler. The important parameters for boiler feed water and average specifications of some are given in Table 3.

Table 3 Boiler feed water specifications

Parameters	Specification
Hardness	<0.2 ppm
Caustic alkalinity	0.15–0.45 ppm
Soda alkalinity	0.15–1.0 ppm
Soda ash	0.3–0.55 ppm
pH	7.5–10
Dissolved oxygen	0.02 ppm
Dissolved solids	
Suspended solids	
Silicates	
Concentration of organics	

Boiler Troubles/Problems

Scale and Sludge Formation

In boilers, water is heated under high pressures to high temperatures which causes the water to evaporate. Due to this, the impurities present in the water get progressively concentrated. When the impurities reach a saturation point, they get precipitated out. This precipitation may be in the form of an adherent deposit, in which case, it is termed as *scale*; or it may be a loose, silky precipitate, in which case, it is termed as *sludge* (Figure 6).



Figure 6 Scale and sludge formation in boiler pipes.

1. **Scales:** These are hard deposits which stick to inner wall/surface of the boiler and are difficult to remove. The impurities in water that lead to formation of scales are $\text{Ca}(\text{HCO}_3)_2$, CaSO_4 , $\text{Mg}(\text{HCO}_3)_2$, MgCl_2 and silica.

Calcium bicarbonate decomposes on action of heat or an increase in pH as follows:



This calcium carbonate formed has low solubility and forms a tenacious scale. As the boiler temperature increases, the solubility of calcium sulphate decreases and it gets precipitated out in form of scales.

Magnesium salts lead to scale formation due to formation of Mg(OH)_2 .



Silica forms a hard, glassy scale on the boiler surface. It reacts with calcium or magnesium present in water to form calcium and magnesium silicates which form hard scales on the boiler.

The scale formation can have the following harmful effects on boilers:

- **Danger of explosion:** Scales form a coating on the inner walls of the boiler. When the boiler is heated, the metal heats up faster than the scales. The metal takes up heat and expands, while the scales do not expand as much. Due to this, the scales crack and water from inside the boiler comes in contact with the hot metal and immediately forms steam. This steam exerts a pressure on the boiler walls, which may crack under pressure and burst.
 - **Lowering of boiler efficiency:** Boiler parts may get plugged or choked by deposition of scales, thus lowering the efficiency of the boiler.
 - **Wastage of fuel:** Scales being insulators do not conduct heat to the boiler water. Thus, there is wastage of fuel.
 - **Increase in cleaning expense:** Scales need to be cleaned often, hence the cleaning expense is substantial.
2. **Sludge:** It is a loose accumulation of suspended solids, found in the colder and less turbulent sections of the boiler and in the distribution pipes. It is formed by substances that have greater solubility in hot water than in cold water. For example, salts like magnesium chloride and magnesium carbonate MgCl_2 , MgCO_3 , MgSO_4 , CaCl_2 are soluble in hot water but precipitate out in colder portions of boiler pipes. Iron and silica are also commonly found in sludge. They can be removed by blow-down operation. Sludge, if not periodically removed, may settle down to form scales.

Some harmful effects of sludge formation are:

- Colder parts of the boiler and distribution lines may get plugged by sludge.
- Wastage of fuel, since sludges are bad conductors of heat.
- Sludges lower the boiler efficiency.
- Sludges cause an increase in cleaning expenses.

Formation of scales and sludges may be prevented by using near zero hardness boiler feed water.

Priming and Foaming

When water is heated in the boiler, it produces steam which evaporates from the surface of water. The steam may sometimes carry with it a few droplets of water with dissolved impurities. Such a steam is called wet steam or carryover. This wet steam or carryover reduces the heating efficiency of steam and also causes corrosion to the surfaces it comes in contact with. The boiler water is transferred with the steam, leading to the formation of one of the two conditions: Priming and foaming.

1. **Priming:** It is the discharge of large drops of water into the outlet steam. This lowers the energy efficiency of the steam and leads to the deposition of salt crystals on the heaters and in the turbines.

Priming may be caused by presence of impurities in the boiler feed water and improper construction of boiler. High level of water in the boiler and high steam velocities may also cause priming. It may be prevented by making boiler feed water free from impurities. Proper construction of boiler, maintaining proper level of water and slow discharge of steam also prevents priming.

2. **Foaming:** It is the formation of persistent bubbles on the surface of the boiler water, which may completely or partially fill the steam space of the boiler.

Foaming is caused by alkalis, oils, fats, certain types of organic matter and suspended solids in boiler feed water. The suspended solids collect in the surface film surrounding a steam bubble and make it tougher, resist breaking and build up foam. It can be prevented by

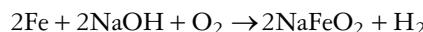
- use of anti-foaming agents;
- removal of oils and greases using sodium aluminate;
- removal of clay and suspended matter using coagulating agents;
- removal of silica using ferrous sulphate or sodium aluminate.

Caustic Embrittlement

It is the phenomenon in which the boiler material becomes brittle due to exposure to caustic solutions (like NaOH) at high temperature and high pressure conditions. Sodium carbonate is often used in softening of boiler feed water by the lime-soda process. There is concentration of residual amounts of Na_2CO_3 in boiler feed water as the water evaporates on boiling. It then undergoes hydrolysis to form sodium hydroxide making the water alkaline.



The alkaline water then seeps inside the cracks on the boiler walls. The concentrated sodium hydroxide solution reacts with iron of the boiler walls causing caustic embrittlement. At high temperatures, the water evaporates and sodium hydroxide concentration increases. It then reacts with the iron present in the boiler walls forming sodium ferrate.



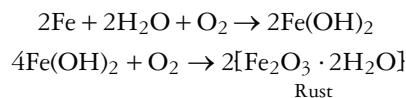
The embrittlement of boiler parts which are under stress might cause the boiler to explode. Caustic embrittlement may be prevented by the following measures:

1. Using sodium phosphate for softening, instead of sodium carbonate.
2. Adding lignins and tannins to the boiler water which seal the small cracks and prevent direct contact of the boiler wall with the alkali.
3. Adding sodium sulphate to the boiler feed water to prevent the formation of cracks.
4. Maintaining pH between 8 and 9 which stops the feed from becoming very alkaline.

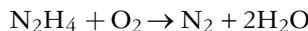
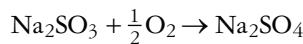
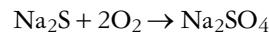
Boiler Corrosion

Boiler corrosion is a decay process in which the boiler surface gets degraded by the attack of feed water. It is caused due to the presence of dissolved gases such as oxygen and carbon dioxide in the boiler feed water.

Raw water generally has about 8–9 ppm of dissolved oxygen. Oxygen levels of more than 7 ppm cause boiler corrosion, and so have to be kept in check. The dissolved oxygen can attack the iron in the boiler and produce rust.



In modern boiler systems, dissolved oxygen is first removed using vacuum degasifiers deaerating heaters at boiler system. The remaining traces of oxygen are chemically scavenged by treating feed water with a reducing agent that serves as an oxygen scavenger. Hydrazine and sodium sulphite are widely used for this purpose. The removal of residual oxygen is shown by the following reactions:



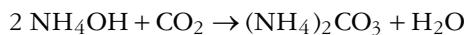
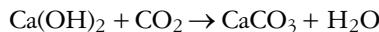
Carbon dioxide is found in the boiler water either from air or due to the presence of residual temporary hardness.



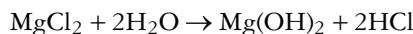
It dissolves in water to produce carbonic acid, which is slightly acidic and corrosive in nature.



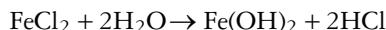
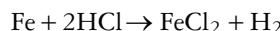
Carbon dioxide may be removed mechanically by deaeration. Chemical elimination may be achieved by treatment with lime or ammonium hydroxide.



When the pH of boiler water drops below 7, corrosion may occur due to acidic nature of feed water. The acid may get formed due to the presence of magnesium compounds in the feed water.



This acid may then attack the boiler to form rust:



Acidic corrosion exhibits as rough pitted surfaces and may be contained by adding alkaline agents like ammonium hydroxide.

Concept Check

- Why is hard water hazardous for boilers?
- What is scale and sludge formation? What are the harmful effects on boilers due to their formation?
- Distinguish between priming and foaming. How can their occurrence be prevented?
- What is caustic embrittlement? What are its causes and effects?
- How are dissolved oxygen and carbon dioxide removed from boiler feed water?

2.12 Techniques for Water Softening

Water softening is the process of reducing the dissolved calcium, magnesium, and to some extent manganese and ferrous ion concentrations in water, thereby reducing hardness. Water that is used in the chemical industry should be free from calcium and magnesium salts, as these tend to precipitate out as hard deposits on the pipes and heat exchanger surfaces. The resulting build-up of scale can restrict water flow in pipes. In boilers, the deposits act as an insulation that impairs the flow of heat into water, reducing the heating efficiency and in some cases leading to failure of the boiler. In industrial boilers, most of the troubles with the boilers, such as scale and sludge formation, priming, foaming, corrosion, arise due to hardness of boiler feed water. It thus becomes important to remove hardness causing salts from boiler feed water. The two kinds of treatments for removal of hardness causing salts are:

1. **Internal treatment:** In this method, the conditioning of water is carried out inside the boiler by treating with different chemicals. The processes include colloidal, calgon, carbonate and phosphate conditioning. It is normally carried out to remove the residual salts which could not be removed by external treatment.
2. **External treatment:** In this method, the water is treated before it enters the boilers. The processes include lime–soda process, ion-exchange process and zeolite process.

Internal Treatment for Softening Water

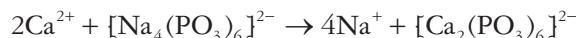
The modern-day high-pressure and heavy-duty boilers have zero tolerance for hardness in water. Hence, even after subjecting water to external treatment for hardness removal, the residual hardness has to be removed using conditioning agents. This treatment can be carried out inside the boiler itself, and is called internal treatment. The reagents added for this can act in two ways:

1. They can precipitate scale-forming impurities, and the sludge formed can be removed by blow-down operation.
2. These can convert the scale-forming impurities to form more soluble complexes, which stay in dissolved form without causing any harm.

The various conditioning treatments are described as follows:

Calgon Treatment

Calgon, or sodium hexametaphosphate similarly forms soluble complexes with calcium and magnesium ions at pH 10, thus ensuring the smooth running of the boiler.



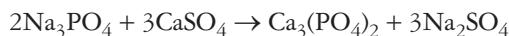
The complex $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ is water soluble so there is no problem of sludge disposal. Calogen conditioning is better than phosphate conditioning.

Colloidal Treatment

This treatment involves addition of conditioning agents such as glue, seaweed extract, agar–agar, tannin, etc., to the boiler water. The residual precipitates get surrounded by molecules of the conditioners and are effectively maintained in the colloidal state. Once the colloidal solution becomes concentrated, the colloids can be removed by blow-down operations.

Phosphate Treatment

Sodium orthophosphate may be added to the boiler water to precipitate out the residual calcium and magnesium as loose calcium and magnesium phosphates which can be easily removed by blow-down operations.

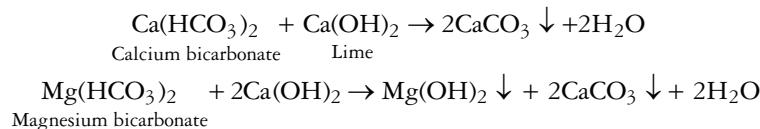


External Treatment for Softening Water

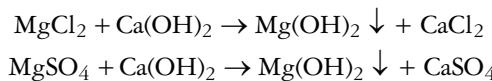
Lime–Soda Process

The lime–soda treatment involves the use of lime (calcium hydroxide) and soda (sodium carbonate) to remove hardness from water. The treatment with these reagents converts all hardness causing salts dissolved in water into insoluble precipitates, which are then removed by settling and filtration.

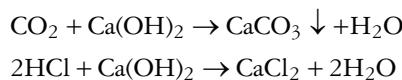
1. **Lime:** It is used to remove temporary hardness in water, as it reacts with soluble calcium and magnesium bicarbonates to form insoluble precipitates.



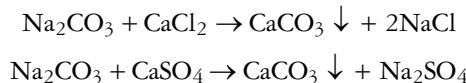
Lime is effective in removing the permanent magnesium hardness from water. It reacts with magnesium sulphate and chloride to form insoluble precipitate of magnesium hydroxide, but in the process, soluble calcium sulphate and calcium chloride are also formed.



Lime also reacts with free dissolved carbon dioxide and free mineral acids present in water.



2. **Soda ash:** A calculated amount of sodium carbonate is added to remove the calcium permanent hardness.



From the reactions involved in lime–soda process, the amount of lime and soda required for the softening process can be calculated as follows:

1. Removal of one equivalent of calcium temporary hardness $[\text{Ca}(\text{HCO}_3)_2]$ requires one equivalent of lime. Therefore, lime requirement is

$$\frac{74}{100} \times [\text{Amount of Ca}(\text{HCO}_3)_2 \text{ in terms of CaCO}_3 \text{ equivalent}]$$

2. Removal of one equivalent of magnesium temporary hardness $[\text{Mg}(\text{HCO}_3)_2]$ requires two equivalent of lime. So, requirement is

$$2 \times \frac{74}{100} \times [\text{Amount of } \text{Mg}(\text{HCO}_3)_2 \text{ in terms of } \text{CaCO}_3 \text{ equivalent}]$$

3. Removal of one equivalent of permanent calcium hardness (CaSO_4 and CaCl_2) requires one equivalent of soda. Therefore, soda requirement is

$$\frac{106}{100} [\text{Amount of } (\text{CaSO}_4 + \text{CaCl}_2) \text{ in terms of } \text{CaCO}_3 \text{ equivalent}]$$

4. Removal of one equivalent of permanent magnesium hardness requires one equivalent of lime and one equivalent of soda. Therefore,

$$\text{Lime requirement} = \frac{74}{100} \times [\text{Amount of } (\text{MgSO}_4 + \text{MgCl}_2) \text{ in terms of } \text{CaCO}_3 \text{ equivalent}]$$

$$\text{Soda requirement} = \frac{106}{100} \times [\text{Amount of } (\text{MgSO}_4 + \text{MgCl}_2) \text{ in terms of } \text{CaCO}_3 \text{ equivalent}]$$

5. Apart from these, lime and soda equivalents can be added to the total requirement if aluminium sulphate and ferrous sulphate are present. Similarly, lime and soda equivalents need to be subtracted from the total requirement if sodium aluminate is present as coagulant or sodium bicarbonate is present as impurity, respectively.

The calcium carbonate formed by the reaction precipitates as sludge and can be filtered out. The resulting sodium sulphate and chloride are highly soluble in water and do not form scales.

The lime–soda process can be carried out in two ways: Older method of batch softening and the modern method of continuous softening.

1. **Batch softening:** In this method, lime and soda are mixed with feed water in a tank. Sufficient time for completion of reactions and formation of precipitates is allowed before the sludge is filtered and soft water is obtained.

The precipitates formed are often fine and do not filter easily. A small amount of coagulant is added to entrap the fine precipitates. One of the most commonly used coagulating agents for the lime–soda process is sodium aluminate, which itself being alkaline makes the softening more effective. Coagulants also help to remove silica present in water. It gets absorbed on the sludge during coagulation of precipitate.

2. **Continuous softening:** In this method, tanks holding the hard water are divided into compartments for addition of lime and soda, for retention time, completion of reaction and precipitate formation, and outflow of soft water. The process gives continuous supply of soft water.

Lime–soda softening is also classified as hot or cold, depending on the temperature of water at which softening reactions are carried out. Hot process softeners (Figure 7) are added at almost the boiling point of water and increase the rate of precipitation reactions, decreases the viscosity of water, eliminates the need of adding coagulants and produces overall better quality water.

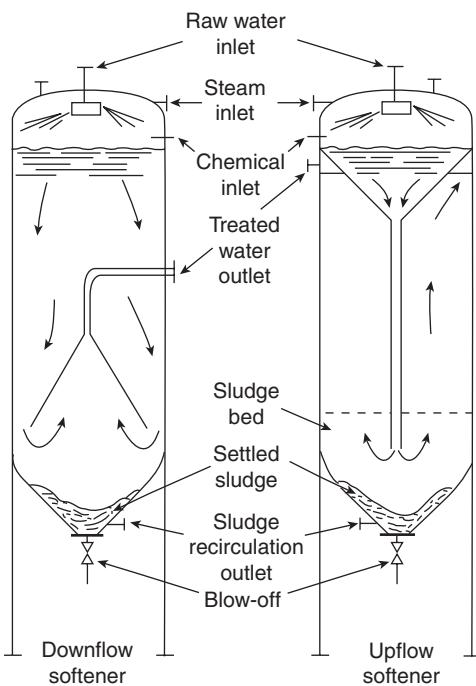


Figure 7 Equipment used in hot process softening.

The lime-soda softening process offers the following advantages:

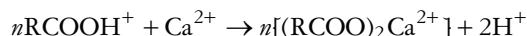
1. It not only reduces hardness but also reduces alkalinity, TDS and silica of the feed water.
2. Feed water need not be clarified completely before the softening process.
3. The levels of carbon dioxide can also be reduced using the hot softening process.

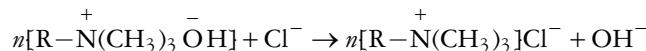
However, the lime–soda process has the following disadvantages:

1. It can reduce the hardness of water, but cannot totally remove it.
2. The feed water quality may change from source to source, which makes adjusting the amounts of soda and lime very cumbersome.

Ion Exchange Process (Demineralization)

Ion exchange is the process of softening of water by exchanging the harmful ions of water with harmless ions from an ion exchange resin. It is also known as demineralization of water. Ion exchange resins are high molecular weight, cross-linked polymers with a porous structure. The ion-exchange properties arise due to the presence of acidic (sulphonic or carbonyl) or basic (substituted amino group) functional groups present attached to the polymeric chains. The acidic groups exchange their H^+ (or Na^+) ions for cations (Ca^{2+} , Mg^{2+}) present in water and are known as cation exchange resins. The basic groups exchange OH^- for anions present in water and are known as anion exchange resins. For example,

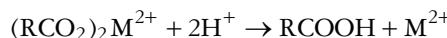




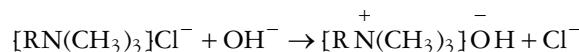
The H^+ and OH^- ions released combine to form demineralized water.

In the process, the cation and anion exchange resins are packed in separate columns (Figure 8). The water is first passed through the cation exchange resin where cations like Ca^{2+} , Mg^{2+} are exchanged with H^+ . It is then passed through anion exchange resin where ions like SO_4^{2-} , Cl^- , etc., are exchanged with OH^- . The sequence of water flow is important and cation exchange resin needs to be used first. This is because if water is passed first through anion exchange resin, alkali is produced which can harm the cation exchange resin in the subsequent step. When the resins are exhausted and lose their capacity to exchange H^+ and OH^- ions, they are regenerated.

The process of regeneration is the reversal of the reaction taking place for ion exchange. The exhausted cation exchange column is regenerated by passing a solution of dilute HCl or H_2SO_4 and then washing with deionized water.



Similarly, for anion exchange resins, hydroxyl ions are provided for exchange, and ammonium hydroxide or sodium hydroxide can be used as regenerating agents.



The advantages of ion exchange process are:

1. The ion exchange apparatus, once set up, is easy to operate and control.

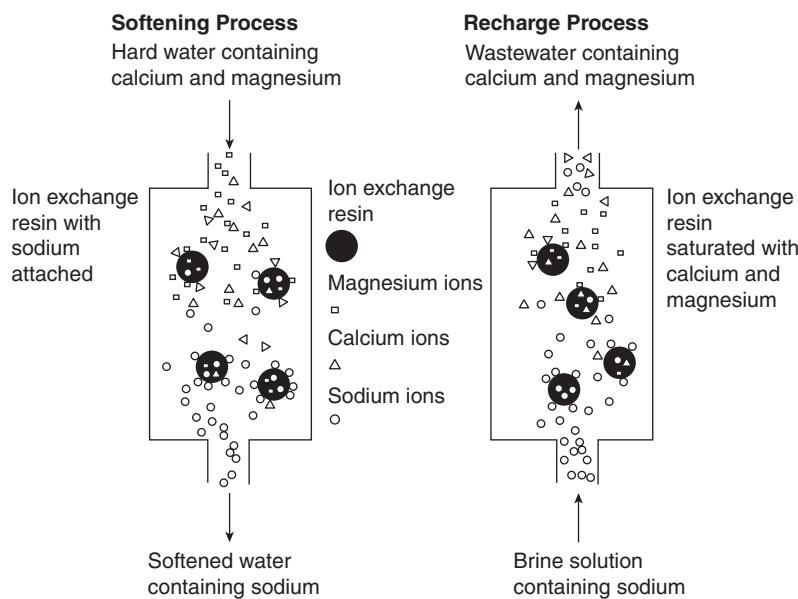


Figure 8 Ion exchange column.

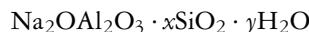
2. It works well for variations in hardness of water which do not have to be uniform at all times.
3. In comparison with lime–soda process, the entire unit takes up less space, produces better quality water and is more economical.

The disadvantages of ion exchange process are:

1. When cation exchange is carried out with a hydrogen exchanger, the pH of the effluent reduces and may result in corrosion; whereas, if a sodium exchanger is used, the TDS, alkalinity and silica are not reduced.
2. Effective pretreatment needs to be carried out to make the feed water suitable for ion exchange. The ion exchange material should not be allowed to get contaminated with suspended and colloidal matter, which could result in degradation of the exchange column and difficulties in its regeneration.

Zeolite (Permutit) Process

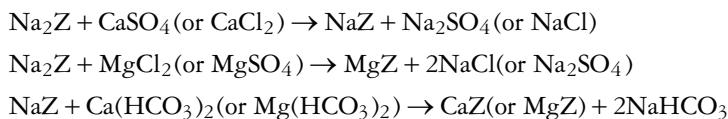
Zeolites are naturally occurring hydrated aluminosilicate minerals which may be represented as:



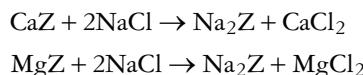
where $x = 2$ to 10 and $y = 2$ to 6. These are also known as permutit (in Greek) or boiling stones.

Zeolites may also be prepared synthetically by heating together sodium silicate, aluminium sulphate and sodium aluminate to yield crystalline and porous material with higher ion exchange capacity than natural zeolites. In the zeolite crystal, there exists a framework of linked tetrahedral of SiO_4 , with each tetrahedral sharing the corner oxygen with the other tetrahedral. Some Si^{4+} ions are replaced by Al^{3+} ions, which are accompanied by Na^+ ions to balance the charge. These sodium ions in zeolites can exchange with hardness-causing divalent ions. The ion exchanging capacity increases with increase in charge and atomic number of exchanging ions.

For the softening water by permutit process, the water is percolated through the bed of zeolite packed in a vertical cylinder (Figure 9). The zeolite may be represented as Na_2Z and the following reactions occur in the zeolite bed:



The ion exchange process will continue till all the exchangeable sodium ions are used up. The exhausted zeolite bed then needs to be regenerated for further use. Regeneration is carried out by treating the bed with a concentrated solution of sodium chloride:



The bed is then washed with deionized water to remove calcium and magnesium chlorides.

Zeolite process of softening water offers the following advantages:

1. It removes hardness effectively with residual hardness 10 ppm in softened water.
2. The process can adjust for variation in hardness in water.
3. It is a clean process in which no sludge is formed.
4. The working unit is compact, simple and easy to operate.

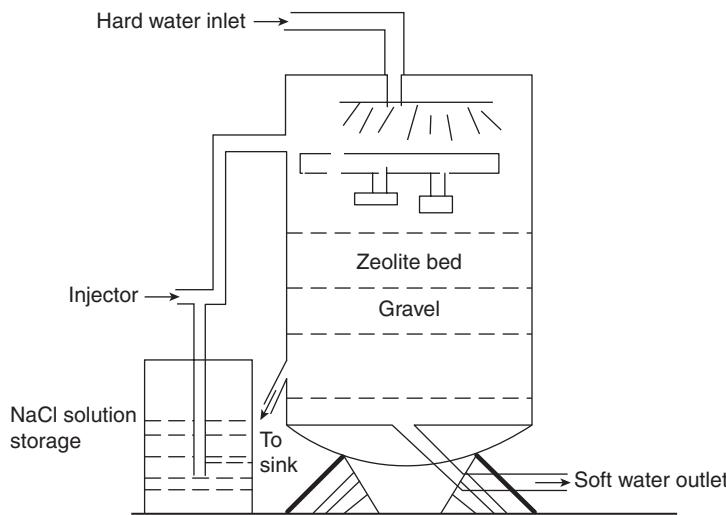


Figure 9 Schematic representation of zeolite process.

However, the process has a few disadvantages:

1. Mineral acids if present in water will disintegrate the zeolite bed.
2. The effective concentration of sodium ions in water is increased.
3. Zeolite bed may get clogged by turbidity.

Problem 12

Calculate the amount of lime and soda required for softening 50,000 l of water containing the following salts:

$$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg/l}; \text{Mg}(\text{HCO}_3)_2 = 7.5 \text{ mg/l} \text{ and } \text{CaSO}_4 = 13.6 \text{ mg/l}$$

$$\text{MgSO}_4 = 12.0 \text{ mg/l}; \text{MgCl}_2 = 2.0 \text{ mg/l} \text{ and } \text{NaCl} = 4.7 \text{ mg/l}$$

Solution

The hardness of water due to dissolved salts expressed in terms of CaCO_3 equivalent is:

$$8.1 \text{ mg/l of Ca}(\text{HCO}_3)_2 = \frac{8.1}{162} \times 100 = 5 \text{ mg/l of CaCO}_3$$

$$7.5 \text{ mg/l of Mg}(\text{HCO}_3)_2 = \frac{7.5}{146} \times 100 = 5.13 \text{ mg/l of CaCO}_3$$

$$13.6 \text{ mg/l of CaSO}_4 = 13.6 \times \frac{100}{136} = 10 \text{ mg/l of CaCO}_3$$

$$12.0 \text{ mg/l of MgSO}_4 = 12 \times \frac{100}{120} = 10 \text{ mg/l of CaCO}_3$$

$$2.0 \text{ mg/l of MgCl}_2 = 2 \times \frac{100}{95} = 2.10 \text{ mg/l of CaCO}_3$$

NaCl does not contribute to hardness. The amount of lime and soda required are as follows:

$$\begin{aligned}\text{Lime requirement} &= [\text{Temporary hardness of Ca} + 2 \times \text{Temporary hardness of Mg} \\ &\quad + \text{Permanent hardness of Mg}] \times \frac{\text{Molecular weight Ca(OH)}_2}{\text{Molecular weight of CaCO}_3} \\ &= [5 + 2 \times 5.13 + 10 + 2.10] \times \frac{74}{100} = 20.25 \text{ mg/l}\end{aligned}$$

$$\begin{aligned}\text{Soda requirement} &= [\text{Permanent hardness}] \times \frac{\text{Molecular weight of Na}_2\text{CO}_3}{\text{Molecular weight of CaCO}_3} \\ &= [\text{CaSO}_4 + \text{MgSO}_4 + \text{MgCl}_2 \text{ hardness as CaCO}_3] \times \frac{106}{100} \\ &= [10 + 10 + 2.10] \times \frac{106}{100} \\ &= 23.43 \text{ mg/l}\end{aligned}$$

Lime and soda requirement for 50,000 l water is as follows:

$$\text{Lime} = 20.25 \times 50000 \text{ mg} = 1.01 \text{ kg}$$

$$\text{Soda} = 23.43 \times 50000 \text{ mg} = 1.17 \text{ kg}$$

Problem 13

Calculate the quantity of quick lime and soda ash required to soften 10,000 liters of water containing:

- (a) 219 ppm of magnesium bicarbonate and 234 ppm of sodium chloride.
- (b) 36 ppm of Mg^{2+} and 18.3 ppm of HCO_3^- .
- (c) 1.5 ppm of free acids, 144 ppm of sulphate ions and 71 ppm of chloride ions.

Solution

- (a) One equivalent of magnesium temporary hardness requires two equivalents of lime. Therefore,

$$\begin{aligned}\text{Lime required for Mg(HCO}_3)_2 &= [2 \times \text{Mg(HCO}_3)_2 \text{ hardness in terms of CaCO}_3] \\ &\quad \times \frac{\text{Molecular weight Ca(OH)}_2}{\text{Molecular weight of CaCO}_3}\end{aligned}$$

The hardness in terms of CaCO_3 equivalent is:

$$219 \text{ ppm or } 219 \text{ mg/l of Mg(HCO}_3)_2 = 219 \times \frac{100}{146} = 150 \text{ mg/l of CaCO}_3$$

Therefore,

$$\text{Lime required} = \frac{74}{100} \times (2 \times 150) \text{ mg/l} = 222 \text{ mg/l}$$

For 10,000 l of water, lime required = $222 \times 10000 \text{ mg} = 2.2 \text{ kg}$.

NaCl does not contribute to hardness of water and does not react with lime. Also temporary hardness due to magnesium does not require any soda.

(b) Now,

$$\text{Lime required} = [\text{Mg}^{2+} + \text{HCO}_3^- \text{ hardness in terms of } \text{CaCO}_3] \times \frac{\text{Molecular weight of } \text{Ca(OH)}_2}{\text{Molecular weight of } \text{CaCO}_3}$$

The hardness in terms of CaCO_3 equivalent is:

$$36 \text{ ppm or } 36 \text{ mg/l of } \text{Mg}^{2+} = 36 \times \frac{100}{24} = 150 \text{ mg/l of } \text{CaCO}_3$$

$$18.3 \text{ ppm or } 18.3 \text{ mg/l of } \text{HCO}_3^- = 18.3 \times \frac{100}{122} = 15 \text{ mg/l of } \text{CaCO}_3$$

Therefore,

$$\text{Lime required} = (150 + 15) \times \frac{74}{100} = 122.1 \text{ mg/l}$$

For 10,000 l of water, lime required = $122.1 \times 10000 \text{ mg} = 1.2 \text{ kg}$. Now,

$$\begin{aligned} \text{Soda required} &= [\text{Mg}^{2+} \text{ hardness as } \text{CaCO}_3 \text{ equivalent}] \times \frac{\text{Molecular weight } \text{Na}_2\text{CO}_3}{\text{Molecular weight } \text{CaCO}_3} \\ &= [150] \times \frac{106}{100} \text{ mg/l} = 159 \text{ mg/l} \end{aligned}$$

For 10,000 l of water, soda required = $159 \times 10000 \text{ mg} = 1.59 \text{ kg}$.

(c) Now,

$$\text{Lime required} = [\text{Free acid hardness as } \text{CaCO}_3 \text{ equivalent}] \times \frac{\text{Molecular weight of } \text{Ca(OH)}_2}{\text{Molecular weight of } \text{CaCO}_3}$$

$$\begin{aligned} \text{Soda required} &= [\text{Free acid} + \text{chloride ion} + \text{sulphate ion hardness as } \text{CaCO}_3 \text{ equivalent}] \\ &\quad \times \frac{\text{Molecular weight of } \text{Ca(OH)}_2}{\text{Molecular weight } \text{CaCO}_3} \end{aligned}$$

The hardness in terms of CaCO_3 equivalent is:

$$1.5 \text{ ppm or } 1.5 \text{ mg/l of free acids} = 1.5 \times \frac{100}{1 \times 2} = 75 \text{ mg/l of } \text{CaCO}_3$$

$$144 \text{ ppm or } 144 \text{ mg/l of sulphate ions} = 144 \times \frac{100}{96} = 150 \text{ mg/l of } \text{CaCO}_3$$

$$71 \text{ ppm or } 71 \text{ mg/l of chloride ions} = 71 \times \frac{100}{35.5 \times 2} = 100 \text{ mg/l of } \text{CaCO}_3$$

Using the above values,

$$\text{Lime required} = [75] \times \frac{74}{100} = 55.5 \text{ mg/l}$$

For 10,000 l of water, the amount of lime required is $55.5 \times 10000 \text{ mg} = 0.555 \text{ kg}$.

$$\text{Soda required} = [75 + 150 + 100] \times \frac{106}{100} = 344.5 \text{ mg/l}$$

For 10,000 l of water, the amount of water soda required is $344.5 \times 10000 \text{ mg} = 3.445 \text{ kg}$.

Problem 14

Calculate the quantities of lime and soda required for treatment of 125,000 l of water with the following analysis using 10 ppm of sodium aluminate as coagulant.

Analysis of raw water: $\text{Ca}^{2+} = 95 \text{ ppm}$, $\text{Mg}^{2+} = 36 \text{ ppm}$, $\text{CO}_2 = 66 \text{ ppm}$, $\text{HCO}_3^- = 244 \text{ ppm}$, $\text{H}^+ = 2 \text{ ppm}$.

Analysis of treated water: $\text{CO}_3^{2-} = 45 \text{ ppm}$, $\text{OH}^- = 34 \text{ ppm}$.

What would be the quantities required for treatment of same water if purity of lime is 74% and soda is 92%?

Solution

Since the treated water shows presence of OH^- and CO_3^{2-} ions, it implies that excess of lime and soda was added for treating the water. So the quantities of lime and soda required would be the sum of the quantities required to treat the raw water and the quantities present in treated water.

$$\begin{aligned} \text{Lime required} &= [\text{Mg}^{2+} + \text{CO}_2 + \text{HCO}_3^- + \text{H}^+ + \text{OH}^- - \text{Na AlO}_2 \text{ hardness as CaCO}_3 \text{ equivalent}] \\ &\quad \times \frac{\text{Molecular weight of Ca(OH)}_2}{\text{Molecular weight of CaCO}_3} \end{aligned}$$

$$\begin{aligned} \text{Soda required} &= [\text{Mg}^{2+} + \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}^+ + \text{OH}^- - \text{HCO}_3^- \text{ hardness as CaCO}_3 \text{ equivalent}] \\ &\quad \times \frac{\text{Molecular weight of Na}_2\text{CO}_3}{\text{Molecular weight of CaCO}_3} \end{aligned}$$

Hardness in terms of CaCO_3 equivalent:

$$(a) \text{Ca}^{2+}: 95 \text{ ppm or } 95 \text{ mg/l } \text{Ca}^{2+} = 95 \times \frac{100}{40} = 237.5 \text{ mg/l of CaCO}_3$$

$$(b) \text{Mg}^{2+}: 36 \text{ ppm or } 36 \text{ mg/l } \text{Mg}^{2+} = 36 \times \frac{100}{24} = 150 \text{ mg/l of CaCO}_3$$

$$(c) \text{CO}_2: 66 \text{ ppm or } 66 \text{ mg/l } \text{CO}_2 = 66 \times \frac{100}{44} = 150 \text{ mg/l of CaCO}_3$$

$$(d) \text{HCO}_3^-: 244 \text{ ppm or } 244 \text{ mg/l } \text{HCO}_3^- = 244 \times \frac{100}{61 \times 2} = 200 \text{ mg/l of CaCO}_3$$

$$(e) \text{H}^+: 2 \text{ ppm or } 2 \text{ mg/l } \text{H}^+ = 2 \times \frac{100}{1 \times 2} = 100 \text{ mg/l of CaCO}_3$$

$$(f) \text{CO}_3^{2-}: 45 \text{ ppm or } 45 \text{ mg/l } \text{CO}_3^{2-} = 45 \times \frac{100}{60} = 75 \text{ mg/l of CaCO}_3$$

$$(g) \text{OH}^-: 34 \text{ ppm or } 34 \text{ mg/l } \text{OH}^- = 34 \times \frac{100}{2 \times 17} = 100 \text{ mg/l of CaCO}_3$$

$$(h) \text{Na}_2\text{AlO}_2: 10 \text{ ppm or } 10 \text{ mg/l} \text{Na}_2\text{AlO}_2 = 10 \times \frac{100}{164} = 6.09 \text{ mg/l of CaCO}_3$$

Using above values,

$$\text{Lime required} = [150 + 150 + 200 + 100 + 100 - 6.09] \times \frac{74}{100} = 513.49 \text{ mg/l}$$

For 12,5000 l of water, the amount of lime required is $513.49 \times 125000 \text{ mg} = 64.18 \text{ kg}$.

$$\text{Soda required} = [150 + 237.5 + 75 + 100 + 100 - 200] \times \frac{106}{100} = 490.25 \text{ mg/l}$$

For 12,5000 l of water, the amount of soda required is $490.25 \times 125000 = 61.28 \text{ kg}$.

Therefore, the quantity of lime required if purity is 74% is

$$60.48 \times \frac{100}{74} = 86.72 \text{ kg}$$

The quantity of soda required if purity is 92% is

$$61.28 \times \frac{100}{92} = 66.61 \text{ kg}$$

Problem 15

A zeolite bed was exhausted after completely removing the total hardness of 10,000 l of hard water. The zeolite bed was regenerated using 8 l of NaCl containing 150 g/l of NaCl. Calculate the hardness of water.

Solution

For the process of regeneration, 8 l NaCl containing 150 g/l of NaCl was used. Therefore, the amount of NaCl used = $150 \times 8 = 1200 \text{ g}$. Now, the CaCO₃ equivalent of 1200 g of NaCl is

$$1200 \times \frac{100}{58.5 \times 2} = 1200 \times \frac{100}{117} = 1025.64 \text{ g of CaCO}_3$$

The total hardness removed by the zeolite in 10,000 l of water is 1025.64 g. The hardness of water in terms of CaCO₃ equivalent is

$$\frac{1025.64}{10000} = 0.1025 \text{ g/l} = 102.5 \text{ mg/l}$$

Problem 16

An exhausted zeolite softener was regenerated by passing 150 l of sodium containing 100 g/l of NaCl. How many liters of water having hardness of 500 ppm have been softened by this zeolite bed?

Solution

Amount of NaCl used for regeneration is $150 \times 100 = 15000 \text{ g}$.

Therefore CaCO₃ equivalent of 15000 g of NaCl is

$$15000 \times \frac{100}{58.5 \times 2} = 12820.51 \text{ g of CaCO}_3 = 1.282 \times 10^7 \text{ mg of CaCO}_3$$

Let volume of softened water be V . Therefore,

$$\text{Hardness in mg/l of CaCO}_3 = \frac{1.282 \times 10^7}{V}$$

and so

$$V = \frac{1.282 \times 10^7}{500} = 2564.11$$

Concept Check

- Why is hard water considered hazardous for boilers? How is hard water softened?
- What is the lime-soda method of softening? Enumerate its advantages and disadvantages.
- How is hard water softened using ion exchange method?
- What is the internal treatment of hard water? Which ions can be removed using this treatment?

2.13 Wastewater

Liquid waste that is carried away from a community in sewers is called sewage. This wastewater may be from domestic or industrial sources. Domestic wastewater results from washing, laundering and other domestic activities and carries with it microorganisms and various impurities. The wastewater from industries is much more concentrated and needs appropriate treatment for removal of impurities.

Characteristics of Wastewater

Wastewater has distinct physical characteristics, such as color, odor, taste and suspended solids. The chemical characteristics that describe wastewater are dissolved solids, dissolved gases (oxygen), pH, chemical oxygen demand (COD) and biological oxygen demand (BOD). The disease-causing micro-organisms in wastewater determine its biological value and toxicity to animal life and plant life. Biological and chemical oxygen demands are described as follows:

1. **Biological oxygen demand:** It is the amount of oxygen required by aerobic microorganisms for the biological breakdown of organic matter present in wastewater. It is determined by measuring the difference in dissolved oxygen (DO) levels in wastewater sample before and after incubation with aerobic microorganisms for 5 days at 20°C. The magnitude of BOD is expressed in mg/l and is a measure of biodegradable impurities in water sample.
2. **Chemical oxygen demand:** It is the amount of oxygen consumed in oxidation of organic and oxidizable inorganic material present in wastewater. COD is expressed in mg/l and determined as follows:

The oxidizable (organic and inorganic) material present in a known volume (V) of water is oxidized by excess of potassium dichromate. The unconsumed amount of dichromate (V_{sample}) is determined by titrating against standard solution of ammonium sulphate of normality N using

diphenylamine as indicator. A blank titration is carried out with distilled water and the volume of water used (V_{blank}) is determined. Then

$$\text{COD} = \frac{(V_{\text{blank}} - V_{\text{sample}})}{V} \times N \times 8 \times 100$$

Sewage Treatment

Sewage treatment involves the removal of a wide range of impurities such as grease, oil, pesticides, scum, heavy metals, pathogenic organisms, inorganic compounds, plastics, etc., from wastewater to produce a liquid safe enough to be discharged into the environment. The most important characteristics that determine the methodology for treatment of waste are BOD and COD. Primary, secondary and tertiary treatments are used for treatment of sewage (Figure 10). These are described as follows.

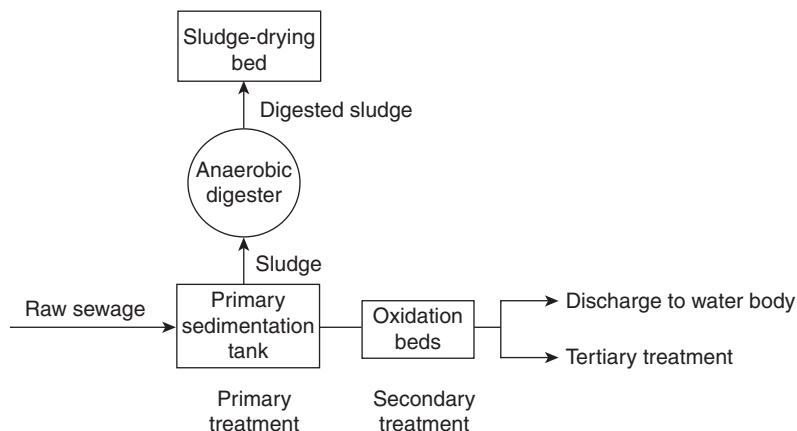


Figure 10 Sewage treatment flowchart.

Primary Waste Treatment

Primary treatment of wastewater consists of the removal of insoluble matter such as grit, grease and scum from water. Wastewater is passed through screens to remove floating impurities and then it is sent for sedimentation for settling of colloidal impurities.

Primary sedimentation involves the sedimentation of floatable and settleable impurities. As explained earlier, some coagulants may be added to aid faster and better sedimentation. The sludge that is so formed can be removed from the bottom and the grease which is still floating can be removed using a skimming device.

When wastewater is put through primary treatment, it generates huge quantities of sediments called sludge. Sludge contains soil particles, organic matter and some inert material. The sludge contains aerobic bacteria that consume the organic matter present in the waste, and because of the higher presence of soil and organic matter in sludge, it is an effective fertilizer for plants. In certain cases, the sludge contains heavy metals and is too polluted to be used in soil. In such cases, sewage is pretreated to remove heavy metals, and resulting sludge can be safely used for soil improvement. The foul smell emanating from sludge can be removed by drying it in air and sun, after which it can be used to fertilize gardens and crop fields.

Secondary Waste Treatment

Sewage is usually very high in organic pollutants which deplete the oxygen levels of water in which it is released. Hence, to prevent this, the BOD levels of sewage have to be brought within the acceptable range before it is discharged into the environment. The secondary treatment of water involves biodegradation of such material under aerobic or anaerobic condition.

Addition of such microorganisms in an aerobic environment breaks down the organic waste into less harmful products which can be removed, thus bringing the BOD levels of sewage down to an acceptable range. The wastewater may be treated by biological process by any of the following methods:

- Trickling filter:** In this method, a 2 m deep cylindrical tank is filled with a bed of either crushed rock, coarse clinkers or anthracite coal (Figure 11). The sewage is allowed to trickle over this filtering material by means of rotary feeder arm. Air is pumped into the filter to counter current the downward flow of sewage growth and cover the surface of filter medium. These further feed on the organic waste present in sewage and release carbon dioxide and water. The purified sewage is removed from the bottom and complex organic material that does not undergo microbial oxidation is separated. This process removes about 85–90% of BOD.

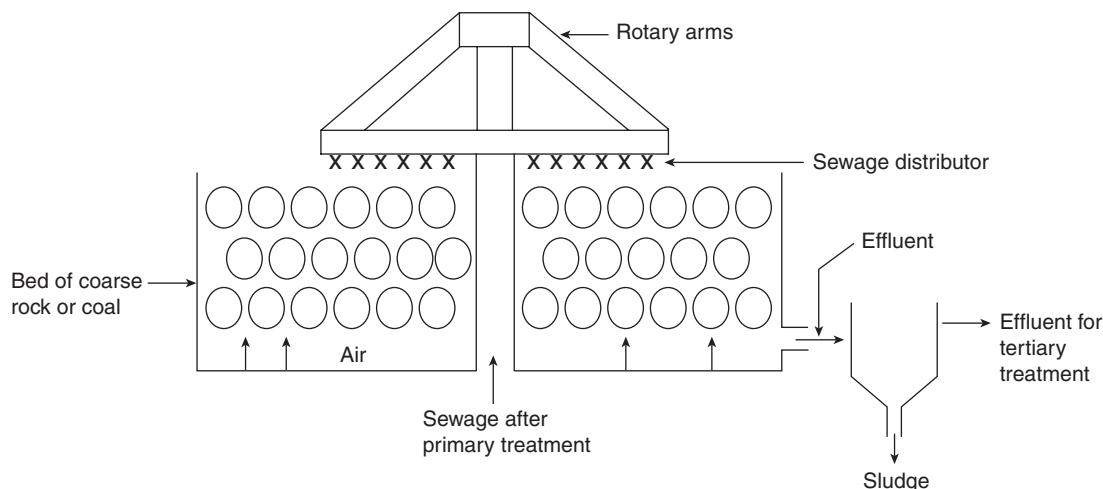


Figure 11 Schematic diagram of trickling filter.

- Rotating biological contactor (RBC):** This contactor has a number of rotating disks made of high-density polythene or polystyrene, closely mounted on a shaft. These disks are coated with microorganisms and keep rotating, ensuring that the wastewater comes in contact with microorganisms as well as the air and organic waste gets degraded.
- Activated sludge process (ASP):** In this process, wastewater is pumped into an aeration tank and air or oxygen is passed through it (Figure 12). An activated sludge is generated by aeration of sewage which consists of organic material containing large number of micro-organisms. This is then added as a floc to wastewater coming in after primary treatment. The mixture is aerated and agitated. The microorganisms feed on the organic matter in the wastewater and degrade it. After a sufficient period of time, the water is taken to a settling tank and allowed to settle. The supernatant is used for the next treatment. The healthy sludge is then returned to the aeration chamber, for it to react with a fresh batch of wastewater and the waste sludge is taken up for sludge treatment.

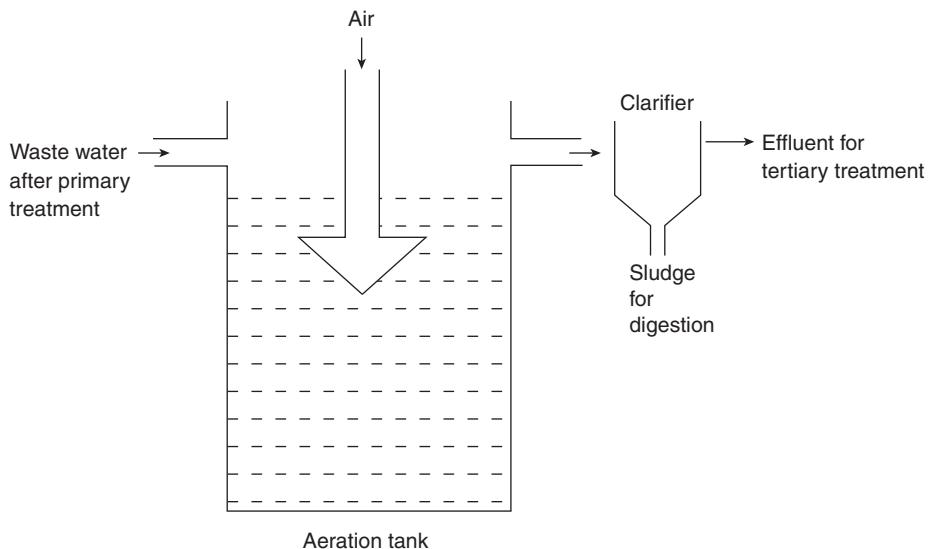


Figure 12 Schematic representation of activated sludge process.

Water is taken for secondary sedimentation to remove suspended impurities. Primary and secondary treatment together can remove upto 90% of the BOD causing impurities.

Tertiary Waste Treatment

After the primary and secondary treatments, the sewage still contains dissolved organic and inorganic compounds, nitrogen and phosphorus, and microorganisms like algae, bacteria and viruses.

For tertiary treatment, it is filtered using sand filter or passed through activated carbon filter to remove finely suspended impurities. It is then fed into lagoons where a number of microorganisms remove fine particulates. It is then taken up for denitrification which releases nitrates as nitrogen gas. Phosphorus can be removed by biological process or chemical treatment. Water is then disinfected using chlorination or UV light or ozonation. Odor from water is then removed using carbon reactors or chemical treatments.

By sludge treatment, sludge formed throughout is digested to reduce the amount of organic substances and microorganisms which may be present in it. It is then subjected to aerobic digestion, anaerobic digestion and composting.

Recycling Wastewater

Though development of wastewater treatment plants has sanitized the process of water conservation by reducing biological oxygen demand and use of chlorination, the need for resource recovery arises, which is also known as water recycling. This can be done by

1. Return of treated wastewater after primary treatment to crops using sprinkler or other irrigation systems.
2. Natural purification by slow percolation of the wastewater into the soil, which eventually recharges the groundwater with clean water.
3. Reuse of the water pumped out of the ground for municipal, industrial, institutional, or agricultural activities.

Through recycling technique, various resources can be produced, such as methane gas (which can be burned as a fuel), as well as ornamental plants and flowers that have commercial value. The processes involved are as follows:

1. The wastewater is run through filters to remove large particles.
2. The water then undergoes anaerobic processing to produce methane gas.
3. The nutrient-rich water flows over an incline surface containing plants, so that the plants can use the nutrients.
4. The water may be further processed by other living plants before being discharged into the environment.

This recycling process is thought to clean the water to the same extent as done by secondary wastewater treatment.

Rainwater Harvesting

Rainwater harvesting has become an important method adopted for water conservation. It has also become mandatory in many cities. It involves collection of rainwater from roofs, terraces and balconies, etc. and storage into large water tanks for future use. This harvested water recharges groundwater, and can be used to meet our daily requirements, as well as for agricultural use. The implementation of this technique dates back to the period of Indus Valley civilization, and has been practiced in arid and semi-arid zones to satisfy water requirements for domestic use, livestock, irrigation, and to replenish ground water.

The main objectives of rainwater harvesting are:

1. Improve moisture content of the soil for planting more and more trees, and thereby reducing air pollution.
2. Increase ground water table through artificial means.
3. Prevent floods and reduce soil erosion.
4. Improve quality of groundwater to avoid its contamination.
5. Reduce water loss.
6. Store water to meet the needs of large populations, as well as for future requirements.

Though rainwater harvesting has many advantages, it can be heavily contaminated by dust particles, air and water pollutants, salts of Ca, Mg, Na, etc. from the sea, dissolved gases such oxides of carbon, nitrogen, sulphur, bacteria, animal and bird faeces. Thus, water must be pretreated for use, especially for drinking and bathing purposes. The water can be boiled in solar cookers, or chlorine may be added as a disinfectant.

Problem 17

A sewage sample of 20 ml was diluted to 500 ml and equal volumes filled in two BOD bottles. About 100 ml of one of the water samples was titrated immediately and it required 5.5 ml of 0.02 N sodium thiosulphate solution. The second sample was incubated for 5 days and it required 2.5 ml of 0.02 N sodium thiosulphate solution for titration. Calculate the BOD of water.

Solution

Given that

Volume of sewage water (A) = 20 ml.

Volume of sewage water after dilution (B) = 500 ml.

Volume of sample used for titration = 100 ml.

Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution for blank titration = 7.5 ml.

Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution for sample after 5 days = 2.5 ml.

Normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution = 0.02 N.

In the blank titration,

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 100 = 0.02 \times 7.5$$

Therefore,

$$N_1 = \frac{0.02 \times 7.5}{100}$$

$$\begin{aligned} \text{Normality of dissolved oxygen in blank } (D_1) &= \frac{0.02 \times 7.5}{100} \times \text{equivalent weight of oxygen} \\ &= \frac{0.02 \times 7.5}{100} \times 8 = 0.012 \text{ g/dm}^3 = 12 \text{ mg/dm}^3 \end{aligned}$$

In titration after 5-day incubation,

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 100 = 0.02 \times 2.5$$

Therefore,

$$N_1 = \frac{0.02 \times 2.5}{100}$$

$$\text{Normality of dissolved oxygen after 5 days } (D_2) = \frac{0.02 \times 2.5}{100} \times 8 = 0.004 \text{ g/dm}^3 = 4 \text{ mg/dm}^3$$

Now, BOD is calculated as follows:

$$\text{BOD} = \frac{D_1 - D_2}{A} \times B = \frac{12 - 4}{20} \times 500 = 8 \times 25 = 200 \text{ mg/dm}^3$$

Problem 18

A sewage water of 25 ml for COD reacts with 25 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ solution and the unreacted $\text{K}_2\text{Cr}_2\text{O}_7$ requires 8 ml of N/4 ferrous ammonium sulphate (FAS) solution. Under similar conditions, in blank titration, 15 ml of N/4 ferrous ammonium sulphate is used up. Calculate the COD of the sample.

Solution

Given that

Volume of water sample = 25 ml.

Volume of N/4 FAS used for unreacted $\text{K}_2\text{Cr}_2\text{O}_7$ = 8 ml.

Volume of N/4 FAS used for blank titration = 15 ml.

Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed to meet the COD in terms of FAS solution = $15 - 8 = 7$ ml.

Now, normality of COD sample is calculated as follows:

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 25 = 0.25 \times 7$$

$$N_1 = \frac{0.25 \times 7}{25} = 0.07$$

The COD sample is

$$0.07 \times \text{Equivalent weight of O}_2 = 0.07 \times 8 = 0.56 \text{ g/dm}^3 = 560 \text{ mg/dm}^3$$

Concept Check

- What is sewage? What are the major steps involved in treatment of sewage?
- What is meant by BOD? How is BOD removed from sewage?

Key Terms

Hard and soft water	Sedimentation	Boiler corrosion
Degree of hardness	Disinfection	Lime–soda process
Temporary and permanent hardness	Brackish water	Ion exchange process
Alkalinity of water	Saline water	Demineralization
Bicarbonate alkalinity	Chlorination	Ion exchange resins
Carbonate alkalinity	Ozonization	Permutit process
Hydroxyl alkalinity	Reverse osmosis	Zeolites
Argentometric method	Electrodialysis	Calgon, carbonate, colloidal, phosphate conditioning
SPADNS method	Flash evaporation	Sewage treatment
Phenol disulphoinic method	Boiler feed water	Biological and chemical oxygen demands
Winkler method	Scales	Primary and secondary waste treatments
Gravimetric method	Sludge	Rainwater harvesting
Potable water	Priming	
Flocculation	Foaming	
	Caustic embrittlement	

Objective-Type Questions

Multiple-Choice Questions

1. Bicarbonates of calcium and magnesium cause
 - a. softness.
 - b. permanent hardness.
 - c. temporary hardness.
 - d. all of the above.

2. Temporary hardness of water can be removed by
 a. boiling.
 b. filtration.
 c. solvent extraction.
 d. sedimentation.
3. Hardness in water is caused by
 a. sodium chloride
 b. sodium carbonate.
 c. calcium chloride.
 d. potassium nitrate.
4. Hard water contains
 a. Ca^{2+} , Mg^{2+} or Fe^{2+} .
 b. NO_3^- and PO_4^{3-} .
 c. Na^+ , K^+
 d. dissolved gases.
5. The presence of which of the following salts of hardness producing metal ions causes permanent hardness of water?
 a. Bicarbonate
 b. Carbonate
 c. Chloride
 d. Hydroxide
6. Temporary hardness is due to
 a. MgSO_4
 b. $\text{Ca}(\text{HCO}_3)_2$
 c. $\text{Ca}(\text{NO}_3)_2$
 d. Na_2SO_4
7. Hardness in water is expressed in terms of equivalent of
 a. CaCl_2
 b. MgCl_2
 c. CaCO_3
 d. MgCO_3
8. Which of the following dissolved salts in water will cause the most hardness in water sample?
 a. 10 ppm CaSO_4
 b. 10 ppm CaCO_3
 c. 10 ppm MgCl_2
 d. 10 ppm $\text{Mg}(\text{OH})_2$
9. Which of the following is not a unit of hardness of water?
 a. ppm
 b. mg
 c. ${}^\circ\text{Fr}$
 d. mg/l
10. Which of the following is equal to 1 ppm in hardness?
 a. 0.07°Cl
 b. 0.7°Cl
 c. 0.1°Cl
 d. 2.0°Cl
11. Hardness due to 13.6 mg/l of CaSO_4 can be expressed in terms of CaCO_3 as
 a. 10 mg/l.
 b. 5 mg/l.
 c. 20 mg/l.
 d. 2 mg/l.
12. Alkalinity in water cannot be due to the presence of
 a. OH^- only.
 b. CO_3^{2-} and HCO_3^- .
 c. OH^- and CO_3^{2-} .
 d. OH^- and HCO_3^- .
13. When $P > M/2$, what type of alkalinity present in water?
 a. OH^- , CO_3^{2-}
 b. CO_3^{2-} and HCO_3^-
 c. OH^- , HCO_3^-
 d. OH^- , CO_3^{2-} and HCO_3^-
14. The end point of the complexometric determination of hardness by EDTA is
 a. colorless to wine red.
 b. clear blue to colorless.
 c. wine red to clear blue.
 d. colorless to clear blue.
15. In the titration of water sample with 0.1 N H_2SO_4 using phenolphthalein indicator, 0 ml of H_2SO_4 was used. This indicates that alkalinity of water is due to the presence of
 a. CO_3^{2-}
 b. OH^-
 c. HCO_3^-
 d. CO_3^{2-} and OH^-

16. Which of the following processes is not involved in potable water treatment?
 - a. Disinfection
 - b. Demineralization
 - c. Coagulation
 - d. Sedimentation
17. Brackish water mostly contains dissolved
 - a. Ca salts.
 - b. Mg salts.
 - c. NaCl salts.
 - d. suspended impurities.
18. Which of the following is not a method for disinfection of water?
 - a. Chlorination
 - b. Ozonization
 - c. Electrodialysis
 - d. UV treatment
19. Sterilization of water can be done by using
 - a. ozone.
 - b. oxygen.
 - c. hydrogen peroxide.
 - d. caustic potash.
20. Ultraviolet rays are used in water treatment for
 - a. illumination.
 - b. disinfection.
 - c. coagulation.
 - d. sedimentation.
21. Which of the following is not a hazardous chemical present in water?
 - a. Cadmium
 - b. Calcium
 - c. Chromium
 - d. Arsenic
22. Chlorides should be removed from potable water as they render it
 - a. highly toxic.
 - b. carcinogenic.
 - c. teratogenic.
 - d. unaesthetic and peculiar in taste.
23. The optimum concentration for fluoride ion is
 - a. <0.1 mg/l.
 - b. 0.8–1.0 mg/l.
 - c. 5 mg/l.
 - d. 10 mg/l.
24. For the determination of fluoride by SPADNS method, wavelength used is
 - a. 570 nm.
 - b. 670 nm.
 - c. 750 nm.
 - d. 760 nm.
25. For the determination of nitrate by phenol disulphonic method, the wavelength used is
 - a. 240 nm.
 - b. 290 nm.
 - c. 320 nm.
 - d. 410 nm.
26. Flocculating agents include
 - a. iron (III) hydroxide.
 - b. aluminium hydroxide.
 - c. polyDADMAC.
 - d. all of the above.
27. Which of the following is not a requisite condition for water used for steam generation in boilers?
 - a. It should be free from pathogens.
 - b. It should be free from dissolved salts.
 - c. It should be free from suspended impurities.
 - d. It should be free from dissolved gases.
28. Which of the following gases dissolved in water cause boiler corrosion?
 - a. Oxygen
 - b. Carbon dioxide
 - c. Sulphur dioxide
 - d. All of the above
29. The presence of which of the following substances leads to the formation of scales?
 - a. $Mg(OH)_2$
 - b. $MgCl_2$
 - c. $MgSO_4$
 - d. $MgCO_3$

30. Desalination of water can be carried out by
 a. lime-soda process.
 b. ion exchange.
 c. reverse osmosis.
 d. all of the above.
31. For the removal of $\text{Ca}(\text{HCO}_3)_2$, temporary hardness by lime-soda process, which substance is required?
 a. Lime
 b. Soda
 c. Lime and soda
 d. None of the above
32. A blow-down operation causes the removal of
 a. scales.
 b. sludges.
 c. both scale and sludge.
 d. hot water only.
33. Calgon is a trade name given to
 a. sodium silicate.
 b. calcium phosphate.
 c. sodium hexametaphosphate.
 d. sodium zeolite.
34. Which of the following can be used as coagulant?
 a. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
 b. $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$
 c. $\text{Na}_2\text{Al}_2\text{O}_4$
 d. all of the above.
35. Colloidal conditioning of a boiler is done by using
 a. calgon.
 b. EDTA.
 c. ion-exchangers.
 d. lignin.
36. Which of the following ions is not found in naturally occurring zeolite?
 a. Na^+
 b. Al^{3+}
 c. Si^{4+}
 d. Ca^{2+}
37. Distilled water can be obtained by
 a. boiling.
 b. the zeolite process.
 c. the lime-soda process.
 d. the ion-exchange process.

Fill in the Blanks

- _____ is due to the presence of bicarbonates, carbonates and hydroxides of the hardness producing metal ions.
- The degree of hardness of a sample containing 20 ppm MgSO_4 is _____ mg/l equivalents of CaCO_3 .
- The estimation of hardness of water by EDTA method involves a _____ titration.
- Phenolphthalein alkalinity equal to zero implies that alkalinity of water is due to _____ ions.
- The chloride content of water can be determined by _____ method.
- The conditioning of water in the boiler itself by the addition of chemicals is called _____.
- Dissolved CO_2 may be removed from water by addition of _____.
- The exhausted zeolite can be regenerated by use of _____ solution.
- In the ion exchange process, exhausted cation exchanger can be regenerated by using _____ solution.
- In calgon conditioning, _____ is added to boiler water to prevent the scale and sludge formation.
- Sterilization of water can be done by using _____.

Review Questions

Short-Answer Questions

1. What are different types of impurities present in water?
2. What are the parameters determined in analysis of water to ascertain the quality and utility of water?
3. What is hard water? What are the causes of hardness?
4. Distinguish between temporary and permanent hardness of water.
5. What is meant by carbonate and non-carbonate hardness of water?
6. Explain why hard water does not produce lather with soap?
7. What is degree of hardness of water? Why is it conventional to express degree of hardness of water in terms of CaCO_3 ?
8. What are different units used to express degree of hardness of water? What is the relationship between the units?
9. Define ppm of hardness.
10. How is temporary hardness eliminated?
11. What is permanent hardness of water? What ions cause permanent hardness?
12. What is total hardness?
13. How do you determine the temporary hardness of water?
14. How many grams of MgCO_3 dissolved per liter give 84 ppm of hardness?
15. State any two disadvantages of using hard water for domestic purpose.
16. Mention the disadvantages of using hard water for industrial purpose.
17. What is the principle in estimation of hardness by EDTA method?
18. Which indicator is used during the determination of hard water by the EDTA method, and what is the color change at the end point?
19. Why is $\text{NH}_3-\text{NH}_4\text{Cl}$ buffer solution added in EDTA titration for determination of hardness of water?
20. Discuss chemistry involved in EDTA complexometric method of determining hardness of water.
21. Write the structure of EDTA and its complex with Ca^{+2} ion.
22. Define alkalinity of water. What are the types of alkalinity in water?
23. Alkalinity of water cannot be due to the simultaneous presence of OH^- , CO_3^{2-} and HCO_3^- ions. Explain.
24. What are the characteristics of potable water? List the steps involved in treatment of water for municipal supply.
25. Why is boiled water not always 100% safe for drinking purposes?
26. Write short notes on sedimentation and coagulation.
27. What is brackish water?
28. What is meant by desalination? What is its significance? List the methods employed for desalination.
29. Explain the principle of reverse osmosis for desalination of water.
30. What is the main advantage of reverse osmosis process over ion exchange?

31. Explain disinfection of water. List various methods and chemicals used for disinfection of water.
32. What is break-point chlorination? What are its advantages?
33. Why chlorination is preferred over bleaching powder treatment?
34. What are the implications of presence of following impurities in water: (a) Fluoride (b) nitrate and (c) chloride.
35. What are the sources and ill effects of lead, cadmium and mercury as pollutants in water?
36. What is the principle of determining nitrate content of water by phenoldisulphonic acid method?
37. Explain the difference between municipal water and the water used for industrial purposes such as the one used in steam boilers.
38. What are the requirements of boiler feed water?
39. What are the disadvantages of using hard water in a boiler operation?
40. What are the defects caused by hard water in boilers?
41. What is the effect of dissolved oxygen in boiler feed water? How can it be removed?
42. Why should the presence of CO_2 be avoided in boiler feed water? How is dissolved CO_2 removed from water by chemical means?
43. What are the boiler problems caused by the presence of silica in water?
44. Differentiate between scale and sludge.
45. Write a short note on scale and sludge formation.
46. Write a short note on caustic embrittlement.
47. How can caustic embrittlement be controlled by addition of sodium sulphate or sodium phosphate?
48. Explain disadvantages of scale formation and two prevention methods for it.
49. Distinguish between priming and forming.
50. Distinguish between external and internal treatments of boiler feed water.
51. What is the principle behind internal treatment?
52. How can scale formation be prevented by colloidal conditioning?
53. What are the advantages of phosphate conditioning over carbonate conditioning?
54. Why is calgon conditioning better than phosphate conditioning?
55. How does calgon treatment prevent scale formation in boilers?
56. What is the ideal pH for phosphate conditioning? What phosphate is used for conditioning of (a) alkaline water, (b) weakly alkaline water and (c) acidic water?
57. Write a short note on phosphate conditioning.
58. Name the various methods used for softening of water. Explain with reactions which is the best method and why.
59. Write the chemical reaction involved in water softening by lime–soda process.
60. Write a brief account of lime–soda process.
61. Give equations to explain the following:
 - a. $\text{Mg}(\text{HCO}_3)_2$ requires double amount of lime for softening;
 - b. $\text{Al}_2(\text{SO}_4)_3$ requires equivalent amount of lime for softening.
62. What are zeolites? Why is water softened by zeolite process unfit for use in boilers?
63. Discuss the following:
 - a. Regeneration of zeolite
 - b. Disadvantages of zeolite process

64. Write a comparative statement on lime-soda and zeolite process.
65. Compare the advantages and disadvantages of permutit process with those of lime-soda process.
66. What are ion exchange resins and how are they classified? Write the chemical reactions involved in ion exchange process.
67. Write a brief account of ion exchange process.
68. Explain why in the deionization process, water is usually first passed through the cation exchanger and then through the anion exchanger.
69. How can exhausted cation and anion exchange resins be regenerated?
70. Define BOD and state its significance.
71. Define COD and state its significance.
72. What are the steps involved in the primary treatment of sewage?
73. What are the steps involved in tertiary treatment of sewage?
74. How do you estimate dissolved oxygen in water?
75. Deoxygenation of water using hydrazine is better than sodium sulphite. Why?
76. Write brief note on secondary treatment of sewage.
4. What is the principle of EDTA titration? How is the permanent hardness of water determined using EDTA method?
5. How is hardness of water determined by the EDTA method? Write the necessary calculations.
6. How do you estimate the temporary hardness of water by complexometric method?
7. Explain the determination of total hardness of water by EDTA method.
8. How alkalinity of water sample containing hydroxide and carbonate ions is determined using indicator method?
9. Describe a method to determine various alkalinites in a given sample of water.
10. For a water sample containing hydroxyl and carbonates show that (a) $A_{ph} > 0.5A_{mo}$; (b) $A_h = 2A_{ph} - A_{mo}$; $A_c = 2(A_{mo} - A_{ph})$
11. Describe how water is made suitable for domestic use.
12. a. Explain the following steps involved in purification of water: Sedimentation and filtration.
b. Describe the sand filter used for the purification of municipal water.
13. Why is sterilization of water necessary? Discuss any two methods of sterilization.
14. What is meant by sterilization of water? Explain how sterilization of water is carried out by using chlorine and ozone.
15. What is meant by disinfection? What is its significance? Explain the different methods used for disinfection of surface waters.
16. Compare the process of purification of drinking water, free from micro-organisms using (a) bleaching powder, (b) chlorine and (c) ozone.
17. Define desalination. Explain briefly the different methods used for the desalination of brackish water.

Long-Answer Questions

1. a. What do mean by hardness of water? How is it classified?
b. Mention the disadvantages of using hard water for domestic purposes.
2. How will you determine the total, permanent and temporary hardness of a water sample in the laboratory?
3. Explain the soap titration method for the estimation of total hardness of water.

18. With the help of a neat diagram, explain the reverse osmosis method for desalination of brackish water.
19. Briefly describe the following methods for desalination of water: (a) Flash distillation and (b) electrodialysis.
20. What is potable water? Discuss the purification of water by reverse osmosis process.
21. What is flocculation? Explain what happens when alum is added to water for its purification.
22. Explain the function of the following in water treatment: (a) calgon, (b) hydrazine, (c) bleaching powder and (d) ozone.
23. Explain the method of determining sulphate content in water by gravimetric method.
24. Explain the determination of dissolved oxygen by Winkler method. Give the reactions involved.
25. Explain the principle and method of determination of chloride content in water.
26. Briefly describe the principle and method of determining the amount of following substances in water: (a) fluoride by SPADNS method and (b) sulphate by gravimetric method.
27. Describe the argentometric method of estimation of chloride content for a water sample.
28. What are the major disadvantages of hard water when used for (a) domestic purposes; (b) industrial purposes and (c) steam generation in boilers?
29. What disadvantages are expected if hard water is used for steam generation in boilers? What processes may be used to overcome these problems?
30. a. Distinguish between the internal and external treatments of water.
b. Discuss the different methods of internal treatment for boiler feed water.
31. What are scales? How are they formed? What are the disadvantages and the methods of prevention of scale formation?
32. Explain the process of scale and sludge formation in boilers and methods for their prevention.
33. What is caustic embrittlement and how can it be avoided?
34. Explain the factors responsible for the corrosion of a boiler. Discuss the measures for its prevention.
35. Write short notes on (a) phosphate conditioning of boiler and (b) priming and foaming.
36. Describe the lime–soda process for water softening. Give the chemistry involved during the softening.
37. What is the principle applied to removal of hardness of water by lime–soda process? Write the chemical reaction involved in the process. What is the role of addition of NaAlO_2 in the process?
38. Briefly explain the construction and working of continuous hot lime–soda water softener.
39. Explain the cold and hot lime–soda processes. What are the advantages of lime–soda process?
40. Describe the hot lime–soda process for softening water. Mention its advantages over the cold lime–soda process.
41. Explain the basic principles involved along with the chemical reactions for (a) lime–soda and (b) zeolite processes and their advantages.
42. Describe the principle and procedure involved in the zeolite process for the

- treatment of water. What are the advantages and disadvantages of the process?
43. What is the chemical composition of zeolite? How are they classified? Explain the mechanism of treatment of hard water by zeolites.
 44. With a neat diagram explain the ion-exchange process for the purification of water. Discuss the merits and demerits of this process.
 45. What are ion-exchange resins? How will you purify water by using the resins? What are the advantages of this method over other methods?
 46. Explain the ion-exchange method for the removal of dissolved impurities and its advantages over lime-soda process.
 47. Compare the resin process with permuntit process for softening of water.
 48. Discuss the demineralization process in detail.
 49. Discuss the principle and processes involved in determination of (a) biological and (b) chemical oxygen demands.
 50. Describe the activated sludge process used in biological (secondary) treatment of sewage.
 51. Justify the following:
 - a. COD is greater than BOD.
 - b. Chloramine is a better disinfectant compared to chlorine and bleaching powder.
 - c. Sedimentation with coagulation is a better process than sedimentation alone.
52. Explain the terms BOD and COD. What are the steps involved in the tertiary treatment of sewage?
 53. Write short notes on:
 - a. Priming and foaming
 - b. Phosphate conditioning
 - c. Caustic embrittlement.
 54. Write short notes on: (a) ozonization, (b) caustic embrittlement and (c) zeolite softeners.
 55. Write short notes on: (a) breakpoint chlorination, (b) dissolved oxygen, (c) hardness of water and (d) sedimentation and coagulation.
 56. What are the major disadvantages of hard water when used for (a) domestic purposes, (b) industrial purposes and (c) steam generation in boilers?
 57. Differentiate between:
 - a. hard water and soft water;
 - b. temporary and permanent hardness;
 - c. osmosis and reverse osmosis;
 - d. electrodialysis and flash evaporation;
 - e. ion exchange and reverse osmosis.

Numerical Problems

1. How many grams of FeSO_4 dissolved per liter of water give 210.5 ppm of hardness?
2. A water sample on analysis was found to contain the following:
 $\text{Mg}(\text{HCO}_3)_2 = 22.5 \text{ ppm}$, $\text{CaSO}_4 = 7.5 \text{ ppm}$,
 $\text{NaCl} = 3.6 \text{ ppm}$
 Calculate the permanent and temporary hardness in $^{\circ}\text{Cl}$.
3. A water sample (500 ml) has a hardness equivalent to 10.5 ml of 0.5 N CaSO_4 . What is the hardness in ppm?
4. Calculate the calcium carbonate equivalent hardness in the given water sample containing 204 g of CaSO_4 per liter.
5. A sample of water on analysis has been found to contain following in ppm: $\text{Ca}(\text{HCO}_3)_2 = 4.86$; $\text{Mg}(\text{HCO}_3)_2 = 5.84$; $\text{CaSO}_4 = 6.80$; $\text{MgSO}_4 = 8.40$. Calculate the temporary and permanent hardness of the water (atomic weights are: Ca = 40, Mg = 24, C = 12, S = 32, O = 16, H = 1).

6. A sample of hard water contains the following dissolved solids per liter.
 $\text{Ca}(\text{HCO}_3)_2 = 16.4 \text{ mg}$, $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mg}$, $\text{CaCl}_2 = 11.1 \text{ mg}$, $\text{MgSO}_4 = 12 \text{ mg}$, $\text{CO}_2 = 4.4 \text{ mg}$ and $\text{CaSO}_4 = 13.6 \text{ mg}$. Calculate temporary and permanent hardness of water in ppm and in $^{\circ}\text{Cl}$.
7. Determine the total hardness of a sample of water in $^{\circ}\text{Fr}$ and $^{\circ}\text{Cl}$ which showed the following analysis: Suspended matter = 100 mg; $\text{Ca}(\text{NO}_3)_2 = 16.4 \text{ mg/l}$; $\text{MgSO}_4 = 24 \text{ mg/l}$; $\text{MgCl}_2 = 19 \text{ mg/l}$; $\text{NaOH} = 40 \text{ mg/l}$; $\text{KOH} = 56 \text{ mg/l}$ (atomic masses of Na = 23, Mg = 24, K = 39 and Ca = 40).
8. Two liters of water obtained from a bore well in Patancheru near Hyderabad gave the following analysis for salts: $\text{FeSO}_4 = 30.4 \text{ mg}$; $\text{CaSO}_4 = 13.6 \text{ mg}$; $\text{MgCl}_2 = 38 \text{ mg}$; $\text{Ca}(\text{HCO}_3)_2 = 32.4 \text{ mg}$; $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mg}$; $\text{NaCl} = 11.7 \text{ mg}$. Find out the total hardness of water in ppm units, giving temporary and permanent hardness assuming the atomic masses of Fe = 56, Ca = 40, Mg = 24 and Na = 23.
9. What is the total hardness of a sample of water in $^{\circ}\text{Fr}$ and $^{\circ}\text{Cl}$ having the following salts: $\text{CaCl}_2 = 11.1 \text{ mg/l}$; $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/l}$; $\text{Mg}(\text{NO}_3)_2 = 14.8 \text{ mg/l}$; $\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg/l}$. Given that the atomic weights of Mg = 24 and Ca = 40.
10. A sample of hard water contains 150 ppm of temporary hardness and 300 ppm of permanent hardness. Express the above hardness in $^{\circ}\text{Cl}$ and $^{\circ}\text{Fr}$.
11. A 100 ml water sample contains hardness equivalent to 25 ml of 0.08 N MgSO_4 . What is the hardness of water sample in ppm?
12. An amount of 0.28g CaCO_3 was dissolved in dilute HCl, and the solution made up to 1l with distilled water. For titration, 100 ml of the above solution required 28 ml of EDTA solution and 100 ml of the water sample required 33 ml of same EDTA solution. After boiling 100 ml of this water, cooling and filtering, the titration required 10 ml of EDTA solution. Calculate the temporary and permanent hardness of water.
13. When 50 ml of a sample of hard water was titrated against 0.01 M EDTA, 48 ml of EDTA was required for titration. Now, 50 ml of the same hard water after boiling and filtering, etc., required 35 ml of the EDTA for titration. Calculate the total and temporary hardness of water in $^{\circ}\text{Cl}$.
14. A standard hard water contains 0.15 g of CaCO_3 per liter. About 20 ml of this sample required 25 ml of EDTA solution and 100 ml of the sample water required 18 ml of EDTA solution. The same sample after boiling required 12 ml EDTA solution. Calculate the temporary hardness of the given sample of water in ppm.
15. A 100 ml water sample required 15.0 ml of 0.01 M EDTA for titration using Eriochrome-T as indicator. In another experiment, 100 ml of the same sample was boiled to remove the carbonate hardness, the precipitate was removed and the cold solution required 8.0 ml of 0.01 M EDTA for titration. Calculate in terms of ppm and $^{\circ}\text{Fr}$, the total hardness, permanent hardness and carbonate hardness.
16. A 0.5 g CaCO_3 was dissolved in dilute HCl and dilute to 500 ml. About 50 ml of this solution required 48 ml of EDTA solution for titration, while 50 ml of given hard water sample required 15 ml of EDTA solution for titration. Calculate total hardness of water sample in ppm.
17. A 50 ml standard hard water containing 1 mg of pure CaCO_3 per ml consumed 25 ml of EDTA. Now, 50 ml of a water sample consumed 25 ml of the same EDTA solution

- using EBT indicator. Calculate the total hardness of water sample in ppm, °Cl and °Fr.
18. One gram of CaCO_3 was dissolved in dilute HCl and the solution was made to 1 l by dilution. Now, 50 ml of this solution required 40 ml of EDTA solution, while 50 ml of the sample water required 20 ml of EDTA solution. Calculate total hardness of water sample.
 19. A 200 ml water sample required 20.0 ml of 0.2 N HCl using methyl orange as indicator. Another 200 ml of the same sample required 8.0 ml of 0.2 N HCl using phenolphthalein as indicator. Express the alkalinites in terms of mg of CaCO_3 per liter.
 20. A water sample is alkaline to both phenolphthalein and methyl orange. From this water sample, 100 ml on titration with 0.02 N HCl required 4.7 ml of acid to reach phenolphthalein end point. When four drops of methyl orange are added to the same solution and titration is further continued, the yellow color of the solution just turned red after addition of another 10.5 ml of acid solution. Describe the type and extent of alkalinity present in water sample.
 21. A 100 ml of a raw water sample on titration with 0.02 N H_2SO_4 required 12.4 ml of the acid to reach phenolphthalein end point and 15.2 ml of the acid to reach methyl orange end point. Determine the type and extent of alkalinity present in the water sample.
 22. Calculate the requirement of CaO and Na_2SO_3 for cold lime-soda process for softening 50,000 l of water having $\text{Ca}^{2+} = 100 \text{ ppm}$; $\text{Mg}^{2+} = 42 \text{ ppm}$; $\text{CO}_2 = 60 \text{ ppm}$; $\text{HCO}_3^- = 212 \text{ ppm}$; $\text{H}^+ = 5 \text{ ppm}$. Sodium aluminate was used as a coagulant at 8 ppm concentration. Analysis of 100 ml of the treated water gave a phenolphthalein end point of 27.5 ml and methyl orange end point of 40 ml with 0.1 N HCl.
 23. Chemically treated water containing NH_4HCO_3 was boiled for 5 min to remove ammonia. The alkalinity was found to change as: A_{ph} from 0 to 0.3 mg equiv./l and A_{mo} from 1.1 to 0.8 mg equiv./l. Find the amount of ammonia that distilled off.
 24. Calculate the temporary hardness of water from the following data by the soap titration method, when 100 ml of the water sample is titrated with soap solution.
Lather factor = 0.6 ml of soap solution
Total hardness = 18.6 ml of soap solution
Permanent hardness = 6 ml of soap solution
Standard hard water (400 mg/l of CaCO_3) = 36 ml.
 25. A sample of hard water gives the following results on analysis: $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ ppm}$, $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$, $\text{CaCl}_2 = 11.1 \text{ ppm}$, $\text{MgCl}_2 = 9.5 \text{ ppm}$, $\text{CaSO}_4 = 13.6 \text{ ppm}$, $\text{MgSO}_4 = 12.0 \text{ ppm}$, $\text{CO}_2 = 4.4 \text{ ppm}$. What is the amount of lime and soda required for the treatment of the water sample?
 26. Calculate the lime and soda needed for softening 10,00,000 l of water containing the following:
 MgSO_4 : 12.00 mg/l, $\text{Mg}(\text{HCO}_3)_2$: 14.6 mg/l, CaCl_2 : 22.2 mg/l, NaCl : 5.85 mg/l.
 27. Calculate the lime and soda needed for softening 50,000 l of water containing the following salts: $\text{CaSO}_4 = 13.6 \text{ mg/l}$; $\text{MgCl}_2 = 9.5 \text{ mg/l}$; $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/l}$; $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/l}$. Given that the molar mass of $\text{Ca}(\text{HCO}_3)_2$ is 162 and that of MgCl_2 is 95.

28. Calculate the quantities of lime and soda required in kilograms for softening 10,000 l of water using 82 ppm of NaAlO_2 as coagulant. Analysis of water was as follows: $\text{CaCl}_2 = 11.1$ ppm; $\text{Mg}(\text{HCO}_3)_2 = 14.6$ ppm; $\text{NaCl} = 58.5$ ppm; $\text{KCl} = 74.5$ ppm; Dissolved $\text{CO}_2 = 44$ ppm (atomic weight of Na = 23, Mg = 24, K = 39, Ca = 40 and Al = 27).
29. Calculate the quantities (in kilograms) of lime and soda required to soften 50,000 l of hard water containing the following salts: $\text{MgCl}_2 = 9.5$ ppm; $\text{Mg}(\text{HCO}_3)_2 = 14.6$ ppm; $\text{CaSO}_4 = 13.6$ ppm; $\text{Ca}(\text{HCO}_3)_2 = 16.2$ ppm.
- Assume that the lime used is only 85% pure and soda is only 95% pure and the molar masses of $\text{Mg}(\text{HCO}_3)_2$ and CaSO_4 are, respectively, 146 and 136.
30. The hardness of 10000 l of sample of water was completely removed by zeolite softener. The zeolite softener required 60 l of NaCl solution containing 1.5 kg/l of NaCl. Calculate the hardness of water solution.
31. A zeolite softener was 90% exhausted by removing the hardness completely when 10,000 l of hard water sample passed through it. The exhausted zeolite bed required 200 l of 3% NaCl solution for its complete regeneration. Calculate the hardness of water solution.
32. When 10,000 l of hard water was softened by passing through a zeolite softener, the exhausted zeolite column required 30 l of 2 N NaCl solution for its regeneration. Calculate the hardness of water.
33. A zeolite softener was exhausted and regenerated by passing 100 l of NaCl solution of strength 585 g/l. Calculate the total hardness of the water sample in ppm, if the zeolite softener can soften 1000 l of water before regeneration.
34. A 50 ml of sample contains 840 ppm of DO after 5 days. The DO value becomes 230 ppm after the sample has been diluted to 80 ml. Calculate the BOD of the sample.
35. A 25 ml of a sewage water sample was refluxed with 10 ml of 0.25 N $\text{K}_2\text{Cr}_2\text{O}_7$ solution in the presence of dilute H_2SO_4 . The unreacted dichromate required 6.5 ml of 0.1 N ferrous ammonium sulphate. Now, 10 ml of the same $\text{K}_2\text{Cr}_2\text{O}_7$ solution and 25 ml of distilled water, under the same conditions as the sample, required 27 ml of 0.1 N ferrous ammonium sulphate. Calculate the COD of the sewage water sample.
36. In a COD experiment, 30 cm^3 of an effluent sample required 9.8 cm^3 of 0.001 M $\text{K}_2\text{Cr}_2\text{O}_7$ for oxidation. Calculate the COD of the sample.
37. Calculate the COD of the effluent sample when 2 cm^3 of the effluent requires 10.5 cm^3 of 0.005 M $\text{K}_2\text{Cr}_2\text{O}_7$ for complete oxidation.
38. About 20 cm^3 of a sample of COD analysis was reacted with 10 cm of 0.25 N $\text{K}_2\text{Cr}_2\text{O}_7$ and 20 cm^3 of distilled water under the same condition as the sample requires 26.0 cm^3 of 0.10 N Mohr's salt. What is the COD of the sample?
39. In a COD experiment, 29.5 cm^3 and 20 cm^3 of 0.025 N Mohr's salt solution were required for blank and sample titrations, respectively. The volume of test sample used was 25 cm^3 . Calculate the COD of the sample solution.

Answers

Multiple-Choice Questions

- | | | |
|---------|---------|---------|
| 1. (c) | 14. (c) | 27. (a) |
| 2. (a) | 15. (c) | 28. (d) |
| 3. (c) | 16. (b) | 29. (a) |
| 4. (a) | 17. (c) | 30. (c) |
| 5. (c) | 18. (c) | 31. (a) |
| 6. (b) | 19. (a) | 32. (b) |
| 7. (c) | 20. (b) | 33. (c) |
| 8. (c) | 21. (b) | 34. (d) |
| 9. (b) | 22. (d) | 35. (d) |
| 10. (a) | 23. (b) | 36. (d) |
| 11. (a) | 24. (a) | 37. (d) |
| 12. (d) | 25. (d) | |
| 13. (a) | 26. (d) | |

Fill in the Blanks

- | | | |
|---------------------|-----------------------|------------------------------|
| 1. alkalinity | 5. argentometric | 9. acid |
| 2. 16.67 | 6. internal treatment | 10. sodium hexametaphosphate |
| 3. complexometric | 7. ammonium hydroxide | |
| 4. bicarbonate ions | 8. brine | 11. ozone |

Numerical Problems

1. 319.96 ppm
2. 0.39°Cl ; 1.08°Cl
3. 525 ppm
4. 150 ppm
5. 7 mg/l; 12 mg/l or ppm
6. Temporary hardness = 20.12 ppm or 1.41°Cl
Permanent hardness = 30 ppm or 2.1°Cl
7. 3.5°Cl ; 5°Fr
8. 50 ppm; temporary hardness = 15 ppm;
permanent hardness = 35 ppm
9. 2.1°Cl ; 3°Fr
10. Temporary hardness = 10.5°Cl ; 15°Fr
Permanent hardness = 21°Cl ; 30°Fr
11. 1000 ppm
12. Permanent hardness = 100 mg/l
Temporary hardness = 230 mg/l

13. Total hardness = 960 mg/l; temporary hardness = 260 mg/l
14. 7.2 ppm
15. Carbonate hardness = 70 ppm, 7°Fr
 Permanent hardness = 80 ppm, 8°Fr
 Total hardness = 150 ppm, 15°Fr
16. 312.5 ppm
17. 1000 ppm, 70°Cl, 100°Fr
18. 2000 ppm, 140°Cl, 200°Fr
19. 1400 mg/l
20. $P < \frac{1}{2} M$, so, the alkalinity is due to carbonate and bicarbonate ions only and is given as $2P(\text{CO}_3^{2-}) = 47 \times 2 = 94$ ppm and for bicarbonate as $M - 2P(\text{CO}_3^{2-}) = 154 - 47 \times 2 = 60$ ppm
21. Since, $P > \frac{1}{2} M$, alkalinity is both due to OH^- and CO_3^{2-} ions.
Alkalinity due to carbonate ions = 56 ppm
Alkalinity due to hydroxyl ions = 96 ppm
22. 27.02 kg; 26.57 kg
23. 7.9 mg/l
24. 142.4 ppm
25. 44.4 mg/l; 42.4 mg/l
26. 22 kg; 31.8 kg
27. 1.11 kg; 1.06 kg
28. 0.148 kg; 0.100 kg
29. 1.74 kg; 1.12 kg
30. 7692.31 mg/l
31. 927.84 mg/l
32. 205.13 mg/l
33. 5×10^5 ppm
34. 976 mg/l
35. 656 mg/dm³
36. 2.613 mg/cm³
37. 210 mg/cm³
38. 20 mg/cm³
39. 30.4 mg/cm³



3

Electrochemistry and Corrosion

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Nature of electrolytic conductance and factors affecting conductivity.
- Strong and weak electrolytes and their behavior.
- Specific, molar and ionic conductances.
- Concept of transport (transference) number and hydrated ions.
- Electrochemical cells and their types.
- Origin and nature of electrode potential.
- Construction and working of a galvanic cell.
- Electrochemical conventions and notations.
- Derivation and significance of Nernst equation.
- Electromotive force (EMF) of a cell and its measurement.
- Different types of reference electrodes and their applications.
- Characteristics and applications of electrochemical series.
- Different types of electrodes, their construction and uses.
- Use of glass electrode in the measurement of pH of a solution.
- Different types of concentration cells and their applications.
- Essential components and characteristics of a battery.
- Construction, working and uses of classical batteries – dry cell, alkaline dry cell, lead–acid battery and nickel–cadmium cell.
- Construction, working and uses of modern batteries – nickel–metal hydride battery and lithium batteries.
- Characteristics and uses of fuel cells and their types.
- Construction, working and applications of hydrogen–oxygen fuel cell.
- Corrosion, its definition, causes and effects.
- Types of corrosion – dry and wet (electrochemical) corrosion – and their differences.
- Types of electrochemical corrosion – differential metal, waterline, pitting and crevice.
- Other types of corrosion – stress, intergranular, microbiological, soil, erosion.
- Factors affecting rate of corrosion – primary and secondary factors.
- Corrosion control methods.
- Protective coatings.
- Metal finishing.
- Electroplating process.
- Electroless plating.

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry that deals with the relation between chemical action and electricity. It deals with the study of electrical properties of electrolytes and also the chemical changes brought about by passage of electricity.

3.1 Electrical Conductance

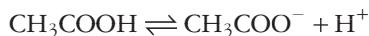
Substances that allow the passage of current through them are called conductors and the phenomenon is called electrical conductance. Conductors are further divided into two categories, namely, metallic and electrolytic conductors.

1. In metallic conductors, the conduction is only due to the presence of free mobile electrons. Hence, these are also referred to as electronic conductors. This electronic conduction is not accompanied by any chemical change. Use of quinhydrone electrode in the measurement of pH of a solution.
2. The substances which conduct electricity both in the fused state and in the aqueous solution are called electrolytic conductors or electrolytes. These substances dissociate in molten state or aqueous solution to furnish ions. The conduction is due to the presence of these mobile ions. For example, molten or aqueous solution of sodium chloride.

Types of Electrolytes

Based on the extent of dissociation, electrolytes are classified into two types:

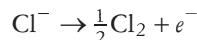
1. **Strong electrolytes:** Those which are almost completely dissociated in their aqueous solutions and have a large value of conductance. For example, HCl, HNO₃, NaOH, KOH, NaCl and KCl.
2. **Weak electrolytes:** Those which do not undergo complete dissociation even in their dilute aqueous solutions and have low value of conductance. In the solution of a weak electrolyte, there exists an equilibrium between the undissociated molecules and their ions. For example, CH₃COOH, HCOOH and NH₄OH. The dissociation of acetic acid is shown as follows:



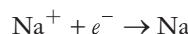
Electrolytic Conductance

Consider the process of conductance of an electrolyte, say, molten NaCl solution (Figure 1).

When electricity is provided by a battery or a DC source, the electrodes acquire electrical charges. They attract ions of opposite charge which take part in redox reactions. At anode, the oxidation reaction occurs. For example, in case of NaCl as electrolyte,



The electrons from the positive electrode are pumped through the external circuit. These electrons are delivered to the negative electrode where reduction occurs:



The overall effect is that as these redox reactions occur, there is a flow of electrons through the external wire resulting from the flow of ions in the solution. The resulting conductance is called the *electrolytic conductance*.

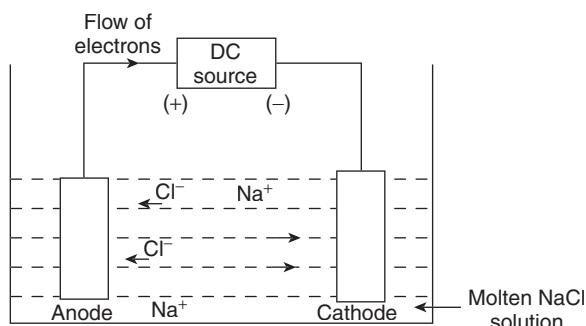


Figure 1 Mechanism involved in typical electrolytic conductance.

Specific Conductance

Like any metallic conductor, electrolytic conductor also offers some resistance to the flow of current. Let R be the resistance offered by an electrolytic conductor. This resistance is directly proportional to the length (l) of the conductor and inversely proportional to the area of cross-section (a) of the conductor. Therefore,

$$R \propto l \quad \text{and} \quad R \propto \frac{1}{a}$$

so,

$$R \propto \frac{l}{a}$$

or

$$R = \rho \cdot \frac{l}{a}$$

where ρ is the proportionality constant. Therefore,

$$\rho = R \cdot \frac{a}{l}$$

If $R = 1 \Omega$, $l = 1 \text{ m}$ and $a = 1 \text{ m}^2$; then $\rho = R$, where ρ is called the *specific resistance*. It is the resistance offered by a conductor of 1 m length and 1 m^2 area of cross-section. In SI system, it has unit of $\Omega \text{ m}$ (ohm-meter). The reciprocal of specific resistance is called the *specific conductance* (k). Therefore,

$$k = \frac{1}{\rho}$$

or

$$k = \frac{1}{R} \times \frac{l}{a}$$

Specific conductance is the conductance of the solution placed between two electrodes having the cross-sectional area of 1 m^2 and placed 1 m apart. In other words, it is defined as the conductance of 1 cm^3 of the solution and has units Siemens per centimeter (S/cm) in SI system. As the specific conductance does not involve the concentration term, it is expressed in the other modes.

The ratio of length to the cross-sectional area is called the *cell constant*.

$$\text{Cell constant} = \frac{l}{a}$$

It is the characteristic parameter of conductivity of cell used for the experiments.

Equivalent Conductance

It is the conductance of an electrolytic solution due to all the ions obtained from 1 gram-equivalent (g-equiv.) mass of the electrolyte at a given concentration. Therefore,

$$\Lambda = kV$$

where k is the specific conductance of the solution and V is the volume of the solution containing 1 g-equiv. of the substance. In terms of concentration and normality,

$$\Lambda = \frac{k}{1000 \times c} \quad \text{or} \quad \Lambda = \frac{k (\text{S/cm}) \times 1000 (\text{cm}^3/\text{l})}{\text{Normality (g-equiv./l)}}$$

In SI system, equivalent conductance has $\text{Sm}^2/\text{equiv.}$ as the unit.

Molar Conductance

It is defined as the conductance of an electrolytic solution due to all the ions obtained from 1 mole of electrolyte at a given concentration. Mathematically,

$$\Lambda_m = \frac{k}{1000 \times c} \quad \text{or} \quad \Lambda_m = \frac{k (\text{S/cm}) \times 1000 (\text{cm}^3/\text{l})}{\text{Molarity (mol/l)}}$$

where k is the specific conductance of the solution and c is the molar concentration of the solution. The units of molar conductance in SI system are Sm^2/mol .

Ionic Conductance

Conductance of a solution depends on the number of ions. It is observed that molar conductance increases upon dilution. This may be due to the increase in the degree of dissociation of the electrolyte or due to decreased ion-ion force of attraction.

With dilution, the influence by other ions on the movement of an ion decreases. At a particular dilution, the ion becomes totally independent of other ions. At this point, it contributes maximum towards the conductance of the solution. The part of the conductance of the solution due to movement of an ion is referred to as ionic conductance. Under the conditions, the molar conductance of the solution reaches the maximum value. This value is called *molar conductance* at infinite dilution (Λ_0).

Kohlrausch observed certain very interesting relation between the value of Λ_0 of different electrolytes having common anion or cation (Table 1).

This observation has made him to formulate the law which states that at infinite dilution when all the interionic effects disappear, each ion makes a definite contribution towards the molar conductance

Table 1 Molar conductance at infinite dilution of different electrolytes at 298 K, in Sm^2/mol

Electrolytes	Λ_0	Difference	Remarks
KCl	14.99×10^{-3}		
NaCl	12.65×10^{-3}	2.34×10^{-3}	Difference in conductance is due to difference in conductance of K^+ and Na^+ ions
KNO ₃	14.5×10^{-3}		
NaNO ₃	12.16×10^{-3}	2.34×10^{-3}	
KCl	14.99×10^{-3}		
KNO ₃	14.5×10^{-3}	0.49×10^{-3}	Difference in conductance is due to difference in conductance of Cl^- and NO_3^- ions
NaCl	12.65×10^{-3}	0.49×10^{-3}	
NaNO ₃	12.16×10^{-3}		
HCl	42.62×10^{-3}	0.49×10^{-3}	
HNO ₃	42.13×10^{-3}		

of the electrolyte irrespective of the nature of the other ion with which it is associated. Mathematically, the law can be stated as:

$$\Lambda_o = \lambda_o^+ + \lambda_o^-$$

where Λ_o , λ_o^+ and λ_o^- are molar conductance at infinite dilution, ionic conductance of the cation at infinite dilution and ionic conductance of the anion at infinite dilution, respectively.

Applications of Kohlrausch Law of Independent Ionic Migration

The law has various utilities like evaluating molar conductance at infinite dilution of weak electrolytes:

1. **To calculate the Λ_o of weak electrolytes:** The Λ_o values of strong electrolytes can be graphically obtained, while those of weak electrolytes are calculated indirectly by knowing Λ_o values of selected strong electrolytes. For example, if Λ_o of HCl, NaCl and CH_3COONa are known then Λ_o of acetic acid and can be calculated as:

$$\begin{aligned}\Lambda_o(\text{CH}_3\text{COOH}) &= \lambda_o^+(\text{CH}_3\text{COO}^-) + \lambda_o^-(\text{H}^+) \\ &= \Lambda_o(\text{HCl}) + \Lambda_o(\text{CH}_3\text{COONa}) - \Lambda_o(\text{NaCl}) \\ &= \lambda_o(\text{H}^+) + \lambda_o(\text{Cl}^-) + \lambda_o(\text{CH}_3\text{COO}^-) + \lambda_o(\text{Na}^+) - [\lambda_o(\text{Na}^+) + \lambda_o(\text{Cl}^-)]\end{aligned}$$

2. **To calculate the ionic conductance:** The ionic conductance (λ_o^+) can be calculated provided the transport number and molar conductance at infinite dilution are known.

$$t_+ = \frac{\lambda_o^+}{\Lambda_o}$$

where t_+ is the transport number (discussed in the next section) of the ion.

3. **To calculate the solubility of the sparingly soluble salt:** A saturated solution of a sparingly soluble salt is a very dilute solution. If the specific conductance of the solution is determined, the concentration of the solution can be calculated.

$$\Lambda_o = \frac{k}{1000 \times c} \quad \text{or} \quad \Lambda_m^\circ = \frac{k (\text{S/cm}) \times 1000 (\text{cm}^3/\text{l})}{\text{Molarity (mol/l)}} \times \text{Solubility}$$

The molar conductance at infinite dilution can be obtained from literature.

Factors Affecting Conductance

Among the various factors, the following greatly influence the conductance of a solution:

1. **Temperature:** In case of strong electrolytes, increase in temperature increases the speed of the ions. This results in increased conductance. In case of weak electrolytes, increase in temperature increases the degree of dissociation. There is increase in both the number of ions as well as their speed. Hence, the conductance increases.
2. **Concentration:** Generally, the conductance of a solution depends on the number of ions present in the solution and the speed of the ions. At higher concentration, the force of attraction between the ions increases, which decreases the speed of the ions. Hence, conductance decreases

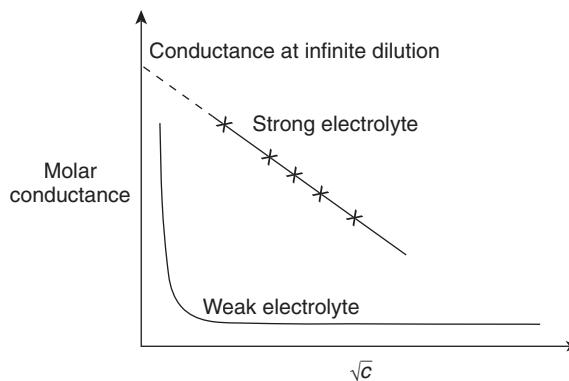


Figure 2 Plot of molar conductance vs. (concentration)^{1/2}.

with concentration. The graphical representation of molar conductance vs. square root of the concentration reinforces this conclusion (Figure 2).

It can be found from the graph that for a strong electrolyte, as the concentration approaches the zero value, the molar conductance approaches a limiting value called *molar conductance* at infinite dilution. The *y*-intercept made by the curve indicates the molar conductance at infinite dilution.

The curve for a weak electrolyte is a rectangular hyperbola and does not intercept the *y*-axis. Even though the concept of molar conductance at infinite dilution exists for a weak electrolyte, graphically the value cannot be evaluated.

Transport (Transference) Number

It is an established fact that during electrolysis, the current is carried by both anions and cations. The fraction of the total current carried by the cation or anion is termed as transport number. Suppose Q is the total current carried through the solution by cations and anions, a portion of it (q_+) is carried by the cation. Therefore, the current carried by the anion is

$$q_- = (Q - q_+)$$

or
$$t_+ = \frac{\text{current carried by the cations}}{\text{total current carried by both the ions}}$$

so,
$$t_+ = \frac{q_+}{Q} \quad (3.1)$$

where t_+ is the transport number of the cation.

Similarly,

$$t_- = \frac{q_-}{Q} \quad (3.2)$$

where t_- is the transport number of the anion.

Now, adding Eqs. (3.1) and (3.2), we get

$$t_+ + t_- = 1$$

The current carried by an ion depends on the charge, speed and molar concentration of the ion. Therefore,

$$t_+ \propto Z_+ m_+ v_+ \quad \text{and} \quad t_- \propto Z_- m_- v_-$$

For an electrolyte, $m_+ Z_+ = m_- Z_-$. The solution is electrically neutral, but

$$t_+ = \frac{q_+}{q_+ + q_-} = \frac{v_+}{(v_+ + v_-)}$$

$$t_- = \frac{v_-}{(v_+ + v_-)}$$

The speeds of the ions are proportional to molar conductance, that is,

$$\frac{t_+}{t_-} = \frac{v_+}{v_-} = \frac{\lambda_+}{\lambda_-}$$

Interionic Attraction Theory of Conductance

It is a general observation that molar conductance of a solution increases on dilution. Arrhenius postulated in his theory of electrolytic dissociation, that in an aqueous solution of an electrolyte, there will be an equilibrium between the ions and the dissociated molecules. This, however, exclusively accounts for the ionic behavior of weak electrolytes only.

In case of a weak electrolyte, addition of water increases the degree of dissociation because water has a high dielectric constant. Increase in the number of ions increases the molar conductance enormously. However, molar conductance of a strong electrolyte increases marginally on dilution.

A strong electrolyte contains ions, even in a concentrated solution. The conductance of such a solution is low as each ion is under the influence of other oppositely charged ions. As a result, the ion experiences a *pull* or *drag* in a direction opposite to the direction of flow. The mobility of the ion and hence its conductance will decrease upon dilution, as the distance between the ions increases. The ions experience lesser force of attraction than before. Dilution will not increase the population of ions in the solution but only reduce the force of attraction between them. Hence, the conductance increases marginally.

Hydration of Ions

The molar conductance at infinite dilution of an electrolyte is the maximum value that an electrolyte can offer. At this point, the conductance is either due to increase in concentration of ions (in a weak electrolyte) or decrease in interionic attraction (in a strong electrolyte).

Each ion is solvated in the medium, and solvated positive and negative ions move in the solution (Figure 3). These ions move in opposite directions, under the influence of electric field. Each solvated ion has to move through the atmosphere of the other ion. The counter currents which slow down the ions in the same way lead to an effect referred to as the *electrophoretic effect*.

In case of aqueous medium, ions are surrounded by water molecules and are known as hydrated ions. The degree of hydration depends on the size and charge of the ion and greatly influences the conductance of ions. For example, mobility and transport number of Li^+ in LiCl solution is less than that of Na^+ in NaCl . This is because Li^+ being smaller than Na^+ is hydrated to a greater extent than Na^+ .

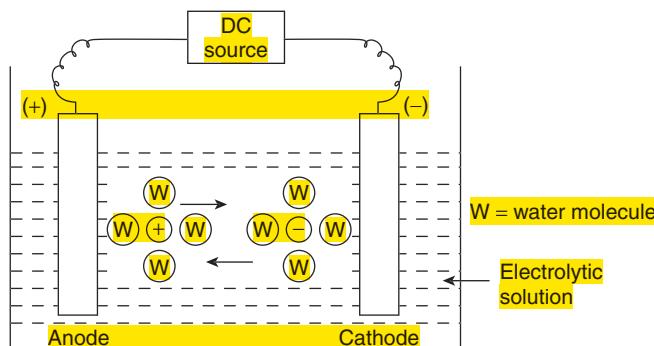


Figure 3 Electrophoretic effect.

Problem 1

Calculate the specific conductance (k) of a solution which is placed between two electrodes $1.63 \times 10^{-2} \text{ m}$ apart and having cross-sectional area $3.996 \times 10^{-4} \text{ m}^2$. The resistance offered by the solution is 17.69Ω .

Solution

If the resistance offered by the solution is 17.69Ω , then

$$k = \frac{1}{R} \cdot \frac{l}{\alpha} = \frac{1}{17.69} \times \frac{1.63 \times 10^{-2}}{3.996 \times 10^{-4}} = 2.3058 \text{ S/m}$$

Problem 2

At 298 K , the specific conductance of 0.1 N NaCl is 1.1 S/m . Calculate the equivalent conductance at the same temperature.

Solution

Given that $c = 0.1 \text{ N}$ and $k = 1.1 \text{ S/m}$. Therefore,

$$\Lambda = \frac{k}{1000 \times c} = \frac{1.1}{1000 \times 0.1} = 1.1 \times 10^{-2} \text{ S m}^2 / \text{equiv.}$$

Problem 3

Calculate the specific conductance and molar conductance of 0.0469 M NaOH , if the resistance offered and the cell constant are 60.2Ω and 89.6 m^{-1} , respectively.

Solution

Given that $R = 60.2 \Omega$, $l/\alpha = 89.6 \text{ m}^{-1}$ and $c = 0.0469 \text{ M}$. Therefore,

$$k = \frac{1}{R} \times \frac{l}{a} = \frac{1}{60.2} \times 89.6 = 1.4883 \text{ S/m}$$

$$\Lambda_m = \frac{k}{1000 \times c} = \frac{1.4883}{1000 \times 0.0469} = 0.03173 \text{ S m}^2/\text{mol}$$

Problem 4

Calculate the molar conductance of infinite dilution of acetic acid at 298 K using the given data: $\Lambda_o(\text{HCl})$, $\Lambda_o(\text{CH}_3\text{COONa})$ and $\Lambda_o(\text{NaCl})$ at 298 K as $42.62 \times 10^{-3} \text{ Sm}^2/\text{mol}$, $9.1 \times 10^{-3} \text{ Sm}^2/\text{mol}$ and $12.65 \times 10^{-3} \text{ Sm}^2/\text{mol}$, respectively.

Solution

We know that

$$\begin{aligned}\Lambda_o(\text{CH}_3\text{COOH}) &= \Lambda_o(\text{HCl}) + \Lambda_o(\text{CH}_3\text{COONa}) - \Lambda_o(\text{NaCl}) \\ &= 42.62 \times 10^{-3} + 9.1 \times 10^{-3} - 12.65 \times 10^{-3}\end{aligned}$$

So,

$$\Lambda_o(\text{CH}_3\text{COOH}) = 39.07 \times 10^{-3} \text{ Sm}^2/\text{mol}$$

Problem 5

Calculate the transport number of sodium ion in 0.1 M NaCl at 298 K, if its ionic conductance is $50.1 \times 10^{-4} \text{ Sm}^2/\text{mol}$. Given that molar conductance of NaCl at infinite dilution is $126.44 \text{ Sm}^2/\text{mol}$.

Solution

The transport number of Na^+ is calculated as:

$$t_{\text{Na}^+} = \frac{\lambda_{\text{Na}^+}^o}{\lambda_{\text{NaCl}}^o} = \frac{50.1 \times 10^{-4}}{126.44 \times 10^{-4}} = 0.3962$$

Concept Check

- Metallic conductivity decreases with temperature. Justify the statement.
- Specific conductance of a solution decreases with dilution. Justify the statement.
- Molar conductance of an acetic acid solution increases drastically with dilution. Explain.
- Equivalence conductance at infinite dilution of lithium ion is less than that of sodium ions. Explain.

3.2 Electrochemical Cells

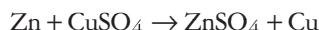
The devices which convert electrical energy into chemical energy or vice versa are called *electrochemical cells*. Based on the activity taking place in them, these devices are classified into two major categories:

1. **Electrolytic cells.**
2. **Galvanic (voltaic cells):** These are further divided into
 - chemical cells;
 - concentration cells.

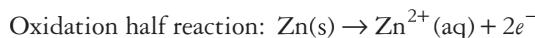
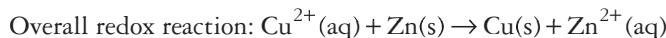
The devices in which chemical changes occur in the presence of applied electrical energy are referred to as *electrolytic cells*. The devices in which electrical energy is generated on account of the chemical reactions occurring in them are known as *galvanic cells*. These may be further classified into chemical and concentration cells. Further, chemical cells are classified into two categories, namely primary and secondary cells.

Redox Reactions

In any reaction, a substance can lose electrons to be oxidized, only if there is another present, which will readily accept these electrons and get reduced. Such reactions in which oxidation and reduction take place simultaneously are known as redox reactions. For example, in the reaction:



Zn loses two electrons and gets oxidized, whereas copper gains two electrons and is reduced from Cu^{2+} to Cu. Redox reactions may be termed as direct or indirect redox reactions depending on whether both oxidation and reduction are taking place in the same or different vessels, respectively. In most of electrochemical cells, indirect redox reactions take place and can be expressed in terms of half cell reactions. The overall reaction is represented in terms of two reactions, one representing the oxidation and the other representing the reduction. For instance, in the earlier example, the half-cell reaction may be written as:



Concept Check

- Differentiate between electrolytic and galvanic cells.
- Using the cell reaction,

$$3\text{X} + 4\text{Y}^{3+} \rightleftharpoons 3\text{X}^{4+} + 4\text{Y}$$
 write down the half cell reactions.

3.3 Electrode Potential

Origin of Electrode Potential

An electrode is a metal plate or rod dipped in a solution of its own ions. A galvanic cell is made up of two such electrodes and current flows from one electrode to the other. This indicates that the two electrodes of the cell are at different potentials. Also, redox reactions occur in a galvanic cell. It is necessary to draw a relation between all these observations to help us know how potential arises in an electrode.

In order to understand the origin of potential of an electrode, consider a zinc electrode which consists of a Zn strip dipped in ZnSO_4 of any concentration. Nernst proposed that in the electrode, there will appear two tendencies – oxidation and reduction processes. If the tendency, say oxidation occurs in the electrode, the Zn atoms on the surface of the metal undergo oxidation, leaving behind electrons on the surface.

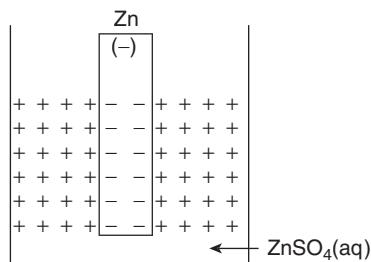
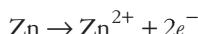


Figure 4 Origin of electrode potential (oxidation).



The Zn^{2+} ions pass into the solution, hence the metal strip becomes negatively charged. The positively charged metal ions in the solution would accumulate around the metal in an order (Figure 4). If the other tendency – reduction occurs in this electrode, then Zn^{2+} ion in the solution would undergo reduction by grabbing electrons from the metallic surface (Figure 5).

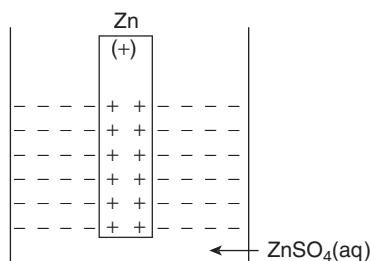
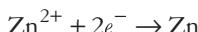
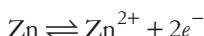


Figure 5 Origin of electrode potential (reduction).



With this, the metallic surface becomes positively charged. The negatively charged ions in the solution would accumulate around the metal. The two tendencies happen simultaneously on the same electrode. As the two tendencies oppose each other, it can be visualized that equilibrium exists between them:



Hence, an electrical double layer called *Helmholtz electrical double layer (HED)* is established at the metal–aqueous solution interface. The actual tendency of the electrode (to gain or lose electrons) depends on which direction the equilibrium would shift to. If the equilibrium shifts in the forward direction, oxidation occurs. If the equilibrium shifts in the backward direction, reduction occurs.

Across the HED layer, there is movement of charges. This results in the potential called *electrode potential*. It is defined as the potential that exists between the metal or a gas and its ions in aqueous solution, at their equilibrium when they are in contact with each other. The electrode potential of a metal is thus a measure of its tendency to lose or gain electrons when in contact with a solution of its own salt.

Oxidation Potential

If oxidation occurs at the electrode, at equilibrium the potential of the electrode can be termed as oxidation potential. For the zinc electrode, the reaction can be represented as:



The electrode in which oxidation occurs at equilibrium is referred to as a negative electrode. For example, zinc electrode with 1 M ZnSO_4 at 298 K offers an oxidation potential of +0.76 V.

Reduction Potential

If reduction occurs at the electrode, at equilibrium the potential of the electrode is referred to as reduction potential. For the zinc electrode, the reaction can be represented as:



If reduction occurs at equilibrium in an electrode, it is termed as positive electrode. The reduction potential of a zinc electrode with 1 M ZnSO_4 at 298 K is -0.76 V.

By comparing the oxidation and reduction potential values of the same electrode, the spontaneous reaction occurring in the electrode can be predicted. In case of zinc electrode, the oxidation potential is more positive than its reduction potential. Thus, oxidation is a spontaneous reaction. However, polarity of an electrode depends on the other electrode to which it is connected.

Standard Electrode Potential (E°)

It is defined as the potential that exists between the metal or the gas and its aqueous solution of unit concentration at 298 K when the sum of all partial pressures of the gaseous reactants and products, if any, is equal to 1 atm pressure. This value is considered to compare the relative abilities of different electrodes to undergo oxidation or reduction.

Concept Check

- Explain the origin of electrode potential.
- The standard reduction potential of zinc is -0.76 V. Explain.
- Two electrodes A and B have potentials of -0.28 V and -0.44 V, respectively. Identify the oxidation and reduction electrodes, if they are coupled.

3.4 Galvanic Cells

A galvanic cell consists of two electrodes immersed in solutions of their respective salts. When the two electrodes are connected externally, a redox reaction occurs in which one of the electrodes undergoes oxidation while the other undergoes reduction.

Construction and Working

A galvanic cell consists of anode compartment and a cathode compartment, connected by a salt bridge. Oxidation occurs at anode (negative electrode) while reduction occurs at the cathode (positive electrode). Daniel cell is the most popular galvanic cell. It has two electrodes Zn in ZnSO_4 and Cu in CuSO_4 connected by a salt bridge (Figure 6).

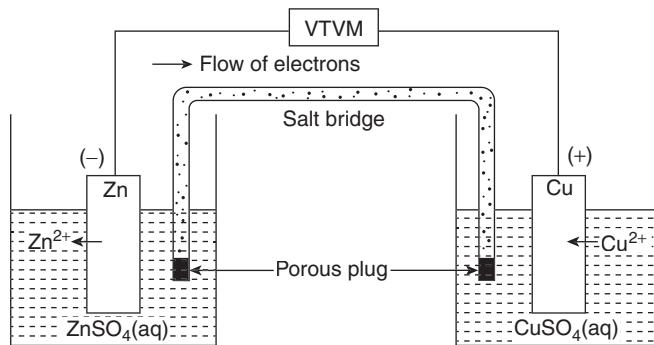
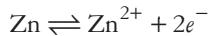
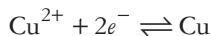


Figure 6 Galvanic cell.

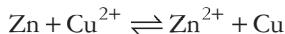
If the electrodes are externally connected, then at zinc electrode, oxidation will occur.



The electrons liberated move along external connection to the other electrode and this results in generation of current. At the copper electrode, reduction reaction will occur.



The net reaction taking place in the cell is



Hence, a redox reaction takes place in a galvanic cell. Electrodes are named in accordance with the reaction occurring at them. In a Daniel cell, zinc electrode is called *oxidation electrode* and copper electrode is called *reduction electrode*.

Salt Bridge

If the electrodes in a galvanic cell are not connected internally, initially the cell generates electrical energy. The electrodes get polarized with passage of time and the cell stops working. For continuous generation of electrical energy, the electrodes need to be internally connected.

A salt bridge is usually used to connect the electrodes of a galvanic cell. It is easy to construct and consists of a gel drawn into a clean U-tube. The gel is formed by adding agar-agar into boiling water containing a suitable electrolyte like KCl. Generally, KCl is preferred because the ionic conductances of K^+ and Cl^- are almost the same. The gel holds the electrolyte in the tube as shown in Figure 7.

As the reactions proceed in the galvanic cell, there will be accumulation of particular ions around the electrodes. This results in a slowdown of the electrode reactions. From the electrolyte of the salt

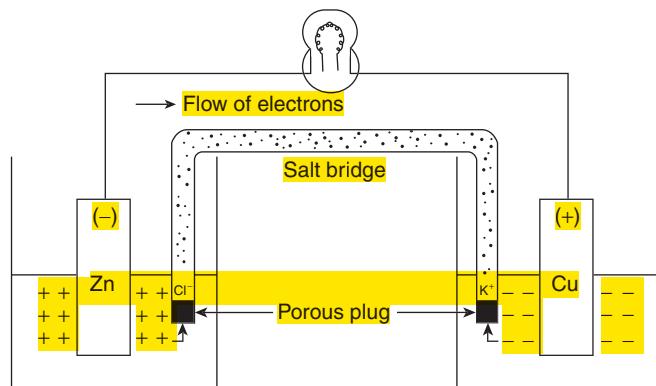


Figure 7 Salt bridge and electrolyte.

bridge, say KCl, the K^+ and Cl^- ions migrate towards the ends of the salt bridge: K^+ ions would migrate towards the reduction electrode (cathode) while Cl^- ions would migrate towards the oxidation electrode (anode). At the oxidation electrode (anode), ions would polarize (attract) some of the oppositely charged ions towards themselves. Simultaneously, the K^+ ions would move towards the reduction electrode (cathode) and polarize the negatively charged ions surrounding the metal. Thus, the cell works as usual.

Hence, a salt bridge helps to

1. bring about internal contact between the electrodes;
2. to minimize liquid junction potential;
3. to minimize polarization.

EMF of the Cell and Free Energy Change

In a galvanic cell, oxidation reaction occurs at the anode and reduction occurs at the cathode. Both the electrodes are at different potential values. The difference in potential of the electrodes is known as the electromotive force (EMF). It is also referred to as the vigor with which the cell works and is the measure of chemical reactions occurring in the cell. In a spontaneous reaction, change in free energy (ΔG) decreases. Larger the decrease in free energy, greater would be the EMF. Mathematically, it can be expressed as:

$$-\Delta G = nEF$$

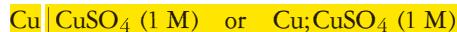
where the negative sign indicates the decrease in the free energy; n is the number of electrons involved in the redox reaction; E is the EMF of the cell and F is the Faraday's constant.

Electrochemical Conventions and Notations

There are some universal conventions and notations to be adopted in describing and representing an electrode or a galvanic cell.

1. There are two electrodes in a galvanic cell. Each of these electrodes is referred to as a half cell.
2. If reduction occurs at an electrode, it is called a *reduction electrode* or a *positive electrode*. It is also named as the cathode.

3. If oxidation occurs at an electrode, it is called an *oxidation electrode* or a *negative electrode*. It is also named as the anode.
4. Oxidation and reduction potential values of an electrode are numerically the same, with opposite signs. For example, oxidation potential of a zinc electrode with 1 M ZnSO_4 at 298 K is +0.76 V. The reduction potential of the same electrode at 298 K is -0.76 V.
5. As per IUPAC, the potential of an electrode is always expressed as reduction potential only, irrespective of the reactions occurring at the electrode.
6. The interphase across which a potential develops is denoted by either a single vertical line (|) or a semicolon (;). For example, copper electrode containing 1 M CuSO_4 is represented as:



7. Representation of a cell will have the oxidation electrode (anode) on the LHS and the reduction electrode (cathode) along the RHS. The salt bridge used to connect the electrodes is represented by double vertical lines. For example, a Daniel cell can be represented as:



8. The EMF of a cell is represented as:

$$E_{\text{cell}} = E_R - E_L$$

where E_R and E_L are the reduction electrode potentials of RHS and LHS electrodes, respectively.

Concept Check

- Describe the working and construction of a Daniel cell.
- What are the reactions taking place at cathode and anode in a galvanic cell with zinc and copper electrodes?
- A salt bridge reduces polarization of a Zn–Ni cell. Explain.
- Express the mathematical relation between EMF of a cell and change in free energy and give its significance.
- The EMF of a Zn–Al cell is 2.46 V at 298 K. Calculate the change in free energy in the cell.

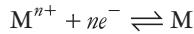
3.5 Nernst Equation

The potential of an electrode depends on concentration and temperature. Therefore, a quantitative equation relating the electrode potential with these parameters can be tailored. Walter Herman Nernst has deduced such an equation for the electrode potential.

Derivation

Arriving at the expression involves the following steps:

1. Consider an electrode assembly undergoing a spontaneous reaction.



2. If this system is in equilibrium, then as per law of mass action, the equilibrium constant (K) can be evaluated as

$$K = \frac{[M]}{[M^{n+}]}$$

3. As the reaction proceeds, there is the formation of HED. Across the HED, there is movement of charges. Hence, some amount of electrical work is done. This value becomes maximum at equilibrium. It is referred to as W_{\max} .
4. W_{\max} depends on
- the number of coulombs of charges flowing across the interphase and
 - the energy available per coulombs of charge.

The expression for W_{\max} can be written as

$$W_{\max} = (\text{Number of coulombs of charge flowing across the HED}) \\ \times (\text{Energy available per coulombs of charge})$$

Therefore,

$$W_{\max} = (nF)(E)$$

or

$$W_{\max} = nEF \quad (3.3)$$

Note:

- As per Faraday's second law, 1 mole of electrons \equiv 1 Faraday of charge. So, n mol \equiv nF of charge.
 - As per definition, energy available per coulomb is called the *potential*, measured in volts.
5. As the reaction is spontaneous, there is decrease in the free energy. Also, the decrease in free energy appears as work done (W_{\max}). Mathematically,

$$-\Delta G = W_{\max} = nEF$$

where negative sign indicates that ΔG is decreasing. So,

$$\Delta G = -nEF \quad (3.4)$$

Similarly,

$$\Delta G^0 = -nE^0 F \quad (3.5)$$

where ΔG^0 and E^0 are the change in free energy and electrode potential under standard conditions, respectively.

6. ΔG varies with temperature, at equilibrium of the system. Van't Hoff's equations bring about their relation:

$$\Delta G = \Delta G^0 + RT \ln \frac{\alpha_{\text{products}}}{\alpha_{\text{reactants}}} \quad (3.6)$$

where T is the temperature on Kelvin scale and α_{products} and $\alpha_{\text{reactants}}$ are activities of products and reactants.

7. Substituting Eqs. (3.3), (3.4), and (3.5) in Eq. (3.6) gives:

$$-nEF = -nE^0 F + 2.303RT \log \frac{\alpha_{\text{products}}}{\alpha_{\text{reactants}}}$$

Dividing by nF throughout, we get

$$E = E^0 - \frac{2.303 RT}{nF} \log \frac{a_{\text{products}}}{a_{\text{reactants}}} \quad (3.7)$$

where n is the number of electrons involved and F is 96,500 C.

In dilute solutions, activities may be replaced by molar concentrations. Therefore,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log \frac{[M]}{[M^{n+}]} \quad (3.8)$$

For pure solids, $[M] = 1$. Therefore, Eq. (3.8) can be written as

$$E = E^0 - \frac{2.303}{nF} RT \log \frac{1}{[M^{n+}]} \quad (3.9)$$

In general, for a galvanic cell the EMF is given as:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log K \quad (3.10)$$

where K is the equilibrium constant for the reaction.

For any cell reaction,



$$K = \frac{[\text{M}^{n+}][\text{N}]}{[\text{M}][\text{N}^{n+}]} = \frac{[\text{M}^{n+}]}{[\text{N}^{n+}]}$$

The Nernst equation is a useful tool in electrochemistry and has the following applications:

1. The potential of an electrode and EMF of a cell can be calculated at any temperature and concentration.
2. Knowing potential of an electrode, the concentration of the reactant can be calculated.
3. The concentration of a solution in the galvanic cell can be determined.
4. The pH of a solution can be calculated by measuring the EMF.

Problem 6

All

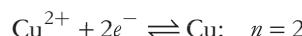
Calculate the electrode potential of copper, if the concentration of CuSO_4 is 0.206 M at 23.1°C . Given that $E_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.34$ V.

Solution

Given that

$$[\text{CuSO}_4] = 0.206; T = 296.1 \text{ K}$$

The reaction taking place is



According to Nernst equation,

$$E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{2.303RT}{nF} \log \frac{1}{[\text{Cu}^{2+}]}$$

or

$$E_{\text{Cu}^{2+}/\text{Cu}} = +0.34 - \frac{2.303 \times 8.314 \times 296.1}{2 \times 96,500} \times \log \frac{1}{0.206} = 0.31984 \text{ V}$$

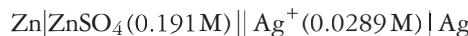
Problem 7

Calculate the EMF of the following Zn–Ag cell at 22.3°C if the concentration of ZnSO_4 and AgNO_3 are 0.191 M and 0.0289 M, respectively. Given that $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$ and $E_{\text{Ag}^+/\text{Ag}} = +0.8 \text{ V}$.

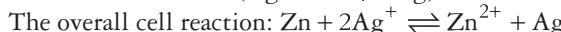
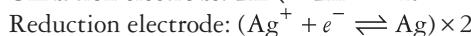
Solution

Here $E_{\text{Zn}^{2+}/\text{Zn}}^0 < E_{\text{Ag}^+/\text{Ag}}^0$.

Hence, zinc electrode is an oxidation electrode, while silver electrode is a reduction electrode. The cell representation is



The reaction occurring in the cell is



Therefore,

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

where Q represents the quotient of reactant and products. According to Nernst equation,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{2.303RT}{nF} \log Q \\ &= \left[E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 \right] - \frac{2.303RT}{nF} \log Q \\ &= [+0.8 - (-0.76)] - \frac{2.303 \times 8.314 \times 295.3}{2 \times 96,500} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \\ &= +1.56 - \frac{2.303 \times 8.314 \times 295.3}{2 \times 96,500} \log \frac{0.191}{(0.0289)^2} \\ &= 1.4908 \text{ V} \end{aligned}$$

Problem 8

Calculate the concentration of NiCl_2 in the nickel electrode having a potential of -0.16942 V at 24.9°C.

Given that $E_{\text{Ni}^{2+}/\text{Ni}}^0 = -0.14 \text{ V}$.

Solution

Applying the Nernst equation,

$$E_{\text{Ni}^{2+}/\text{Ni}} = E_{\text{Ni}^{2+}/\text{Ni}}^0 - \frac{2.303RT}{nF} \log \frac{1}{[\text{Ni}^{2+}]}$$

Here $n = 2$. So,

$$-0.16942 = -0.14 + \frac{2.303 \times 8.314 \times 297.9}{2 \times 96,500} \log(x)$$

where $x = [\text{Ni}^{2+}]$. So,

$$-0.16942 = -0.14 + (0.02955) \log x$$

$$-0.02942 = 0.02955 \log x$$

we get $x = [\text{NiCl}_2] = 0.1010 \text{ M}$.

Problem 9

Calculate the standard electrode potential of lead electrode, if the electrode potential is -0.18025 V at 301 K and a concentration of Pb^{2+} solution is 0.0096 M .

Solution

Given $[\text{Pb}^{2+}] = 0.0096 \text{ M}$; $E_{\text{Pb}^{2+}/\text{Pb}} = -0.18025 \text{ V}$; $T = 301 \text{ K}$. According to Nernst equation,

$$E_{\text{Pb}^{2+}/\text{Pb}} = E_{\text{Pb}^{2+}/\text{Pb}}^0 - \frac{2.303RT}{nF} \log \frac{1}{[\text{Pb}^{2+}]}$$

Therefore,

$$\begin{aligned} E_{\text{Pb}^{2+}/\text{Pb}}^0 &= E_{\text{Pb}^{2+}/\text{Pb}} - \frac{2.303RT}{nF} \log[\text{Pb}^{2+}] \\ &= -0.18025 - \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \log(0.0096) \\ &= -0.18025 - 0.02986 \times (-2.0177) = -0.120 \text{ V} \end{aligned}$$

Problem 10

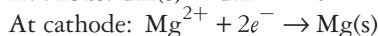
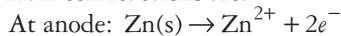
For the cell $\text{Zn}|\text{Zn}^{2+}(\alpha = 10^{-4} \text{ M}) \parallel \text{Mg}^{2+}(\alpha = 10^{-3} \text{ M})|\text{Mg}$, the standard reduction potential for Zn and Mg electrodes are -0.764 V and -2.364 V , respectively.

- (a) Write the half-cell reaction and overall cell reaction.
- (b) Find E_{cell}^0 and ΔG and predict if the cell reaction is spontaneous or not.

Solution

For the cell $\text{Zn}|\text{Zn}^{2+}(\alpha = 10^{-4}) \parallel \text{Mg}^{2+}(\alpha = 10^{-3})|\text{Mg}$,

(a) Half-cell reactions are:



(b) According to Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}][\text{Mg}]}{[\text{Zn}][\text{Mg}^{2+}]}$$

Substituting given values:

$$\begin{aligned} E_{\text{cell}} &= (E_{\text{Mg}^{2+}/\text{Mg}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0) - \frac{0.0591}{2} \log \frac{[10^{-4}]}{[10^{-3}]} \\ &= -2.364 - (-0.764) - \frac{0.0591}{2} \log 10^{-1} \\ &= 1.6 + \frac{0.0591}{2} = -1.6 + 0.0295 = -1.5705 \text{ V} \end{aligned}$$

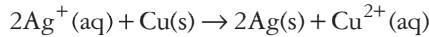
Therefore,

$$\begin{aligned} \Delta G &= -nFE = -2 \times 96500 \times -1.5705 \\ &= 303106.5 \text{ J/mol} = 303.106 \text{ kJ/mol} \end{aligned}$$

Since E_{cell} is negative and ΔG is positive, the reaction is not spontaneous and not feasible.

Problem 11

Calculate the potential of copper-silver cell if $\{\text{Ag}^+\} = 1 \times 10^{-3} \text{ M}$ and $\{\text{Cu}^{2+}\} = 1 \times 10^{-4} \text{ M}$. The standard reduction potentials of silver and copper electrodes are 0.8 V and 0.3 V, respectively. The cell reaction is given by:



Solution

Given that $[\text{Ag}^+] = 10^{-3} \text{ M}$, $[\text{Cu}^{2+}] = 10^{-4} \text{ M}$ and $n = 2$. Also,

$$E_{\text{Ag}^+/\text{Ag}}^0 = 0.8 \text{ V} \quad \text{and} \quad E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.3 \text{ V}$$

According to Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Ag}][\text{Cu}^{2+}]}{[\text{Ag}^+]^2[\text{Cu}]}$$

Substituting given values, we get

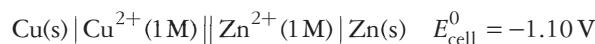
$$\begin{aligned} E_{\text{cell}} &= E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{0.0591}{2} \log \frac{[10^{-4}]}{[10^{-3}]^2} \\ &= 0.8 - 0.3 - \frac{0.0591}{2} \log 100 \\ &= 0.5 - 0.0591 = 0.441 \text{ V} \end{aligned}$$

Problem 12

Calculate the EMF of the cell



Given that

**Solution**

We know that

$$E_{\text{cell}}^0 = E_{\text{Cathode}}^0 - E_{\text{Anode}}^0$$

For $\text{Pb(s)}|\text{Pb}^{2+}(1\text{M})||\text{Cu}^{2+}(1\text{M})|\text{Cu(s)}$

$$E_{\text{cell}}^0 = E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Pb}^{2+}/\text{Pb}}^0 \quad (3.11)$$

For $\text{Pb(s)}|\text{Pb}^{2+}(1\text{M})||\text{Zn}^{2+}(1\text{M})|\text{Zn(s)}$

$$E_{\text{cell}}^0 = E_{\text{Zn}^{2+}/\text{Zn}}^0 - E_{\text{Pb}^{2+}/\text{Pb}}^0 = -0.63 \quad (3.12)$$

For $\text{Cu(s)}|\text{Cu}^{2+}(1\text{M})||\text{Zn}^{2+}(1\text{M})|\text{Zn(s)}$

$$E_{\text{cell}}^0 = E_{\text{Zn}^{2+}/\text{Zn}}^0 - E_{\text{Cu}^{2+}/\text{Cu}}^0 = -1.10 \quad (3.13)$$

Subtracting Eqs. (3.13) from (3.12), we get

$$E_{\text{Zn}^{2+}/\text{Zn}}^0 - E_{\text{Pb}^{2+}/\text{Pb}}^0 - (E_{\text{Zn}^{2+}/\text{Zn}}^0 - E_{\text{Cu}^{2+}/\text{Cu}}^0) = -0.63 - (-1.10)$$

or

$$E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Pb}^{2+}/\text{Pb}}^0 = 0.47 \text{ V}$$

Problem 13

What will be the EMF of a cell at 298 K constructed by dipping zinc rods in 0.001 M and 0.5 M ZnSO_4 solutions?

Solution

For a concentration cell at 298 K,

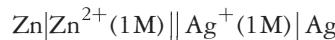
$$E_{\text{cell}} = \frac{0.0591}{n} \log \left[\frac{c_2}{c_1} \right]$$

Substituting given values, we get

$$\begin{aligned} E_{\text{cell}} &= \frac{0.0591}{2} \log \frac{0.5}{0.001} \\ &= 0.0295 \log 500 \\ &= 0.0295 + 2.698 = 0.079 \text{ V} \end{aligned}$$

Problem 14

Calculate the maximum work that can be obtained from the cell



where $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$ and $E_{\text{Ag}^+/\text{Ag}}^0 = 0.8 \text{ V}$.

Solution

The EMF of the cell can be obtained from Nernst equation for cell reaction



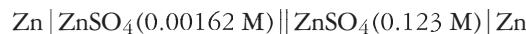
$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}][\text{Ag}]}{[\text{Ag}^+]^2[\text{Zn}]} \\ &= 0.8 - (-0.76) - \frac{0.0591}{2} \log \frac{[1]}{[1]^2} \\ &= 1.56 - \frac{0.0591}{2} \times 0 = 1.56 \text{ V} \end{aligned}$$

As, $\Delta G = -W_{\max} = -nFE$. Therefore,

$$W_{\max} = 2 \times 96500 \times 1.56 = 301080 \text{ J} = 301.080 \text{ kJ}$$

Problem 15

Calculate the valency of copper from the following cell at 294 K, if the EMF of the cell is 0.02571 V.



Solution

The EMF is given by

$$\text{EMF} = \frac{2.303RT}{nF} \log \frac{c_2}{c_1}$$

where $c_2 = 0.0123 \text{ M}$ and $c_1 = 0.00162 \text{ M}$. So,

$$0.02571 = \frac{2.303 \times 8.314 \times 294}{n \times 96500} \cdot \log \frac{0.0123}{0.00162}$$

we get $n = 1.9975 \approx 2.0$. Hence, copper is in divalent state.

Problem 16

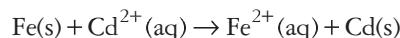
Determine the concentration of Cd^{2+} ions in the following electrochemical cell:



Given that $E_{cell} = -0.02 \text{ V}$ and $E^0 = 0.04 \text{ V}$ at 298 K .

Solution

According to Nernst equation, for the cell reaction



$$E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}][\text{Cd}]}{[\text{Fe}][\text{Cd}^{2+}]}$$

Substituting given values:

$$-0.02 = 0.04 - \frac{0.0591}{2} \log \frac{[0.1]}{[x]}$$

$$-0.06 = -\frac{0.0591}{2} \log \frac{[0.1]}{[x]}$$

$$2.03 = \log \frac{[0.1]}{[x]}$$

$$2.03 = -1 - \log[x]$$

$$3.03 = -\log[x]$$

$$\log x = -3.03$$

On taking antilog, we get $x = 0.00093 \text{ M}$.

Concept Check

- Write the expression for Nernst equation and give the significance of the terms.
- In a particular system M^{3+} is reduced to M^{2+} . Write down the expression for the potential of the electrode system.

3.6 Measurement of EMF of the Cell

EMF and Potential Difference

The terms EMF and potential difference are used indiscriminately, but there is a clear distinction between them. The differences are summarized in Table 2.

Table 2 Differences between EMF and potential difference

EMF	Potential Difference
The difference in electrode potential values of the two electrodes of a cell in an open circuit is called the EMF. An open circuit means when no current flows through circuit	If the difference in potential between the electrodes of the same cell is measured in a closed circuit, it is termed as potential difference. Closed circuit means an activity in which measurement is carried out under load
While measuring EMF, the cell reaction would be in equilibrium. Hence, electrical work done is the maximum	As the cell reaction is not in equilibrium while potential difference is measured, the electrical work done is less
EMF is usually determined by potentiometric method	A simple device like voltmeter is enough to measure the potential difference
EMF is the maximum potential available in a galvanic cell	The potential difference of the same cell is always less than EMF

Potentiometric Measurement

For precise measurement of the EMF of a cell, a voltmeter cannot be used. As the voltmeter draws some amount of current from the cell during the measurement, the EMF so measured is inaccurate. To overcome the error, EMF should be determined only when no current flows through the cell. This condition is achieved by Poggendorff's compensation principle. This principle is also called *null deflection method* which uses a potentiometer.

Compensation Method

An experimental cell whose EMF is to be calculated and a standard cell of known EMF are connected opposite to each other in a potentiometric circuit such that no current flows through the circuit. The EMF of the experimental cell is exactly opposed by the EMF of the standard cell. A potentiometer consists of a wire AB of uniform cross-section and fairly high resistance (Figure 8).

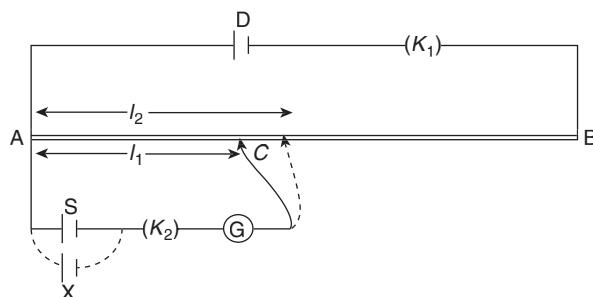


Figure 8 Potentiometer.

The positive of the battery D is connected to the end A of the wire, while the negative terminal is connected to the other end B through a plug key K_1 . Care is taken to select a standard cell (S) of EMF greater than that of experimental cell (X). Similarly, for the experimental cell (X), the positive terminal is connected to end A and the negative terminal is connected to the sliding contact through plug key K_2 and galvanometer (G).

The plug keys K_1 and K_2 are closed. The sliding contact is moved along the wire AB until the galvanometer shows zero deflection. This point C on the potentiometer at which no current flows through the galvanometer is called the *null point*. Let the balancing length, that is, AC be l_1 cm. Therefore, EMF of the experimental cell is

$$E_X \propto l_1 \quad (3.14)$$

Now, replace the experimental cell by a standard cell (S), in the potentiometric circuit. The plug keys K_1 and K_2 are closed, and the sliding contact is again moved from A to B on the potentiometer. The galvanometer shows zero deflection when the sliding contact is at length l_2 . Therefore, the EMF of the standard cell (S) is

$$E_S \propto l_2 \quad (3.15)$$

From Eqs. (3.14) and (3.15), we get

$$\frac{E_X}{E_S} = \frac{l_1}{l_2} \Rightarrow E_X = \frac{l_1}{l_2} \times E_S$$

If the standard cell used is Weston cadmium cell, then $E_S = 1.0098$ V at 293 K. Knowing l_1 , l_2 and E_S , we can easily calculate E_X .

Concept Check

- Explain the basis of Poggendorff's compensation principle for measurement of EMF.
- Null deflection method has a distinct advantage over the direct voltmeter measurement of EMF. Explain.

3.7

Reference Electrodes

The potential of an electrode cannot be accurately, directly measured. It is not feasible to connect a measuring device to the solution of electrode, as it may lead to another equilibrium along with the existing one. The problem can be overcome if the electrode is connected to another electrode of known potential. Such an electrode is termed as reference electrode. From the measured EMF, the potential of the electrode can be obtained by subtracting the potential of the reference electrode.

Any electrode of known potential cannot be treated as a reference electrode. The criteria for an electrode to act as a reference electrode are:

1. The potential of such an electrode should be known, under the conditions of utility.
2. The potential of the electrode should show minimum variation with temperature. In other words, the potential gradient with respect to temperature should be minimum.

The most commonly used reference electrode is the *hydrogen electrode*. The potential of all other electrodes are measured with respect to the hydrogen electrode. Hence, it is called a *primary reference electrode*.

There are a few more reference electrodes available which are standardized using standard hydrogen electrode (SHE) and then used as reference electrodes for measuring potential of other electrodes. Such

reference electrodes are termed as subsidiary or secondary reference electrodes. Calomel electrode and silver–silver chloride electrodes are the most popular secondary reference electrodes.

Standard Hydrogen Electrode (Normal Hydrogen Electrode)

Standard (Normal) Hydrogen Electrode (SHE/NHE) consists of a platinum-foil dipped in 1.0 M HCl. The platinum foil is enclosed in a thick-walled glass tube and connected to an external contact wire. Pure hydrogen is passed into the container at 1 atm pressure through the inlet at the top. Excess of hydrogen leaves the electrode through the outlet at the bottom (Figure 9).

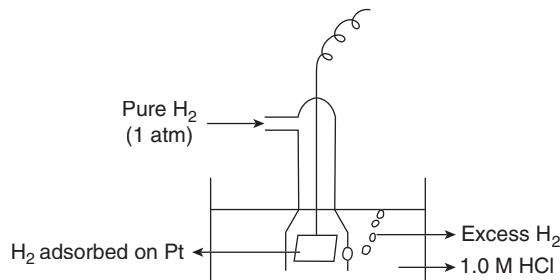
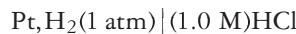
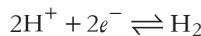


Figure 9 Standard hydrogen electrode.

Pure hydrogen gets adsorbed onto the Pt surface and is in contact with H^+ ions in the solution. It forms a reversible electrode and can be represented as:



If reduction occurs at the electrode, the reaction taking place will be:



As the potential cannot be measured directly, it is conventionally assumed to be zero at 298 K. The EMF of the cell (E_{cell}^0) is determined at a standard condition and since E^0 of SHE is assumed to be zero, the potential of the second electrode can be obtained. The potential of an electrode measured at standard condition (298 K, 1 M concentration of ions and 1 atm pressure) is known as standard electrode potential. The standard electrode potential, as a practice is reported as reduction potential and is a measure of reduction potential of an electrode with respect to SHE.

However, SHE/NHE has its own inherent limitations:

1. Construction of SHE is a difficult activity. It is difficult to maintain unit molar concentration of hydrogen throughout and to pass hydrogen always at exactly 1 atm pressure.
2. Presence of arsenic compounds would easily get absorbed on platinum foil, thereby poisoning the surface. It would affect equilibrium of the reaction.
3. In addition, SHE cannot be used in presence of strong oxidizing and reducing agents.

Calomel Electrode

Calomel electrode is a secondary reference electrode and belongs to the category of metal–sparingly soluble salt electrodes. Calomel is the common name for mercurous chloride and it is sparingly soluble in water. The electrode consists of a thin layer of pure mercury at the bottom of the container. It is covered

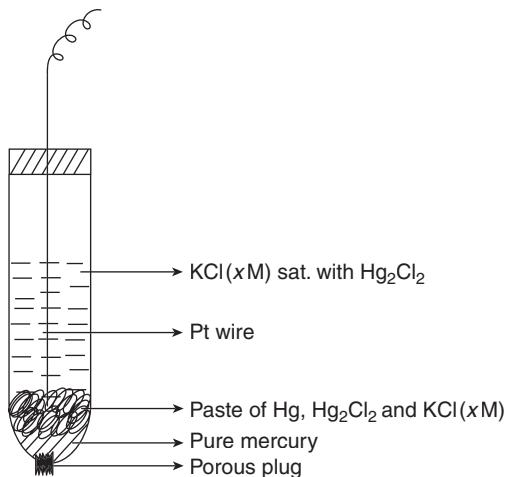
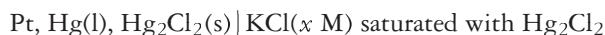


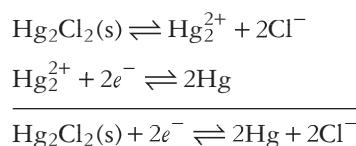
Figure 10 Calomel electrode.

with a paste of Hg, Hg_2Cl_2 and KCl of known concentration. The rest of the container is filled with KCl solution of a known concentration, saturated with Hg_2Cl_2 (Figure 10).

The electrode can be represented as:



It is a reversible electrode. If reduction occurs at this electrode, the reaction can be represented as:



Nernst equation for the calomel electrode is:

$$E_{\text{Hg}/\text{Hg}_2\text{Cl}_2} = E_{\text{Hg}/\text{Hg}_2\text{Cl}_2}^0 - \frac{2.303RT}{nF} \log[\text{Cl}^-]^2$$

The potential of this electrode depends on the concentration of KCl. Calomel electrode with saturated KCl and 1 M KCl have potential values of 0.2412 V and 0.28 V, respectively. It is easy to construct and easy to transport. It provides almost a constant potential value with varying temperature and finds application in laboratories for measuring potential of an electrode. It is used in corrosion studies.

Silver–Silver Chloride Electrode

It belongs to the category of metal-sparingly soluble salt electrodes and is a secondary reference electrode. It consists of a silver wire partially covered with AgCl, dipped in potassium chloride solution of known concentration saturated with AgCl. The porous plug at the bottom provides electrical contact (Figure 11). Partial deposition of AgCl on a Ag wire is electrolytically, anodically carried out, in a solution of chloride ions.

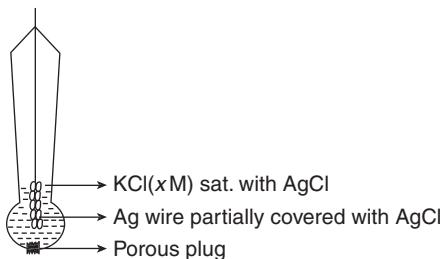


Figure 11 Silver–silver chloride electrode.

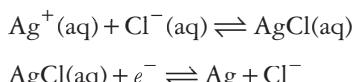
The electrode is represented as:



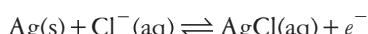
It is a reversible electrode and if oxidation occurs at the electrode, then



If reduction occurs at the electrode, the reaction is:



So, the overall reaction is



As per Nernst, the potential of the electrode is

$$E_{\text{Ag}/\text{AgCl}} = E_{\text{Ag}/\text{AgCl}}^0 - \frac{2.303 RT}{nF} \log [\text{Cl}^-]$$

where $n = 1$. From the equation, it is evident that the potential of the electrode depends on the concentration of chloride ions or KCl. For instance, Ag–AgCl electrode with saturated KCl solution offers a potential of 0.199 V at 298 K, while the electrode with 0.1 M KCl has 0.29 V.

This compact reference electrode is used in corrosion studies and also in laboratories in measuring potential of an electrode.

Concept Check

- Calomel electrode is a reference electrode. Justify.
- Presence of impurities in the hydrogen gas poisons the SHE. Justify the statement.
- The Ag–AgCl electrode is a reversible electrode with respect to chloride ions. Explain.

3.8

Electrochemical Series

The measure of individual potential of metal, for many reversible electrode at standard conditions (1 mole/l or gaseous at 1 atm at 298K) is known as single electrode potential. It is also known as absolute

or half-cell potential. The EMF at the standard conditions for all the combinations can be calculated (Table 3) using the equation, $E_{cell}^0 = E_{RE}^0 - E_{OE}^0$ where E_{RE}^0 and E_{OE}^0 are the standard reduction potentials of reduction electrode and oxidation electrode, respectively.

Table 3 EMF of the cells

<i>Representation of the Cell</i>	$E_{cell}^0 = E_{RE}^0 - E_{OE}^0$ (Volts)	E_{cell}^0 (Volts)
$\text{Li} \mid \text{Li}^+ \parallel \text{Ag}^+ \mid \text{Ag}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Li}^+/\text{Li}}^0 \\&= 0.8 - (-3.0)\end{aligned}$	3.8
$\text{Li} \mid \text{Li}^+ \parallel \text{Zn}^{2+} \mid \text{Zn}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Zn}^{2+}/\text{Zn}}^0 - E_{\text{Li}^+/\text{Li}}^0 \\&= -0.76 - (-3.0)\end{aligned}$	2.24
$\text{Li} \mid \text{Li}^+ \parallel \text{Mg}^{2+} \mid \text{Mg}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Mg}^{2+}/\text{Mg}}^0 - E_{\text{Li}^+/\text{Li}}^0 \\&= -2.36 - (-3.0)\end{aligned}$	0.66
$\text{Li} \mid \text{Li}^+ \parallel \text{Cu}^{2+} \mid \text{Cu}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Li}^+/\text{Li}}^0 \\&= +0.34 - (-3.0)\end{aligned}$	3.34
$\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Zn}^{2+} \mid \text{Zn}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Zn}^{2+}/\text{Zn}}^0 - E_{\text{Mg}^{2+}/\text{Mg}}^0 \\&= -0.76 - (-2.36)\end{aligned}$	1.6
$\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Mg}^{2+}/\text{Mg}}^0 \\&= +0.8 - (-2.36)\end{aligned}$	3.16
$\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Mg}^{2+}/\text{Mg}}^0 \\&= +0.34 - (-2.36)\end{aligned}$	2.7
$\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 \\&= +0.8 - (-0.76)\end{aligned}$	1.56
$\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 \\&= +0.34 - (-0.76)\end{aligned}$	1.1
$\text{Cu}^{2+} \mid \text{Cu} \parallel \text{Ag}^+ \mid \text{Ag}$	$\begin{aligned}E_{cell}^0 &= E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Cu}^{2+}/\text{Cu}}^0 \\&= +0.8 - (-0.34)\end{aligned}$	0.42

When the electrodes are arranged in the increasing order of their standard reduction potential values, the series so formed is termed as electrochemical series. The electrochemical series is given in Table 4.

Table 4 Electrochemical series

Electrode Systems	Reduction Electrode Reaction	Standard Reduction Electrode Potential E^0 (Volts)
Li^+/Li	$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	- 3.024
K^+/K	$\text{K}^+ + e^- \rightleftharpoons \text{K}$	- 2.924
Ca^{2+}/Ca	$\text{Ca}^{2+} + 2e^- \rightleftharpoons \text{Ca}$	- 2.87
Na^+/Na	$\text{Na}^+ + e^- \rightleftharpoons \text{Na}$	- 2.714
Mg^{2+}/Mg	$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	- 2.36
Al^{3+}/Al	$\text{Al}^{3+} + 3e^- \rightleftharpoons \text{Al}$	- 1.7
Zn^{2+}/Zn	$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	- 0.76
Cr^{3+}/Cr	$\text{Cr}^{3+} + 2e^- \rightleftharpoons \text{Cr}$	- 0.74
Fe^{2+}/Fe	$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	- 0.441
Cd^{2+}/Cd	$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}$	- 0.402
Ni^{2+}/Ni	$\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni}$	- 0.236
Sn^{2+}/Sn	$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}$	- 0.14
Pb^{2+}/Pb	$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	- 0.126
Fe^{3+}/Fe	$\text{Fe}^{3+} + 3e^- \rightleftharpoons \text{Fe}$	- 0.045
$\text{H}^+/\frac{1}{2}\text{H}_2$	$\text{H}^+ + e^- \rightleftharpoons \frac{1}{2}\text{H}_2$	- 0.000
Cu^{2+}/Cu	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	+ 0.34
Ag^+/Ag	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+ 0.79
Hg^{2+}/Hg	$\text{Hg}^{2+} + 2e^- \rightleftharpoons \text{Hg}$	+ 0.61
Pt^{2+}/Pt	$\text{Pt}^{2+} + 2e^- \rightleftharpoons \text{Pt}$	+ 1.2
Au^{3+}/Au	$\text{Au}^{3+} + 3e^- \rightleftharpoons \text{Au}$	+ 1.38
F^-/F_2	$\frac{1}{2}\text{F}^- + e^- \rightleftharpoons \text{F}^-$	+ 2.87

The characteristics of electrochemical series are as follows:

1. Lithium is the first member of the series.
2. Highly reactive metal systems are at the top of the series.
3. In other words, good reducing agents are at the top of the series.
4. All good oxidizing agents are at the bottom of the series.
5. Hydrogen system is at the middle of the series. All the elements which displace hydrogen from dilute acids are placed above it.

The electrochemical series has several practical applications in chemistry.

1. Higher the reduction potential, greater is the tendency of the element to get reduced. Hence, the relative oxidizing and reducing abilities of the elements can be compared easily. For instance, among Zn and Cu systems, zinc system has lower reduction potential (-0.76 V) than Cu ($+0.34\text{ V}$). So, zinc system has more reducing ability than Cu. *Lower the reduction potential, greater is the reducing ability.*
2. A metal placed higher in the series is anodic to other metals which lie below it. An element can displace all elements that lie below it in the series, from their salt solutions. For example, zinc shavings added to a hot saturated solution of CuSO_4 can displace copper from the salt. In other words, displacement reactions can be predicted.
3. Knowledge of electrochemical series helps in selection of electrode assemblies, to construct the galvanic cells of the desired EMF.
4. The polarity of the electrode system and the electrode reaction can be easily predicted.
5. Spontaneity and feasibility of the cell under construction can be easily predicted.

Concept Check

- What do you understand by electrochemical series?
- How does electrochemical series help in predicting the feasibility of a redox reaction?

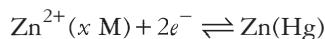
3.9 Types of Electrodes

Electrodes of a galvanic cell can consist of different components or constituents. Based on the constituents, they are classified as follows:

1. **Metal–metal ion electrode:** It consists of a metal in contact with its ions or metallic salt in equilibrium. At the surface of the electrode, a potential arises. For example, zinc in ZnSO_4 and aluminium in AlCl_3 .
2. **Metal–insoluble salt electrode:** It consists of a metal and its sparingly soluble salt, which are in equilibrium with a solution containing the same anion as that of the salt. In addition, the solution should be saturated with the sparingly soluble salt. For example, calomel electrode and silver–silver chloride electrode.
3. **Amalgam electrode:** Amalgam is the alloy of any metal with mercury. An amalgam electrode is a modification of metal–metal ion electrode. In place of a metal, its solution in mercury is used. A typical example of zinc amalgam electrode is represented as:



The electrode reaction is

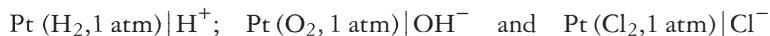


According to Nernst equation, the potential of the electrode is

$$E = E_{\text{Zn}^{2+}|\text{Zn}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Zn}]}{[\text{Zn}^{2+}]}$$

where $[\text{Zn}^{2+}]$ and $[\text{Zn}]$ are the concentrations of Zn^{2+} ions and Zn metal in the amalgam.

4. **Gas electrode:** It consists of a noble metal like platinum which is simultaneously in contact with a gas and a solution of ions of the gas. Since gases cannot conduct electricity, an inert metal is used to make electrical contact. The metal helps in establishing the equilibrium. The potential of the electrode depends on the pressure of the gas and the activity of the solution. Hydrogen, oxygen and chlorine electrodes are examples of this kind and are represented, respectively, as



5. **Redox electrode:** In this electrode, the electrode potential results due to the presence of ions of the same substance present in different oxidation states. Platinum is usually used for electrical contact and attainment of equilibrium between the ions. A solution containing ferrous and ferric ions in contact with platinum is the best example of a redox electrode; this electrode is represented as $\text{Pt}|\text{Fe}^{3+}, \text{Fe}^{2+}$.
6. **Ion-selective electrode (ISE):** In this electrode, a suitable non-porous membrane separates two solutions, containing similar ions of different concentrations, and acts as an electrochemical membrane. The remarkable property of such electrodes is that a potential difference is developed on either side of the membrane (Figure 12).

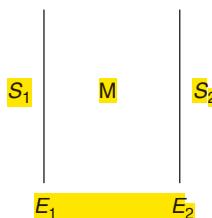


Figure 12 Membrane in ion-selective electrode.

If E_1 and E_2 are the electric potentials of solutions S_1 and S_2 respectively on either side of the membrane (M), the potential experienced by the membrane is termed as boundary potential (E_b) and is given by

$$E_b = E_2 - E_1$$

If the membrane is of uniform composition throughout, the potential on its surface will be proportional to the activities (concentration) of the ions on either side. According to Nernst equation,

$$E_b = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

If one of the two concentrations is known, E_b can be measured; and then the unknown concentration can be calculated. A noteworthy aspect is that these membranes become responsive to one type of ions amidst mixture of ions. Such electrodes are called *ions selective electrodes (ISE)*. In other words, an ISE is an assembly which selectively responds to a particular ion, in presence of many others in a solution and the potential developed is a function of concentration of the solution.

The membrane is the vital component of ISEs and the criteria for the choice of the membrane depends on many aspects:

- It should not be affected by the action of oxidizing and reducing agents.
- It should have sufficient mechanical strength.
- It should have low electrical resistance.
- It should not be attacked by organic solvents.

Based on the nature of the membrane, the ISEs are classified into different categories:

- **Glass electrode:** These electrodes are responsive selectively towards hydrogen ions (H^+). Glass of special variety which has higher electrical conductance than ordinary glass is used. Glass electrodes are used to measure the pH of any solution. A thorough discussion on glass electrode would be taken up in Section 3.10.
- **Crystalline ISEs:** A thin crystalline membrane is used in these ISEs. Fluoride ion-selective electrode is the best example of crystalline ISEs (Figure 13).

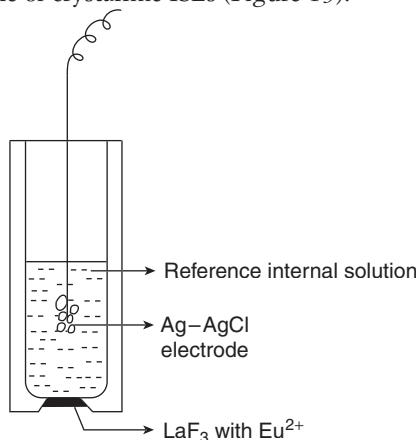


Figure 13 Fluoride ISE.

The membrane used is a single crystal of LaF_3 doped with europium divalent ion (Eu^{2+}) which lowers the electrical resistivity of the membrane.

- **Ion exchange ISEs:** These electrodes consist of an ion-exchange membrane which may be solid or liquid. In case of liquid ion-exchange membrane electrode, the membrane used is immiscible in water and dissolved in suitable organic solvents. The solution so obtained is held in a skeletal matrix which is porous and hydrophobic in nature. The matrix allows contact between the liquid ion exchanger and the test solution in which the electrode is dipped (Figure 14).

In calcium ISE, calcium dialkylphosphate containing 8–10 carbon atoms in the chain is dissolved in dioctyl phenyl phosphate and the resulting solution acts as the membrane.

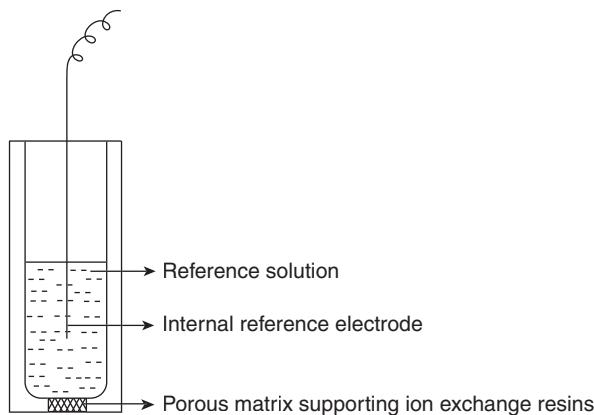


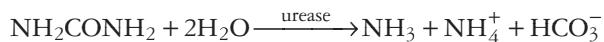
Figure 14 Ion exchange ISE.

A calcium ISE is used in estimating calcium present in blood serum. A nitrate ISE is useful in the analysis of surface and groundwater. In addition, estimation of nitrate in the soil extracts, vegetable and plant materials can be easily, accurately carried out.

- **Enzyme ISE:** An enzyme electrode is identical to a glass electrode. Enzymes like *L*-arginine or *L*-lysine carboxylase will split the corresponding amino acids generating CO_2 . These electrodes are virtually carbonate ion-selective glass electrode which sense CO_2 .

The test solution permeates through the gel holding the enzyme. Amino acids degrade liberating CO_2 or NH_3 and the amount of CO_2 or NH_3 liberated is a measure of the concentration of amino acid used.

In urea enzyme ISE, acryl amide gel holds the enzyme urease, which splits urea into ammonium ion:



Here, NH_4^+ ions are sensed at the electrode. Urea ISEs are used for estimating amount of urea present in blood.

Concept Check

- State the different types of electrodes.
- What are the different types of ion selective electrodes?
- How can calcium and urea present in blood be estimated using ion exchange electrodes?

3.10 Glass Electrode

It is the oldest and the most popular ion-selective membrane electrode available. This ISE is responsive towards H^+ and extensively used to measure the pH of solutions precisely. In 1906, Cremer found that a thin bulb of glass conducted electricity when he put two solutions of different acid strengths inside and outside the bulb. The potential developed at the glass was in accordance with Nernst equation.

Construction

It consists of a thick-walled glass tube with a very thin glass bulb placed at the bottom (Figure 15). The thickness of the bulb is 0.01–0.03 mm. Generally, glass is found to have high electrical resistivity. To make an ion-selective membrane, a special variety of glass called *Corning-015* is used. This variety has the approximate composition of 72% SiO₂, 6%CaO and 22% Na₂O. It also has relatively higher electrical conductance and is highly hygroscopic in nature. The bulb contains 0.1 M HCl and a silver wire partially covered with AgCl is dipped in it.

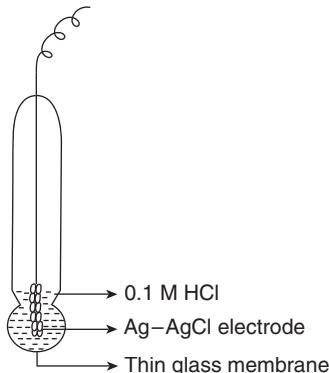
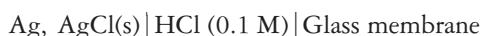


Figure 15 Glass electrode.

The bulb of the glass electrode is dipped in either distilled water or dilute HCl. The glass surface should always be hydrated. The mobility of H⁺ through the hydrated layer is rapid as compared to the dry layer. This helps in quick attainment of equilibrium. The electrode can be represented as:



This glass surface acts as an electrochemical membrane and is non-conducting. The exact mechanism is not clearly known but the following steps are suggested:

1. The glass surface gets hydrated both on the outside and inside.
2. H⁺ ions get absorbed on the hydrated layer.
3. The exchange occurs between alkali metal ions in the glass surface and the H⁺ ions present in the solution.
4. In the dry layer sandwiched between the hydrated layers, electrical conduction occurs by Frankel's mechanism. In other words, Li⁺ or Na⁺ ions move from one interstitial position to another.

Glass Electrode Potential

Consider a glass electrode dipped in a solution of H⁺ ion concentration, c_x . The H⁺ ion concentration of the solution inside the bulb is c_1 . The boundary potential developed across the membrane is

$$E_b = E_x - E_1$$

where E_x and E_1 are the potentials of the solution outside and inside, respectively. As per Nernst equation,

$$E_b = \frac{2.303RT}{nF} \log \frac{c_x}{c_1}$$

If the H^+ ion concentration on either side of the glass membrane is exactly the same, then as per the above equation, $E_b = 0$. Practically, it is found that there is residual potential available in the system. To account for the non-zero potential, the following points are to be considered:

1. Within the glass electrode, there is an internal reference electrode – $\text{Ag}|\text{AgCl}$ in a solution containing chloride ions. It offers some potential ($E_{\text{int.ref.}}$) which has to be considered.
2. With all the care taken in the manufacture and annealing of the glass membrane, strain in the surface and unevenness of the membrane persist. The potential that arises out of these is termed as E_{asymm} .

Hence, the potential of a glass electrode (E_g) has all these aspects and is given by

$$E_g = E_b + E_{\text{int.ref.}} + E_{\text{asymm}}$$

Substituting expression of E_b , we get

$$\begin{aligned} E_g &= \frac{2.303RT}{nF} \log \frac{c_x}{c_1} + E_{\text{int.ref.}} + E_{\text{asymm}} \\ &= \frac{2.303RT}{nF} \log \frac{1}{c_1} + E_{\text{int.ref.}} + E_{\text{asymm}} + \frac{2.303RT}{nF} \log c_x \end{aligned}$$

For a given electrode, the first three terms are constant.

$$\begin{aligned} E_g &= E_g^0 + \frac{2.303RT}{nF} \log [\text{H}^+]_x \\ &= E_g^0 - \frac{2.303RT}{nF} (-\log [\text{H}^+]_x) \\ &= E_g^0 - \frac{2.303RT}{nF} \times \text{pH} \end{aligned}$$

where E_g^0 is constant for a given glass electrode. At 298 K, $n = 1$ and $F = 96,500 \text{ C}$, so

$$E_g = E_g^0 - 0.0591 \text{ pH}$$

Before using the glass electrode, its E_g^0 is determined.

Advantages and Limitations

Glass electrode is a versatile analytical tool and has some distinct advantages:

1. It is portable and compact.
2. Unlike other systems, the equilibrium is easily attained.
3. It gives precise and accurate determination of pH, even in the case of very dilute solutions.
4. Unlike the potentiometric method, a few drops of the solution are enough for measurement.
5. It is a stable electrode system and can be used in presence of strong oxidizing and reducing agents.
6. It can be used in the presence of viscous biological fluids.
7. It can detect and estimate H^+ ions in presence of other types of ions.

Glass electrode is not free from limitations. To cite a few:

1. The glass membrane is very thin and fragile, and so it has to be handled with at most care.
2. Even though care is taken to select the glass of relatively high electrical conductance, it offers fairly high electrical resistance. The current generated is supposed to be of the order of 10^{-12} A , which

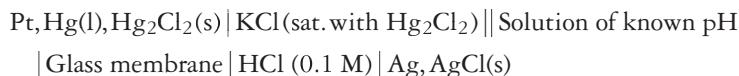
ordinary voltmeters cannot measure. Hence, costlier and highly sensitive electronic equipment like VTVM has to be used.

3. Fluoride ions in the sample attack the glass surface and alter the composition of the membrane.
4. Glass electrodes with Corning-015 cannot be used for accurate measurement of $\text{pH} > 9$. At this pH, the electrode becomes responsive to not only H^+ but also Na^+ . The error so committed is termed as alkaline error. In such cases, the glass membrane with 78% SiO_2 , 15% H_2O and 8% BaO is used.

Determination of pH using Glass Electrode

The pH of a solution can be determined easily, accurately and in less time than the other methods using a glass electrode. This determination is carried out in two stages:

1. **Determination of E_g^0 :** Before using the glass electrode for determining the pH of a solution, its E_g^0 value has to be recorded. The bulb of the glass electrode is thoroughly washed with distilled water and wiped off with a soft cloth. It is dipped in a solution of known pH (say a buffer) taken in a beaker. Usually, buffer of $\text{pH} = 4$ is used. The electrode constructed is connected to a reference electrode (saturated calomel electrode) through a salt bridge. The cell so set up is represented as:



By convention, the glass electrode assembly is always treated as the cathode. The terminals of the cell are connected to the VTVM. Let the EMF recorded be E_1 volts. As per cell representation,

$$E_1 = E_g - E_{\text{SCE}}$$

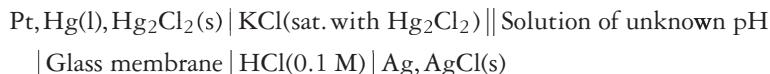
The potential of saturated calomel electrode, $E_{\text{SCE}} = 0.2412$ V at laboratory conditions (say, 298 K). So,

$$E_g = E_1 + 0.2412 \text{ V}$$

But, $E_g = E_g^0 - 0.0591 \text{ pH}$ at 298 K. Now, as E_g and pH are known, E_g^0 can be calculated as

$$E_g^0 = E_g + 0.0591 \text{ pH}$$

2. **Determination of the pH of the given solution:** The glass electrode is taken out of the connection. It is washed again with distilled water and wiped off with a soft cloth. Now, it is dipped in a solution whose pH is to be determined and is coupled in the SCE. The cell so set up (Figure 16) is represented as



The cell constructed is connected to VTVM. The EMF is recorded as E_2 which is given by

$$E_2 = E_g^1 - E_{\text{SCE}}$$

where E_g^1 is the potential of the glass electrode containing the solution of unknown pH. So,

$$E_g^1 = E_2 + E_{\text{SCE}}$$

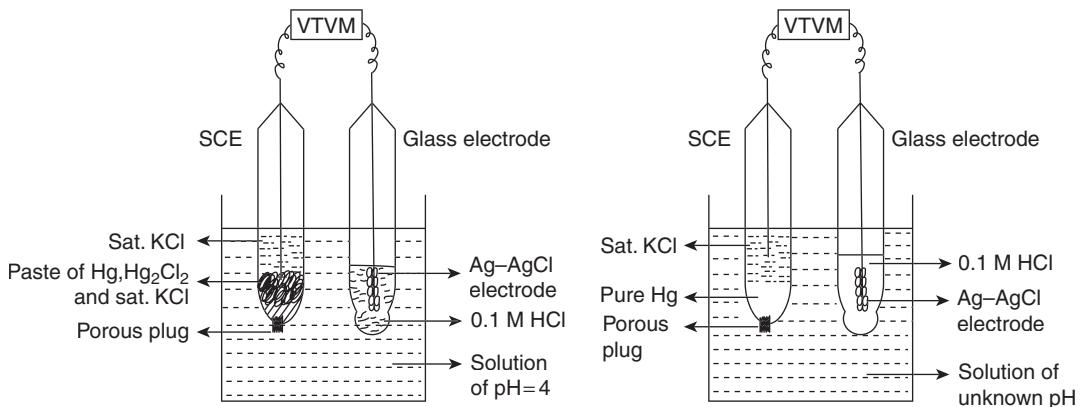


Figure 16 Cell for pH determination.

But, $E_g^1 = E_g^0 - 0.0591 \text{ pH}$, at 298 K from which pH can be easily calculated as

$$\text{pH} = \frac{E_g^0 - E_g^1}{0.0591}$$

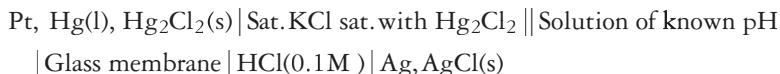
The pH of a solution can also be measured using a pH meter. In this method, the cell constructed using a buffer solution is directly connected to the pH meter. The pH displayed is then adjusted to that of the buffer. This process is termed as the calibration of pH meter. Subsequently, the same glass electrode is formed in a cell with a solution whose pH is to be measured. It is connected to a pH meter. The display on the pH meter directly gives the pH of the solution.

Problem 17

A glass electrode dipped in a solution of pH equal to 4 offered an EMF of 0.2066 V with a saturated calomel electrode (SCE) at 298 K. Dipped in a solution of unknown pH, at the same temperature in contact with SCE, recorded an EMF of 0.1076 V. Calculate the pH of the solution, if $E_{\text{SCE}} = 0.2412 \text{ V}$.

Solution

To find E_g^0 : The cell formed is



So,

$$E_{\text{cell}} = E_g - E_{\text{SCE}}$$

$$0.2066 = E_g - 0.2412$$

or

$$E_g = 0.4478 \text{ V}$$

But, $E_g = E_g^0 - 0.0591 \text{ pH}$. So,

$$E_g^0 = E_g + 0.0591 \text{ pH} = 0.4478 + 0.0591 \times 4 = 0.6842 \text{ V}$$

To find pH of the solution: The cell formed is



$$E_{\text{cell}}^1 = E_g^1 - E_{\text{SCE}}$$

$$E_g^1 = E_{\text{cell}}^1 + E_{\text{SCE}} = 0.1076 + 0.2412 = 0.3488 \text{ V}$$

But, $E_g^1 = E_g^0 - 0.0591 \text{ pH}_{\text{unknown}}$. So,

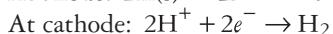
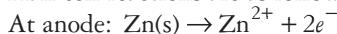
$$\text{pH}_{\text{unknown}} = \frac{E_g^0 - E_g^1}{0.0591} = \frac{(0.6842 - 0.3488)}{0.0591} = 5.675$$

Problem 18

The EMF of a cell corresponding to the reaction $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(0.1\text{M}) + \text{H}_2(\text{g}, 1\text{atm})$ is 0.28 V at 25°C. Write the half cell reactions and calculate the pH of the solution at the hydrogen electrode. Given $E_{\text{Zn}}^0 = 0.76 \text{ V}$ and $E_{\text{H}_2}^0 = 0$.

Solution

Half cell reactions are as follows:



According to Nernst equation,

$$E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^0 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Zn}]}$$

Substituting given values, we get

$$\begin{aligned} E_{\text{Zn}^{2+}/\text{Zn}} &= 0.76 - \frac{0.0591}{n} \log[0.1] \\ &= 0.76 - 0.0295 \times -1 \\ &= 0.76 + 0.0295 = 0.76895 \text{ V} \end{aligned}$$

$$\begin{aligned} E_{2\text{H}^+/\text{H}_2} &= E_{2\text{H}^+/\text{H}_2}^0 - \frac{0.0591}{n} \log \frac{[\text{H}_2]}{[\text{H}^+]^2} \\ &= 0 - 0.0591 \log[\text{H}^+] = -0.0591 \text{ pH} \end{aligned}$$

Therefore, the pH is calculated as

$$E_{\text{cell}} = E_{\text{Zn}^{2+}/\text{Zn}} + E_{2\text{H}^+/\text{H}_2}$$

$$0.28 = 0.76 - 0.0591 \text{ pH}$$

or

$$\text{pH} = \frac{0.76 - 0.28}{0.0591} = 8.12$$

Concept Check

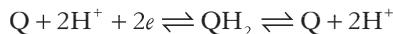
- A glass electrode is dipped in a solution. List out all the possible reasons for potential to arise.
- List the advantages and limitations of glass electrode.
- How is pH of a solution determined using glass electrode?

3.11 Quinhydrone Electrode

Quinhydrone is the name given to an equimolecular compound of quinone and hydroquinone, readily prepared by the gentle oxidation of hydroquinone. Billman and other have shown that quinhydrone may be used to prepare an electrode which in many cases can be used as a very good hydrogen electrode. Such an electrode gives a hydrogen pressure which is extremely weak but in the case of a dilute electrolyte, constant and well-defined at a temperature. The hydrogen pressure results from the transformation of dissolved hydroquinone to dissolved quinone and hydrogen and vice versa. Thus, the quinhydrone electrode is a type of redox electrode which can be used to measure the hydrogen ion concentration (pH) of a solution in a chemical experiment. It provides an alternative to the commonly used glass electrode in a pH-meter.

Construction

The quinhydrone electrode consists from a platinum dipped into a solution saturated with quinhydrone. Quinhydrone (HQ) is a slightly soluble compound formed by the combination of one mole of quinone (Q), a non-electrolyte, and one mole of hydroquinone (H_2Q), a weak dibasic acid. The equilibrium in the solution may be represented by



Quinone is oxidant, and hydroquinone is reductant in this reaction. It is very easy to prepare and handle. Pure solid quinhydrone is dissolved in the solution to be measured until the solution is saturated and an excess is present. A platinum wire is dipped into this solution (Figure 17).

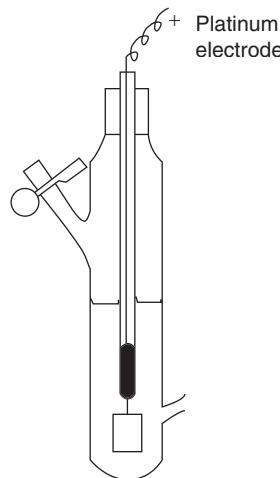


Figure 17 Quinhydrone electrode.

Quinhydrone Electrode Potential

The electrode potential of quinhydrone electrode is given by:

$$E_{Q/H_2Q} = E_{H_2Q}^0 + \frac{RT}{2F} \ln \frac{[\alpha_Q][\alpha_H]^2}{[\alpha_{H_2Q}]} \quad (3.16)$$

Since both quinone and hydroquinone are obtained by dissolving quinhydrone in solution, therefore,

$$\alpha_{H_2Q} = \alpha_Q$$

Also,

$$\ln[\alpha_H]^2 = 2.303 \times 2 \log[\alpha_H] = 2.303 \times (-2)\text{pH} \quad (3.17)$$

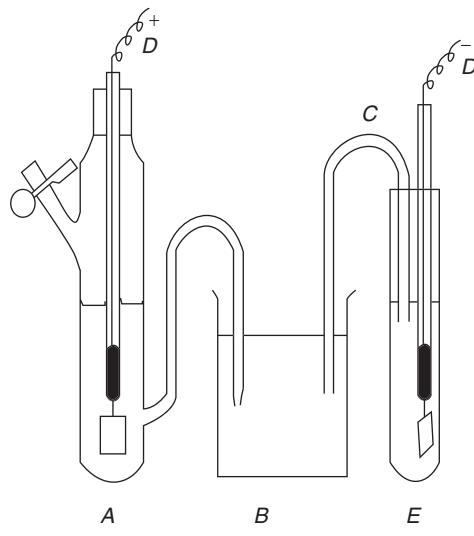
Applying these substitutions to Eq. (3.16), we get

$$E_{Q/H_2Q} = E_{H_2Q}^0 - \frac{2.303RT}{F} \text{pH} \quad (3.18)$$

The standard potential of the quinhydrone electrode is calculated according to the equation

$$E_{H_2Q}^0 = 0.6994 - 7.36 \times 10^{-4}(T - 25)$$

where T is the temperature in degree Celsius.



A Standard quinhydrone electrode vessel.

B Saturated KCl solution.

C Agar-KCl bridge.

D Platinum electrodes.

E Measuring electrode vessel.

Determination of pH using Quinhydrone Electrode

Quinhydrone electrode can be combined with any suitable reference electrode (e.g., saturated calomel electrode) to create an electrochemical cell which is then used for potentiometric measurements (Figure 18). The electrochemical cell that is set up can be represented as $\text{Hg} | \text{HgCl}_2 | \text{KCl}(\text{sat. soln}) \parallel \text{H}_2\text{Q}, \text{Q}, \text{H}^+(\text{known conc.}) | \text{Pt}$

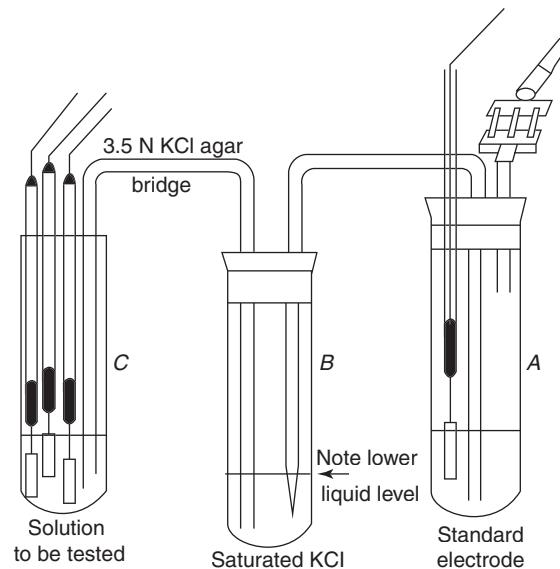


Figure 18 Electrochemical cell using quinhydrone electrode.

The quinhydrone electrode is the positive terminal, and the calomel electrode is negative terminal. The emf of the cell is given by

$$E = E_{\text{Q}/\text{H}_2\text{Q}} - E_{\text{measured}} \quad (3.19)$$

From Eqs. (3.17) and (3.19), the pH of the unknown solution can be calculated as

$$\text{pH} = \frac{E_{\text{Q}/\text{H}_2\text{Q}}^0 - E_{\text{measured}} - E}{2.303 \frac{RT}{F}}$$

The use of quinhydrone electrode for measuring pH of a solutions offers the following advantages:

1. The electrode is simple to prepare and comes to equilibrium rapidly.
2. It can be used for determination of pH volatile acids also, that is, not impacted by the release of CO_2 .

However, there are also some disadvantages associated with its use:

1. It cannot be used in solutions that would react with quinone or hydroquinone, that is in the presence of oxidizing and reducing agents.

2. Hydroquinone must be freshly prepared as it is oxidized by atmospheric oxygen.
3. It cannot be used above pH = 8.5, because hydroquinone being a weak acid, dissociates appreciably above this.

3.12 Batteries

Conversion of chemical energy into electrical energy is the function involved in cells or batteries. A battery is a combination of cells either in series or parallel or both, in order to get the required amount of electrical energy. It is a portable source of electrical energy. In modern times, the words cell and battery are used interchangeably.

With the increased human activities and comforts, a number of battery-dependent appliances or goods have come into existence. Batteries are used in wrist watches, emergency sources of light (UPS), hearing aids, flashlight devices, electric calling bells, calculators, alarm signals, space vehicles and missile firing units.

There is a growing trend in the manufacture of consumer-friendly cells or batteries. In fact, not all the voltaic cells find commercial applications. The general criteria for any cell to be a commercial cell are that they should be cheap, light and portable; should have a long cycle life and high shelf life; should be a continuous and constant source of EMF over a long interval of time and should be a rechargeable unit.

The galvanic cells used to form batteries can be classified as:

1. **Primary cells:** In these cells, the chemical energy is converted into electrical energy as long as the chemical components are active. Once the active chemical components are used up, they cannot be regenerated or reused. These cells are then not rechargeable.
2. **Secondary cells:** In these cells, the redox reaction that converts chemical energy into electrical energy can be reversed by passage of current. These cells can be recharged and reused. The electrical energy is stored in them in form of chemical energy and hence these are also known as storage cells. These cells behave as a galvanic cell during discharge, converting chemical energy into electrical and as electrolytic cell during charging, converting electrical energy into chemical.

A new class of batteries, known as reserve batteries has been designed to meet the conditions of long shelf-life and extreme storage. In these batteries a key component, mainly the electrolyte, is separated from the cell to prevent reaction between cell components and self-discharge. The cell components in these batteries are activated by addition of active components.

The basic components of a battery are:

1. **Anode:** It contains active materials which spontaneously take part in the oxidation reactions.
2. **Cathode:** It contains active materials which spontaneously take part in the reduction reactions.
3. **Electrolyte:** It helps in the migration of the ions leading to the generation of electrical energy.
4. **Separator:** It is a thin polymeric membrane which prevents the mixing of products formed at the electrodes. Usually, polypropylene and polystyrene separators are used.

Discharging and Charging of a Battery

A cell is a battery that is packed with active materials at anode and cathode. As soon as the anode and the cathode are connected to the load, redox reactions occur spontaneously. The electrons liberated at the

anode flow to the cathode through the external wire and take part in the reduction reaction. This process in which spontaneous redox reaction occurs is called *discharging*.

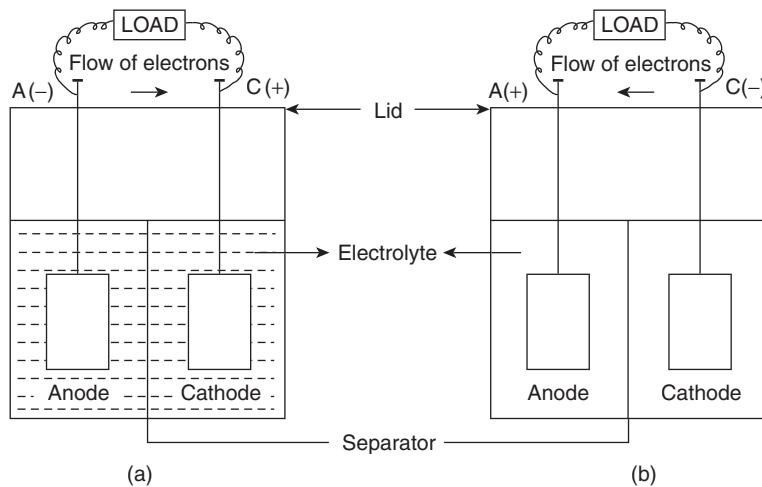


Figure 19 (a) Discharging and (b) charging processes in a battery.

During the discharging process as shown in Figure 19(a), active materials are converted into inactive materials. The cell becomes inactive once the active material is consumed. In case of secondary cells or batteries, the cell reaction is reversed if the external current is passed in the reverse direction. This process of conversion of an inactive material back into active materials in a cell is called *charging* as shown in Figure 19(b). It is a non-spontaneous process.

Characteristics of a Battery

Selection of battery depends on the conditions of working. In fact, cells or batteries are specifically designed for this purpose. The suitability of a battery depends on the following characteristics:

1. **Voltage or EMF:** A good cell is one which offers large and almost constant EMF.

- It depends on the change in free energy of the reaction.

$$\Delta G = -nFE_{\text{cell}}$$

Larger the change in free energy, higher will be the EMF.

- According to Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

where $E_{\text{cell}}^0 = E_R^0 - E_L^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$.

(a) Larger the potential difference between the electrodes, higher is E_{cell}^0 and hence E_{cell} .

(b) As temperature increases, the EMF decreases.

(c) As the value of $[\text{Products}]/[\text{Reactants}]$ increases, EMF of the cell marginally decreases.

- A good battery is one which has a flat discharge rate (constant EMF) (Figure 20).

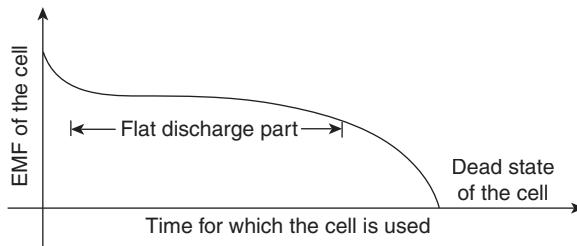


Figure 20 Flat discharge rate.

2. **Current:** It is a measure of the rate of discharge reactions of the cell. It depends on the amount of active materials. Higher the amount of active materials, longer will be the time for which EMF is generated.
3. **Current capacity:** It is defined as the amount of current generated in unit time. It is measured in terms of ampere-hour ($A\text{ h}$) and depends on the discharge conditions. Capacity is inversely proportional to the average molar mass of the active materials. A good battery should have higher current capacity.
4. **Power density:** It is the amount of power output by weight. It is a measure of the power generated in a cell per unit weight of the battery.

$$\text{Power density} = \frac{\text{Amount of power generated in a cell}}{\text{Weight of the cell}} = \frac{iE_{\text{cell}}}{W}$$

where i and E_{cell} are current and EMF generated in a cell, respectively. Lesser the weight of the cell, higher would be the power density.

5. **Energy density:** It is measure of the energy available in the cell per unit weight of the cell.

$$\text{Energy density} = \frac{\text{Amount of energy generated in the cell}}{\text{Weight of the cell}} = \frac{i^2 R t}{W} = \frac{i E_{\text{cell(avg)}} \times t}{W}$$

where i , R and t are the current generated by cell, resistance offered by the cell and time for which the current generated is measured. Always, cells or batteries with higher energy densities are preferred.

6. **Energy efficiency:** It is applicable only to secondary cells. During discharging, electrical energy is released while electrical energy is utilized when the cell is being charged. A good cell is that which liberates more electrical energy than it uses during charging process. The rates of electrical energy released and used in discharging and charging, respectively, is known as

$$\text{Percentage energy efficiency} = \frac{\text{Amount of electrical energy released during discharging}}{\text{Amount of electrical energy used during charging}} \times 100$$

7. **Cycle life:** It is applicable only to rechargeable (secondary) cells. The EMF of cell decreases during discharging. If it is followed by charging process, the amount of active materials in the cell increase and hence the EMF. The discharging and charging processes cannot be repeated perpetually. A discharging followed by charging is referred to as a cycle. The number of times it can be repeated is called cycle life. In other words, cycle life is defined as the number of times the discharging and charging operations can be alternated till such time it performs as designed.

A good cell should have high cycle life. Sometimes, the cycle life would be lower than expected. It may be due to the following reasons.

- The active materials at the electrodes may whither off due to rapid charging conditions.
 - There may be irregular deposition of the products during discharging. It may result in short circuiting.
 - Due to overcharging, the corrosion may occur resulting in severing connections between the contact wire and the active materials.
8. **Shelf life:** The duration of storage under specified conditions at the end of which the cell still has the ability to deliver specified performance. A good battery should possess a long shelf life.
9. **Self-discharge:** Sometimes, the discharge reactions may occur even though the cell is not in use. It is due to the local actions that occur in the cell. It is defined as the loss of active materials of the cell due to localized action on the electrode even when the cell is not in discharge mode. Longer the self-discharge, lower would be the shelf life.

Concept Check

- What are the criteria for a commercial battery?
- How are reserve batteries more efficient than other types of batteries?
- Explain the essential components of a battery.
- Explain the process of charging and discharging of a battery.
- What is meant by the energy efficiency of a battery?
- What are the reasons for the lowering of cycle life of a battery?

3.13 Classical Batteries

Primary Cells

Dry Cell

This cell, also known as Leclanche cell, consists of a cylindrical zinc container which acts as the anode. A graphite rod surrounded by a paste of manganese dioxide acts as the cathode. These are in contact with a thick paste of ammonium chloride and zinc chloride which acts as the electrolyte (Figure 21).

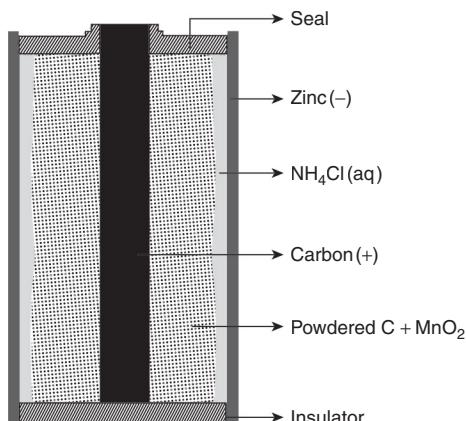
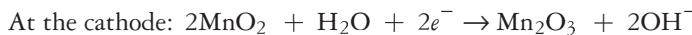
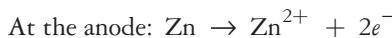


Figure 21 Leclanche cell.

The cell reactions are:

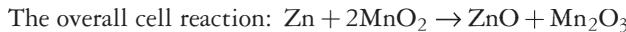
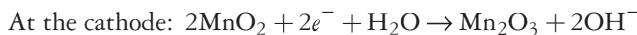


Some secondary reactions take place in the cells which do not contribute to the EMF of the cell as they do not occur at the electrodes. The hydroxyl ions generated at the cathode react with NH_4Cl to liberate ammonia which reacts with Zn^{2+} to form the complex $[\text{Zn}(\text{NH}_3)_2]\text{Cl}_2$. These processes disrupt the flow of current.

A dry cell develops a potential of 1.5 V and the voltage decreases with usage due to accumulation of products at the electrodes. Even when the cell is not in use, the lifetime of the dry cell is not indefinite because acidic NH_4Cl corrodes the zinc cathode. Dry cells are most commonly used batteries that find use in flash lights, radios, tape recorders, transistors, etc.

Alkaline Dry Cell

This cell is same in construction as the dry cell but modified to replace NH_4Cl as electrolyte by sodium hydroxide or potassium hydroxide, hence the name alkaline dry cell. Replacing NH_4Cl with NaOH/KOH prevents corrosion of zinc cathode since it does not dissolve in basic medium. The cell reactions are:



Secondary (Storage) Cells

Lead Storage Cell (Lead–Acid Battery)

This cell, also known as acid storage cell, is the common automobile battery. Its present form is a variant of lead–acid accumulator first designed in 1859. Lead storage cell consists of lead grid filled with spongy lead which acts as the anode and a lead grid packed with lead oxide that acts as the cathode. A number of (generally six) such electrode pairs are dipped in sulphuric acid solution (20%) which acts as the electrolyte and these are separated by inert and porous partitions (Figure 22).

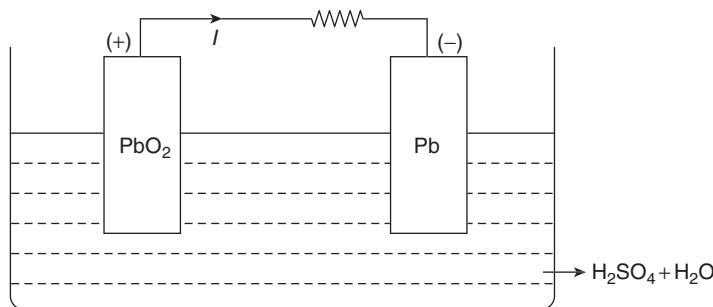
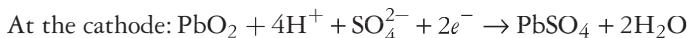


Figure 22 Lead–acid battery.

The cell reactions are:





The cell reaction shows that the electrolyte H_2SO_4 is consumed during the reaction, so as the reaction proceeds, the concentration of H_2SO_4 decreases. Once the concentration of H_2SO_4 has fallen to a certain permissible level, the battery needs to be recharged by reversing the discharge reaction. For this, an external potential higher than the cell potential is applied. The cell then operates like an electrolyte cell and the PbSO_4 deposited on the electrodes is reverted to Pb and PbO_2 by the following reactions:



The cell reactions show that the concentration of H_2SO_4 increases during recharging of the cell. The potential developed by each electrode pair is about 2V and higher potential can be obtained by connecting a number of electrode pairs in series. These batteries find extensive use as automobile batteries, besides being used for electrical supply in trains, hospitals, etc.

Nickel–Cadmium Cell

This cell, also known as alkaline storage battery, consists of anode grid which contains spongy cadmium with cadmium hydroxide. The cathode grid contains nickel oxyhydroxide along with small amounts of graphite and other compounds. A concentrated solution of potassium hydroxide acts as an electrolyte (Figure 23).

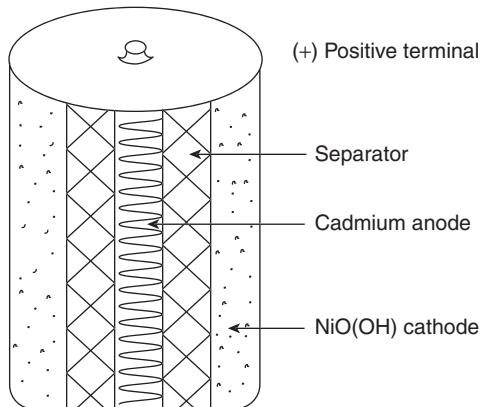


Figure 23 Nickel–cadmium cell.



As the reaction proceeds, the products Ni(OH)_2 and Cd(OH)_2 stick to the surface of the electrode. The cell can be recharged by reversing the reactions. This cell gives potential of about 1.4 V. It can be made into compact button cell type battery and finds use in pocket calculators, electronic flash lights, emergency lights, portable electronics, toys, etc.

Concept Check

- Explain the working of a dry cell along with the redox reactions taking place.
- Explain the construction and working of lead acid battery.
- Separator is not required in a lead acid battery. Justify the statement.
- Explain the functioning of nickel–cadmium battery.

3.14 Modern Batteries

Nickel–Metal Hydride Batteries

These batteries are also alkaline, rechargeable batteries and were commercialized in 1990. Their construction (Figure 24) is done as follows:

1. Anode of the cell is composed of metal hydrides like MH and MH_2 . Active hydrogen storage alloy like LaNi_5 are pasted on a very thin, highly porous nickel sheet.
2. Cathode is composed of NiO(OH) is pasted on a very thin, highly porous nickel sheet.
3. Electrolyte used is aqueous potassium hydroxide.
4. Separator contains a thin layer of polypropylene.
5. All the components are housed in a glass container.

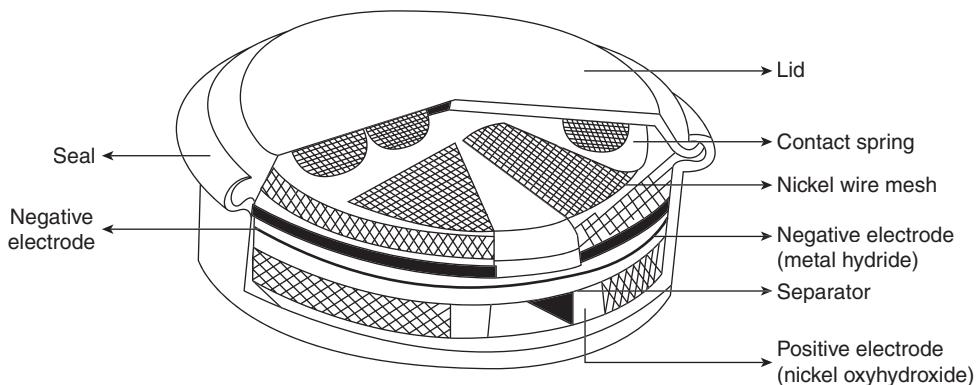
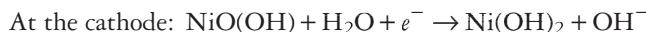


Figure 24 Nickel–metal hydride battery.

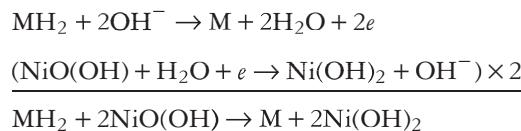
The cell representation is as follows:



The reactions involved in the cell are:



The overall cell reaction is



The battery offers an EMF of 1.3 V.

The characteristics of nickel–metal hydride batteries are as follows:

1. They have long shelf life and cycle life.
2. They have high capacity and rapid recharge capability.
3. They have poor charge detention capacity.

These batteries find application in laptop computers, cellular phones as well as automobiles.

Lithium Batteries

Lithium is a light metal with low electrode potential and good conductivity. It is, therefore, a good material for batteries, and can be expected to have high potential and high energy density. The group of batteries where lithium is used as an anode are known as *lithium batteries* and they were commercialized in 1990. A large number of lithium batteries are available which have lithium as anode but differ in choice of cathode and electrolyte. These may also be classified as primary or secondary. The most well-known of lithium batteries, lithium–manganese dioxide cell is discussed here.

The construction of Li–MnO₂ battery is as follows:

1. Anode is composed of lithium.
2. Cathode is composed of heat treated MnO₂.
3. Electrolyte contains a mixture of LiCl, LiBr, LiAlO₄ and LiClO₄ dissolved in organic solvents like propylene carbonate and is 2-dimethoxyethane.

The cell reactions are as follows:



The battery offers an EMF of 3.0 V.

These batteries have the following characteristics:

1. The batteries are light in weight and compact.
2. They are known for low maintenance and have high energy density.

These batteries find application in memory backups, automatic cameras and calculators.

Lithium Ion Cells

Rechargeable lithium batteries found in many cell phones, digital cameras and laptop computers do not contain metallic lithium. They are called lithium ion cells and use lithium ions instead. In fact, the cell's operation does not actually involve true oxidation and reduction. Instead, it uses the transport of Li^+ ions through the electrolyte from one electrode to the other accompanied by the transport of electrons through the external circuit to maintain charge balance (Figure 25).

Working:

1. During the charging cycle, an external voltage forces electrons through the external circuit and causes lithium ions to travel from the LiCoO_2 electrode to the graphite electrode.
2. During discharge, the lithium ions spontaneously migrate back to the LiCoO_2 electrode, and electrons flow through the external circuit to balance the charge.

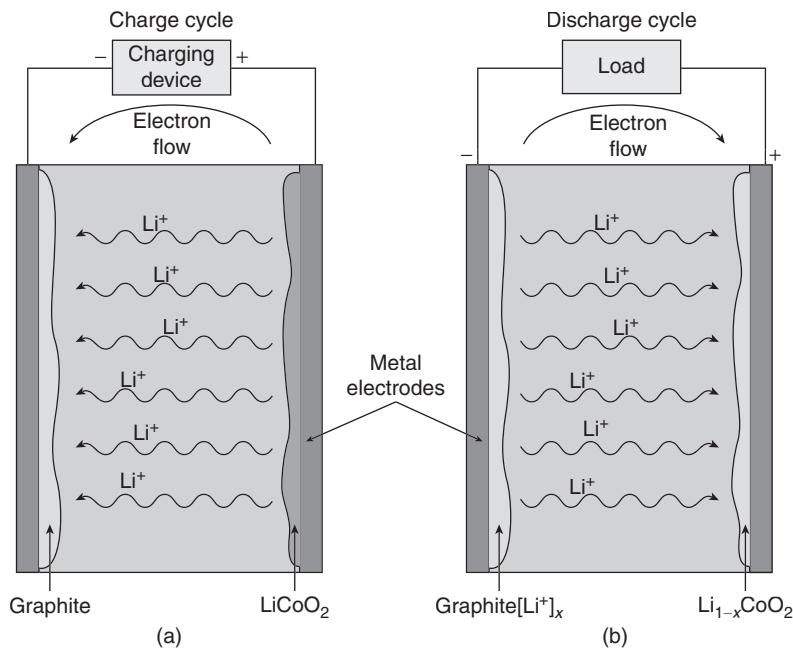


Figure 25 Lithium ion cell.

Concept Check

- Discuss the construction and working of nickel–metal hydride battery.
- Lithium can be the best component of a battery. Substantiate.

3.15 Fuel Cells

Conventionally energy is obtained by the combustion of the fossil fuel. The conversion into electrical energy involves a number of steps and there is loss of energy at every step. The efficiency of the process is

around 40%. There is also a viable way of converting the chemical energy of fuel directly into electrical energy through catalytically activated redox reactions. Such devices are called *fuel cells*. Even though fuel cells were first demonstrated by Sir William Grove in 1839, they became popular only after NASA used them in their space ships (1950s). In other words, fuel cells are galvanic cells in which the electrical energy is directly derived from the redox reactions of the fuel.

Comparison with Conventional Galvanic Cells

Fuel cells differ from the conventional galvanic cells in the following aspects:

1. They consist of two catalytic electrodes.
2. The reagents used are fuel and oxidant.
3. The fuel and oxidant are not stored in the cell. They are stored outside and supplied as and when required.
4. No pollutants and hence fuel cells are environmentally friendly.
5. No toxic species are formed in a fuel cell.
6. They do not need charging.

Advantages and Limitations

Distinct advantages of fuel cells are:

1. They offer high energy conversions (almost 75%).
2. These cells have high energy density.
3. These cells use inexpensive fuels.

Fuel cells suffer from a few limitations:

1. The electrodes used are either Pt, Ag or the alloys of noble metal which are prohibitively costly.
2. The power generated is moderate.

Cell Representation

The representation of the fuel cell is:

Fuel | Electrode | Electrolyte | Electrode | Oxidant

The chemical reactions involved at the electrodes are:

At the anode: Fuel → Oxidation product + ne^-

At the cathode: Oxidant + ne^- → Reduction product

The overall cell reaction: Fuel + Oxidant → Oxidizing product + Reduction product

The frequently used fuels are hydrogen, methanol, ethanol, hydrazine, formaldehyde, carbon monoxide and alkane. The oxidants could be pure oxygen or air.

Hydrogen–Oxygen Fuel Cell

This fuel cell combines hydrogen and oxygen to produce electricity, heat and water. It converts chemical energy to electrical energy and thus can be compared to a battery. The only difference being that as long as hydrogen is supplied, it continues to produce electricity without being discharged.

Design and Working

The whole setup consists of chambers (Figure 26). The first chamber serves as an inlet for hydrogen, while the second one serves as an inlet for oxygen. There are two electrodes: Hydrogen passes over the anode and oxygen passes over the cathode. In the middle, is a proton exchange membrane separating the two electrodes from one another, where these two gases can interact with each other. The electrolyte separating the two electrodes is an ion-conducting material. When electricity is applied, the following reactions take place at the two electrodes:

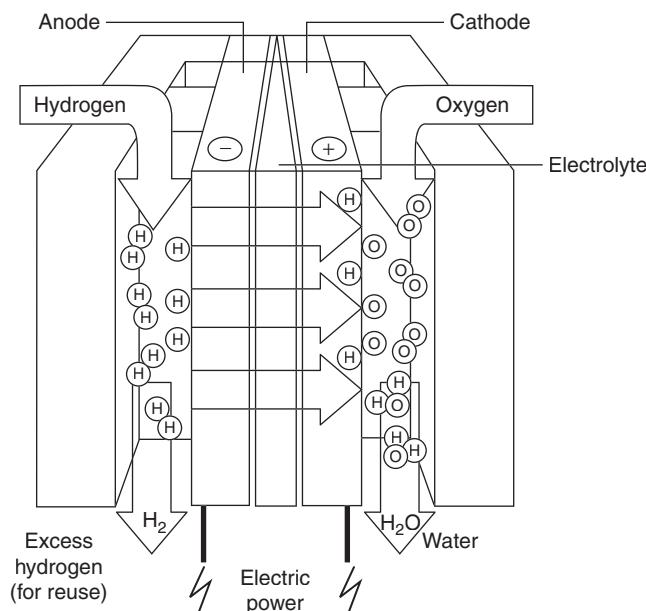
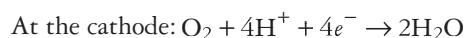


Figure 26 A block diagram of hydrogen–oxygen fuel cell.

The water is released in the fourth chamber. The anodic reaction gives protons and electrons. These are separated and hydrogen ions are allowed to pass through the electrolyte to the cathode while the electrons travel via an external circuit as direct current to power electrical devices. In the cathode, hydrogen ions combine with oxygen to form water along with the heat, thus completing the circuit.

Advantages and Limitations

There are a lot of benefits of using hydrogen as a fuel.

1. It just emits water vapor and no other harmful chemicals to the environment.
2. The efficiency shown is as high as about 75%.

3. Hydrogen is the lightest element and provides a lot of energy, and also it can be transported easily to places where required.
4. Hydrogen fuel can replace the use of batteries and causes less noise pollution.

There are also some limitations:

1. Hydrogen is explosive.
2. For very good efficiency, it turns out to be very expensive, and even the initial research which is to be carried out costs a lot of money.
3. Hydrogen is actually gas, so a large investment of cost and energy is required to compress it into liquefied form.
4. While using these fuel cells in an automobile, a high pressure is created inside the engine, which is quite risky.
5. Another great disadvantage would be that since hydrogen is never present as it is, but always in combined form with either oxygen or some other element, it needs to be separated first.

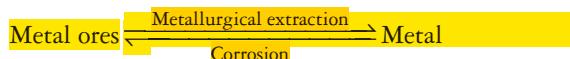
CORROSION AND ITS CONTROL

Corrosion is one of the most significant problems faced by advanced industrial societies. It is estimated that about 30–40% of iron and steel produced annually is used just to replace the rusted iron materials. Corrosion costs of automobiles – fuel systems, radiators, exhaust systems and bodies – are in the billions. Corrosion touches all appliances used inside and outside home, on the road, on the sea, in plants and in aerospace vehicles. Total annual costs of floods, hurricanes, fires, lightning and earthquakes are less than the costs incurred due to corrosion.

3.16 Corrosion in Metals and Alloys

Metals occur in nature in native (free or uncombined) as well as in combined form. The main source of metals is the earth's crust, while some metals exist as dissolved salts in seawater. The metals which have lower reactivity and affinity for oxygen, water or other reagents generally occur in native state. These include silver, carbon, gold, platinum, etc. Other metals exist in combined forms in a variety of compounds as minerals and ores.

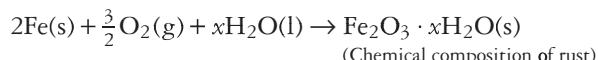
Metals are thermodynamically unstable and found abundantly in nature, so that they require large amounts of energy to get converted into useful engineering materials. Thus, the metals requiring more energy have a greater tendency to corrode, whereas those metals requiring less energy have a lower tendency to corrode. Examples of the former include magnesium, zinc, aluminum and steel; whereas examples of the latter include gold, silver and platinum. Corrosion is a spontaneous slow chemical interaction of metal or alloy with its environment, resulting in the formation of one of its compounds such as oxide, hydrated oxide, carbonate, sulphide, sulphate, etc. Extraction of metals from their ores is an endothermic process. Pure metals, being highly energetic, have natural tendency to revert back to their combined states.



Hence, corrosion can be defined as the destruction of metals or alloys by the surrounding environment through chemical or electrochemical changes.

Causes of Corrosion

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most familiar example of corrosion is rusting of iron exposed to the atmospheric conditions.



Corrosion of metals occurs either by direct chemical attack or by electrochemical attack on the metal by the corrosive environment.

Effects of Corrosion

The effects of corrosion are many and varied. These effects are more pronounced than the simple loss of metal as they affect the safe and efficient functioning of equipments or structures. Even if the loss of metal due to corrosion is small, still it may be required to replace the expensive parts of the equipment. The major harmful effects of corrosion can be summarized as follows:

1. Loss of metal or reduced thickness: This reduced thickness may lead to lack of mechanical strength, leading to structural breakdown. Sudden structure collapse or breakdown may cause hazards or injuries to those working near the site of the structure (e.g., bridges, cars, aircrafts). Loss of metal in localized areas gives a crack-like appearance to the structure. Hence considerable weakness may result from even a small amount of metal loss.
2. Time is lost in making available the parts required for constructing the industrial equipment.
3. The value of the goods is reduced owing to degraded appearance.
4. The fluids stored in pipes or storage tanks get contaminated due to chemical reactions (e.g., beer gets cloudy when small quantities of heavy metals are released by corrosion).
5. Important surface properties of metals are affected. These properties include frictional, bearing properties, ease of fluid flow, electrical conductivity, surface reflectivity and heat transfer. Loss of technically important surface properties of a metallic component.
6. Mechanical damage to valves, pumps, etc., or blockage of pipes by solid corrosion products.

Concept Check

- What do you mean by corrosion?
- Give the chemical composition of rust.
- What are the important causes of corrosion?
- What are the effects of corrosion?

3.17 Corrosion Cell

In general, any type of corrosion cell consists of an anode, a cathode, a metallic (electronic) path between them, and an electrolyte providing ionic path (Figure 27). A voltage difference between the anode and the cathode in the corrosion cell causes a current flow. This DC current flows from the anode through the surrounding environment (electrolyte) to the cathode, and back to the anode through the metallic path (wire) completing the circuit. The corrosion current is carried through this metallic path by electrons; whereas in the electrolyte, it is carried by ions. The electrode that discharges current to the electrolyte (anode) corrodes, while the metal receiving the current from the environment (cathode) remains uncorroded.

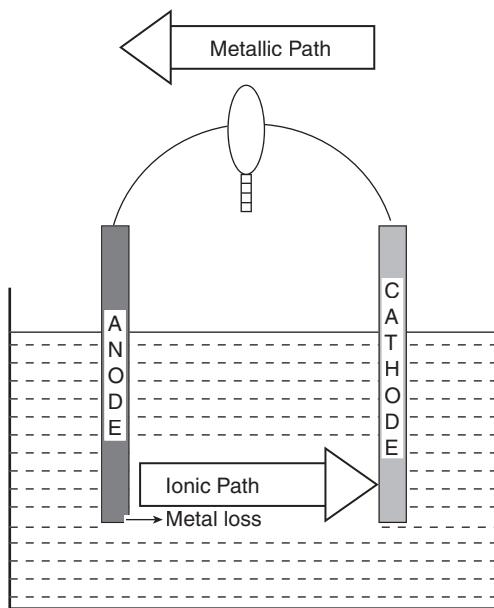


Figure 27 Schematic diagram of corrosion cell.

Concept Check

- What are the essential components in a corrosion cell?

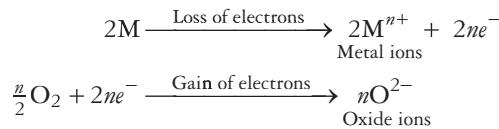
3.18 Theories of Corrosion

Dry Corrosion (Direct Chemical Attack)

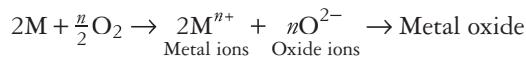
Dry corrosion involves direct attack of atmospheric gases on metal in the absence of moisture liquid phase, that is, conducting (aqueous) medium. The corrosive media include vapors, gases, etc. The example of dry corrosion is the reaction between metal and oxygen (atmosphere) at elevated temperatures in perfectly dry conditions.

Compared to other gases and chemicals, it is found that oxygen is mainly responsible for the corrosion of most metallic substances. Accordingly, corrosion on metallic surface is due to direct reaction of atmospheric gases such as oxygen; halogens; oxides of sulphur, nitrogen; hydrogen sulphide and fumes evolved due to chemical reactions with metal. There are three main types of dry corrosion.

1. **Oxidation corrosion (reaction with oxygen):** Few metals such as alkali and alkaline earth metals react vigorously with oxygen to form oxides at low temperatures even in the absence of moisture. Most other metals react only to a small extent with oxygen under ordinary conditions, in absence of water, to form oxides. However, all metals are oxidized at higher temperatures with the exception of silver, gold and platinum. The corrosion that results from direct attack of oxygen on the metal at low or high temperatures, generally in the absence of moisture is called oxidation corrosion. The reactions taking place during oxidation corrosion involve oxidation of metal by loss of electrons and reduction of oxygen to oxide ions by gain of electrons:



The overall reaction can be given by



The metal atoms on the surface first react with atmospheric oxygen to form the metal oxide. The metal oxide layer is formed perpendicular to the metal surface and forms a barrier for reaction of further metal atoms with the oxygen in the air. So, for the process of oxidation to continue either the metal atoms from the inner layer of metal should diffuse out to the surface or the oxygen atoms should diffuse in to the inner metal layers. Generally, the metal ions being lighter diffuse out more rapidly than the inward diffusion of heavier oxide ion. This can be represented schematically as shown in Figure 28.

The nature of metal-oxide film formed at the interface is important in determining the extent of further corrosion of the metal. The oxide layer formed can be:

- (a) **Stable:** It is fine-grained film that adheres well to the metal layer forming a kind of protective coating. It is impervious in nature and prevents further oxidation of metal. Examples: oxide films of aluminium, lead copper, tin, etc.
 - (b) **Unstable:** The oxide film formed decomposes back to metal and oxygen, so no oxidation corrosion is observed for these metals. Examples: silver and gold.
 - (c) **Volatile:** The metal oxide formed volatizes as soon as it is formed, exposing a fresh layer of metal for oxidation, resulting in rapid corrosion. Examples: molybdenum oxide.
 - (d) **Porous:** The oxide layer formed is porous and allows atmospheric oxygen to travel to inner layers resulting in unobstructed corrosion. Examples: oxide films of lithium, sodium, magnesium, etc.
2. **Corrosion by other gases such as Cl_2 , SO_2 , H_2S , NO_x :** In dry atmosphere, these gases react with metal and form corrosion products, which may be protective or non-protective. Dry Cl_2 reacts with Ag and forms $AgCl$ which is a protective layer, while $SnCl_4$ is volatile. In petroleum industries at high temperatures, H_2S attacks steel forming FeS scale which is porous and interferes with normal operations.

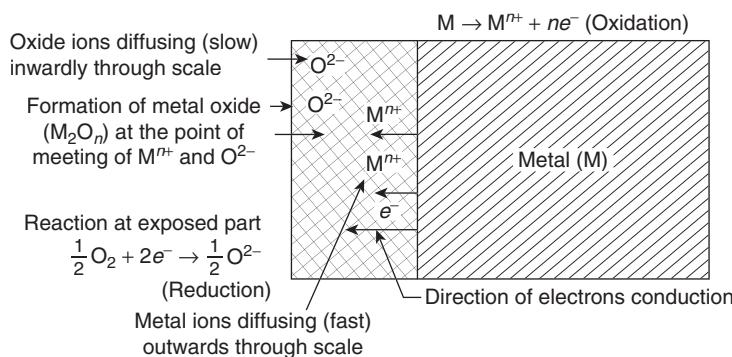


Figure 28 Mechanism for oxidation corrosion.

3. **Liquid metal corrosion:** In several industries, molten metal passes through metallic pipes and causes corrosion due to dissolution or internal penetration. For example, liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.

Wet Corrosion (Electrochemical Theory of Corrosion)

Wet corrosion usually occurs in conducting liquid (aqueous) phase. This type of corrosion occurs when the metal comes in contact with a conducting liquid or when two dissimilar metals are immersed or dipped partly in a solution. In other words, wet corrosion involves electrochemical attack on metals in aqueous environments. This corrosion is more prevalent than dry corrosion.

According to the electrochemical theory of corrosion, the corrosion of a metal like iron exposed to the environment may be thought of as a three-step process.

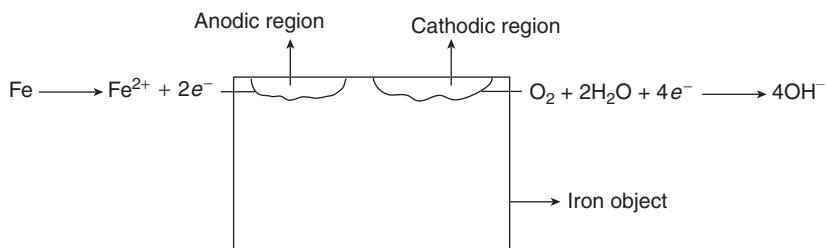
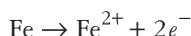


Figure 29 Galvanic cell.

- Formation of large number of galvanic cells (Figure 29), that is, the development of anodic and cathodic regions on the same metal (Figure 29). The electrons released at the anode are absorbed at cathode.
- Corrosion (oxidation) takes place at the anodic region.
- Reduction of O_2 (air) in presence of water to hydroxyl $[\text{OH}^-]$ ions takes place at cathodic region.

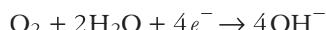
The reactions involved in the galvanic cell are as follows:

- Anodic reaction:** Metal undergoes oxidation (corrosion) with release of electrons:

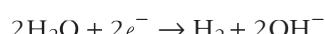


At the cathodic region, electrons are absorbed and cause reduction of constituents.

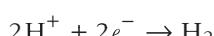
- Cathodic reactions:** These reactions are dependent on the constituents of the corrosion medium. There are three possible ways in which reduction takes place:
 - If the solution is aerated and almost neutral, oxygen is reduced in presence of H_2O to OH^- ions.



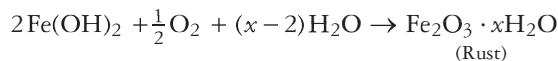
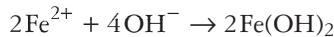
- If the solution is deaerated and almost neutral, H_2 is liberated along with OH^- ions.



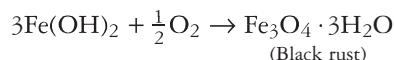
- If the solution is deaerated and acidic, H^+ ions are reduced to hydrogen gas



3. The metal ions formed at the anode combine with hydroxyl ions and form the corresponding metallic hydroxide Fe(OH)_2 , which further gets oxidized to hydrated ferric oxide [rust].



In the presence of limited oxygen, black rust is formed as follows:



Differences between Dry Corrosion and Wet Corrosion

The difference between dry corrosion and wet corrosion are elucidated in Table 5.

Table 5 Comparison between dry corrosion and wet corrosion

<i>Dry Corrosion</i>	<i>Wet Corrosion</i>
Involves direct attack of atmospheric gases on metal in the absence of moisture liquid phase	Involves electrochemical attack on metals in aqueous environments
Less prevalent	More prevalent
The corrosive media include vapors, gases, etc.	The corrosive media is conducting liquid (aqueous) phase
It is of various types: Oxidation corrosion, corrosion by other gases such as Cl_2 , SO_2 , H_2S , NO_x and liquid metal corrosion	It is of three types: differential metal corrosion, differential aeration corrosion and crevice corrosion

Pilling–Bedworth Ratio

On exposure to environment, the metals get oxidized and an oxide layer is formed. The rate of oxidation increases with increase in temperature. This oxide is generally more stable than the metal and protects the metal from further oxidation. The further oxidation corrosion process of the metal is determined by the nature of the oxide formed. In 1923, N.B. Pilling and R.E. Bedworth proposed that the resistance of the metal to further oxidation is determined by the adherence of this oxide layer to the metal surface. They classified metals into two groups: those that form protective oxide layer and those that do not. They suggested that the adherence of the oxide layer formed to the metal is determined by the ratio of the volume of oxide layer formed to the volume of total metal layer used to form this oxide. The oxide layer formed is protective if the volume of the oxide layer is less than the volume of metal reacted.

1. Pilling–Bedworth ratio is represented by R and is given as

$$R = \frac{\text{Molecular volume of oxide}}{\text{Molecular volume of metal}}$$

or

$$R = \frac{M_{\text{oxide}} / d_{\text{oxide}}}{n \times (A_{\text{metal}} / d_{\text{metal}})}$$

where M_{oxide} is the molecular weight of the oxide, A_{metal} is the atomic weight of the metal, d_{oxide} and d_{metal} refer to densities and n is the number of metal atoms per molecule of oxide. If the Pilling–Bedworth ratio is less than 1, the oxide scales are usually non-protective. Scales on metals such as magnesium, potassium, sodium and calcium are porous or cracked due to tensile stress and do not provide efficient barrier to penetration of the air (oxygen) to the metal surface.

2. If the Pilling–Bedworth ratio is more than 1 (iron, nickel, cobalt, chromium, silicon, and aluminum and their alloys), the protective scale may develop and protect the metal or alloy from the air so that oxidation can proceed only by solid-state diffusion, which is slow even at high temperatures.
3. If the Pilling–Bedworth ratio is more than 2, as is the case with silicon and niobium, during the scale growth, large compressive stresses often develop in the oxide that may cause the scale to crack and/or spall off, leaving the metal unprotected.

Table 6 lists Pilling–Bedorth ratio for different metals and their oxides.

Table 6 Pilling–Bedorth ratios (PBRs) for metals and their oxides

Metal	Oxide	PBR
Nb	Nb_2O_5	2.69
Si	SiO_2	2.14
Cr	Cr_2O_3	2.01
Ti	TiO_2	1.77
Ni	NiO	1.66
Zr	ZrO_2	1.51
Al	Al_2O_3	1.28
Mg	MgO	0.804
Ca	CaO	0.638
Sr	SrO	0.611
Ba	BaO	0.670
Li	Li_2O	0.567
Na	Na_2O	0.541
K	K_2O	0.474

It can be seen from Table 2 that each of the alkali and alkaline earth metals has values of Pilling–Bedorth ratio as less than 1 ($R < 1$). Metals which are normally passive have values of R between 1 and 2. The Pilling–Bedorth ratio is greater than 2 for some oxides which provide stable passive films.

If the passive oxide films are very thin, their densities are not necessarily those of the bulk oxides which have been used to calculate the Pilling–Bedorth ratio. So Pilling–Bedorth ratios are more useful in the high-temperature oxidation of metals where the thicker oxide scales which are formed are more closely related to bulk oxide properties. If the metal is subjected to alternate heating and cooling cycles, the stability of the oxide layer is determined by the relative thermal expansion of the oxide and the metal layer. In these cycles, oxides that are prone to thermal spalling form cracks. If the oxide layer formed is volatile at high temperatures, as in case of molybdenum and tungsten, no protection is offered by the oxide layer.

The Pilling–Bedworth ratio or the comparison of molar volumes is only one condition for assessing the mechanical properties of oxide films. Other important factors include inherent stress–strain behavior of the oxide film.

Concept Check

- What is meant by dry corrosion?
- Explain briefly theory of dry corrosion.
- What do you mean by wet corrosion?
- Write a note on electrochemical theory of corrosion.
- Distinguish between dry and wet corrosion.
- What does Pilling–Bedworth ratio equal to 1 indicate?

3.19 Types of Electrochemical Corrosion

Differential Metal Corrosion (Galvanic Corrosion)

Differential metal corrosion occurs when two dissimilar metals are in contact with each other in a corrosive environment. The metal with low reduction potential (anode) undergoes oxidation (corrosion), while metal with high reduction potential (cathode) undergoes reduction. The greater the electrode potential difference, the higher is the corrosion rate. Thus, it is the anodic metal that always undergoes corrosion and cathodic metal is unattacked.

EXAMPLE 1

Consider a bimetallic couple of iron and copper (Figure 30). The electrochemical series is as follows: Mg (−2.52 V); Zn (−0.76 V); Fe (−0.44); Cu (0.34 V) and Ag (0.80 V). As observed, iron is placed above copper in electrochemical series. Therefore, iron is anodic to copper, that is, iron acts as anode and undergoes corrosion, whereas copper acts as cathode and remains unattacked. The reactions involved in the galvanic cell are as follows:

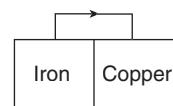
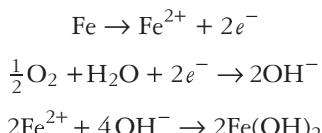


Figure 30 Bimetallic couple of iron and copper.

EXAMPLE 2

Consider a bimetallic sample of iron and zinc as shown in Figure 31.

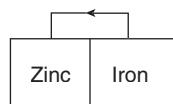


Figure 31 Bimetallic couple of iron and zinc.

As zinc is placed above iron in the electrochemical series, zinc is anodic to Fe. Therefore, zinc undergoes corrosion. Hence, we find that iron corrodes in contact with copper or silver, whereas zinc and magnesium corrode in contact with iron. The rate of differential metal corrosion depends upon the potential difference between the two metals; higher the difference, faster is the rate of corrosion.

EXAMPLE 3

Consider another bimetallic couple of steel and copper as shown in Figure 32.

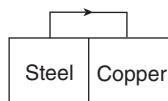


Figure 32 Bimetallic couple of steel and copper.

Steel is anodic in nature thus undergoes corrosion (as iron is above copper in the electrochemical series). The rate of corrosion depends on the potential difference between the two metals (materials).

Other examples of differential metal corrosion (galvanic corrosion) include the following:

1. Buried iron pipeline connected to zinc bar.
2. Steel pipe connected to copper plumbing.
3. Steel propeller shaft in bronze bearing.
4. Zinc coating on mild steel.
5. Lead–tin solder around copper wires.

Preventive Measures

1. Placing a thin layer of an insulator between two metals or materials.
2. Selecting materials having very less potential difference.

Differential Aeration Corrosion

Differential aeration corrosion occurs when a metal is exposed to differential air concentrations or oxygen concentrations. The part of the metal exposed to higher oxygen concentration acts as cathodic region and the part of the metal exposed to lower oxygen concentration acts as anodic region and undergoes corrosion.

EXAMPLE 4

Consider a plate of pure iron which is partially immersed in an aerated solution of sodium chloride (Figure 33).

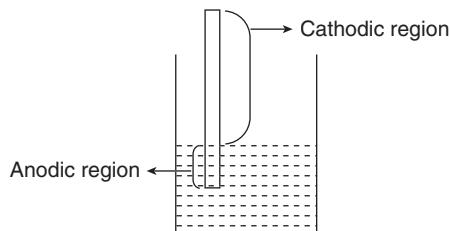
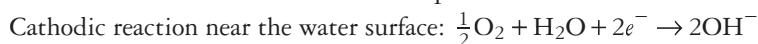


Figure 33 Pure iron partially immersed in an aerated solution of NaCl.

Since cathodic reaction requires oxygen, the part of the metal exposed to higher oxygen concentration always acts as the cathodic region. The portion of the metal immersed in NaCl is anodic region. The reactions involved are as follows:



The examples of differential aeration corrosion include:

1. Half-immersed iron plate in aqueous solution.
2. Steel pipe carrying any liquid exposed to atmosphere.
3. Ocean going ships.
4. Steel storage tanks.

Preventive Measures

1. Using metallic coating, electroless plating or chemical conversion methods.
2. Maintaining the material's own protective film.
3. Controlling the chemistry of fluids and using inhibitors.

Waterline Corrosion

Waterline corrosion is a case of differential aeration corrosion. Ocean going ships and water storage steel tanks undergo this type of corrosion (Figure 34). The metal portion just below the waterline is more anodic to portion above the water line. Therefore, the metal just below the waterline undergoes corrosion.

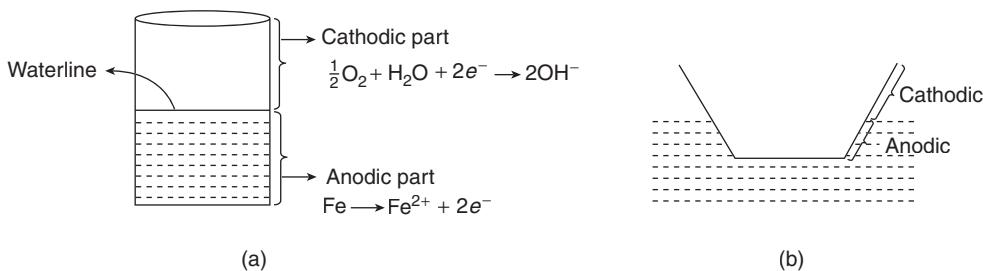


Figure 34 Waterline corrosion: (a) Water storage tank and (b) ocean going ship.

Waterline corrosion is common in water-lifting pipes under water. Ocean going ships also suffer from differential aeration corrosion. Ships sunk under water for several years do not undergo corrosion. For the portion of the ship sunk under water, the difference in O₂ concentration between the top and bottom portions of the ship is negligibly small. Thus, the ship is exposed to almost uniform concentration of air and does not undergo differential aeration corrosion.

Crevice Corrosion

Crevice corrosion is often associated with a small volume of stagnant solution or electrolyte trapped in crevices of joints, rivets, bolts, gasket surfaces, lap joints, nuts, washers or in surface deposits. This

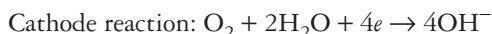
corrosion occurs when oxygen cannot penetrate a crevice, leading to set up of a differential aeration cell. Corrosion occurs rapidly in the area with less oxygen. Also, consider the corrosion occurring when the surface of a painted metal is scratched. The scratched portion would act as a small anode, while the rest of the part would act as cathode, thus forming a local differential aeration cell.

Mechanism

In general, crevice corrosion occurs rapidly in the area with less oxygen. Increase in acidity and chloride content of crevice solution initiates passive film breakdown process, and thereby enhances the rate of corrosion reaction. Finally, corrosion propagation continues leading to further deterioration of the material.

The Fontana and Greene model describes crevice corrosion mechanism. This model consists of four stages.

Stage 1: Corrosion normally occurs both inside and outside the crevice with the following reactions:



The positively charged metallic ions are electrostatically counterbalanced by OH^- ions.

Stage 2: The cathode reaction inside the crevice consumes most of the available oxygen.

Stage 3: The Cl^- and OH^- ions diffuse into the crevice to maintain minimum potential energy, thus forming the metal chloride. Hydrolysis of metal chloride lowers pH and $\text{MCl} + n\text{H}_2\text{O} \rightarrow \text{M(OH)}_n + n\text{HCl}$.

Stage 4: More M^{n+} ions attack more Cl^- leading to lower pH inside crevice. This accelerates the dissolution of metal and more M^{n+} ions will be produced that will further lower the pH.

Preventive Measures

1. Increasing resistance by using alloys that have high percentage of chromium, molybdenum and/or nitrogen.
2. Design and fabricate to avoid crevices.
3. Frequently inspecting for inadvertent crevices and closing crevices by continuous welding, caulking or soldering.

Pitting Corrosion

Pitting corrosion involves localized attack usually in chloride medium. This corrosion arises when a small portion of the metallic surface is either defective (with cracks) or occupied by dust/scale/sand/water drop.

Mechanism

Figure 35 shows the mechanism of pitting corrosion of iron surface in the chloride medium. The metal below the dust (deposit particle) is exposed to lower O_2 concentration and undergoes corrosion. Once a pit is formed, the rate of corrosion increases. The accelerated corrosion takes place below the deposit because of small anodic area and large cathodic area.

Preventive Measures

1. Preparing surfaces with best possible finish. Mirror-finish resists pitting best.
2. Removing all contaminants, especially free-iron by passivation.
3. Designing and fabricating to avoid trapped and pooled liquids.

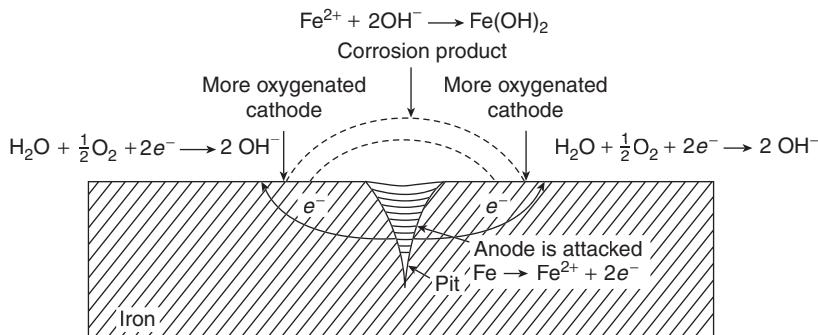


Figure 35 Pitting corrosion on the surface of iron.

Concept Check

- Explain differential metal corrosion.
- Iron corrodes in contact with copper, but not with zinc. Justify.
- How do you prevent differential metal corrosion or galvanic corrosion?
- Write important preventive measures for galvanic corrosion.
- What do you mean by waterline corrosion?
- Explain the mechanism of pitting corrosion?
- Write a note on crevice corrosion.

3.20 Other Types of Corrosion

1. **Stress corrosion:** Mechanical forces within the metal bring about stress corrosion. The internal stress of metal arises when the metal is subjected to mechanical operations such as pressing, hammering, bending, welding or riveting. The stress can also be external stress that acts on the metal during service conditions. The metal atoms under stress are always at higher energy levels as compared to stress-free atoms. The stressed part of the metal, therefore, becomes more reactive than the stress-free part. As a result, a galvanic cell is formed with the stressed part acting as anode, and stress-free part acting as cathode (Figure 36). Under specific corrosion environments, the stressed part undergoes corrosion, initiating the crack. In the presence of continuously acting stress and corrosion medium, the crack propagates through the metal. Cracking of brass and caustic embrittlement of steel boilers are two examples of stress corrosion.

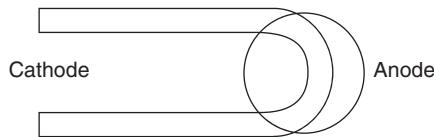


Figure 36 Stress corrosion in metal.

- **Seasonal cracking:** This type of corrosion was first observed during the British rule in India during the monsoon season. Due to diminished military activity during this season, brass cartridges were stored for later usage. After some time, it was found that cracks were developed

on the surface of these cartridges. The seasonal cracking occurs due to the action of (a) susceptible agent like copper and its alloys, (b) attacking agent like ammonia and (c) tensile stress (residual).

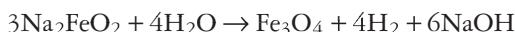
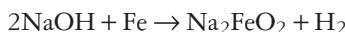
- **Caustic embrittlement of steel boilers:** Mild steel boilers undergo corrosion at the stressed portion when the operating pressures are between 10 atm and 20 atm. Fine cracks may develop at the stressed portion of the boiler. Boiler water containing alkaline impurities pass into these cracks by capillary action. This water evaporates and leaves behind caustic soda in the cracks, whose concentration thus increases. Thus, a galvanic cell is set up between the iron under stress and the iron in the main body. The cell can be represented as follows



Iron under stress acts as the anode and gets corroded resulting in boiler failure. The boiler water contains Na_2CO_3 , which is hydrolyzed at high temperature to give NaOH .



The NaOH formed flows into hair-thin cracks and crevices. There it reacts with iron and forms Na_2FeO_2 (sodium ferroate) which decomposes to give Fe_3O_4 and NaOH .



NaOH thus formed, further reacts with iron to cause corrosion. This is called caustic embrittlement.

Preventive measures

- Applying protective coatings.
 - Using corrosion inhibitors.
 - Performing stress-relief heat treatments.
 - Reducing the overall stress level and designing out stress concentrations.
 - Adding Na_2SO_4 to boiler water in addition to tannin and lignin to boiler water to prevent caustic cracking.
2. **Intergranular corrosion:** Generally observed in alloys, this corrosion involves an attack on the grain boundaries of a metal or alloy, where the formation of a corrosion product takes place. This corrosion is not observed externally, and leads to sudden unanticipated failure of the material. For instance, when stainless steel (18% Cr, 8% Ni) containing more than 0.1% carbon is heated to high temperature and cooled slowly or held at 650°C for a short interval of time, a rapid reaction occurs between carbon and chromium. Chromium carbide, thus formed, precipitates at the grain boundaries and results in the formation of galvanic cells (Figure 37).

Chromium-rich grain centers act as the cathode, while the grain boundaries act as anode and undergo corrosion. This type of corrosion is also called grain-boundary corrosion.

Preventive measures

- Selecting an alloy type resistant to intergranular corrosion.
- Avoiding heat treatments or service exposure that make the material susceptible. Normally, this occurs with austenitic stainless steels when they are held for sometime in the sensitizing temperature range of $470\text{--}915^\circ\text{C}$.
- Applying protective coatings.

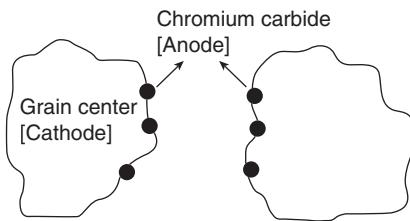
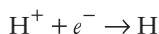


Figure 37 Intergranular corrosion in stainless steel.

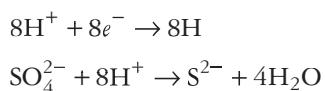
3. **Microbiological corrosion:** This corrosion involves degradation of materials by bacteria, moulds and fungi or their byproducts. Some types of bacteria consume oxygen and cause differential aeration type of system, which results in corrosion. The corrosion occurs at the zones poor in oxygen concentration. For example, the bacillus, algae diatoms. This type of corrosion can occur by a range of actions such as:

- Attack of the metal or protective coating by acid byproducts, sulphur, hydrogen sulphide or ammonia.
- Direct interaction between the microbes and metal that sustains attack.

For example, corrosion of steel pipelines in waterlogged neutral ground containing little oxygen is often much more severe than might be expected. Cast iron pipes of 6 mm wall may perforate in less than 5 years. *Sulphate-reducing bacteria* such as *Desulphovibrio* which flourish in oxygen-free conditions assist the corrosion of iron apparently by consuming hydrogen produced in the cathodic reaction, thus enhancing the rate of the cathodic reaction.



The bacteria make use of H^+ to reduce sulphate SO_4^{2-} concentration. The overall corrosion cell reaction is as follows:



The corrosion product FeS is formed as a result of the above reactions.

Preventive measures

- Selecting resistant materials.
 - Ensuring frequent cleaning.
 - Controlling chemistry of surrounding media and removal of nutrients.
 - Using of biocides.
 - Applying cathodic protection.
4. **Soil corrosion:** Underground pipes, cables, tank bottoms, etc., get corroded due to moisture, pH of soil, ionic species like chlorides and micro-organisms like bacteria. It is further enhanced by differential aeration of various parts of the soil.
5. **Erosion corrosion:** Due to mechanical wear and tear, there is relative motion of the corrosive liquid over the metal surface. This motion increases the rate of corrosion on the surface of a metal and is called erosion corrosion. It is most common in copper tubes.

Concept Check

- Explain caustic embrittlement in boilers.
- Write important preventive measures for the following types of corrosion: (a) stress corrosion and (b) intergranular corrosion.
- Explain very briefly soil corrosion and erosion corrosion.
- Write a note on intergranular corrosion.
- Explain microbiological corrosion.

3.21 Factors Influencing Rate of Corrosion

There are two factors influencing the rate of corrosion: Primary factors related to the metal and secondary factors related to the environment.

Primary Factors

1. **Nature of the metal:** The tendency of metal to undergo corrosion depends on its nature. Metals with low reduction potential exhibit high reactivity, and hence are more susceptible for undergoing corrosion. Thus, the tendency of a metal to undergo corrosion decreases with increase in reduction potential (galvanic potential). Metals such as Li, Na, Mg, Zn, etc., have low reduction potentials and therefore undergo severe corrosion in corrosive environment. The noble metals with high reduction potential, such as Ag, Au, Pt, etc., are less susceptible for undergoing corrosion. However, few metals deviate from the normal tendency, due to their ability to develop passive layers.
2. **Electrode potential difference:** Potential difference between the anodic and cathodic regions is known as open-circuit potential difference. Larger the open-circuit potential, higher is the rate of corrosion. For example, the potential difference between iron and silver is 1.14 V, which is more than 0.3 V between iron and tin. Therefore, iron corrodes faster when in contact with silver than with tin. Thus, farther apart the metals stand from each other in the electrochemical series, greater is the intensity of corrosive attack on the anodic metal. On this account, the use of dissimilar metals should be avoided wherever possible.
3. **Surface state of the metal:** State or condition of the surface of the metal affects the corrosion process rate. For example if part of the surface is covered by oil or dust particles then severe pitting corrosion occurs at the metal surface. Corrosion at the surface is also accelerated by presence of water droplet on the surface. Heterogeneity at the surface of the metal results in high corrosion rate.
4. **Hydrogen overvoltage:** In most of the electrochemical reactions, the competing cathodic reaction is the hydrogen ion reduction to liberate hydrogen gas. Hydrogen overvoltage is the measure of the tendency of the electrode to liberate hydrogen gas. A metal with low hydrogen overvoltage on its surface is more susceptible for corrosion. Low hydrogen overvoltage results in faster cathodic reaction. This even increases the anodic reaction rate, and hence increases the overall rate of corrosion.
5. **Formation of protective films by metals:** A few metals exhibit the tendency to develop passive, but protective films or layers on exposure to corrosive medium. The nature of such a passive layer largely decides the rate of corrosion. The passive layer (usually metal oxide) formed on the surface of the metal is stable, highly insoluble with low conductivities. This allows it to act as a protective layer and prevent further corrosion. Metals like Al, Ti and Cr develop such a layer on their surface, and become passive to corrosion.

On the other hand, if the oxide layer is unstable, soluble, non-uniform and porous, then corrosion continues to take place. For example, metal oxide layers of Fe and Zn cannot control corrosion, as they are porous and cannot completely prevent access to the corrosive environment.

Secondary Factors

- pH:** In general, lower the pH of the corrosion medium, higher is the corrosion rate. At $\text{pH} > 10$, corrosion of Fe practically ceases due to formation of a protective coating of hydrous oxides. However, metals like Al, Zn undergo fast corrosion in highly alkaline solution. If the $\text{pH} < 3$, severe corrosion occurs even in absence of air due to the continuous evolution of hydrogen at the cathodic region.
- Temperature:** The rate of any chemical reaction increases with rise in temperature. Increase in temperature increases the conductance of the medium, reduces passivity of the metal, and thereby increases the rate of corrosion.
- Anodic and cathodic area effect:** The rate of corrosion is greatly influenced by the relative sizes of anodic and cathodic areas.

When the ratio of anodic to cathodic region is small, that is, smaller anodic region and larger cathodic region then, this leads to faster and intensive anodic reaction, thus making the overall corrosion effective. For example, tin-coated iron material with some pinholes or uncovered areas on the surface where tin is cathodic to iron (Figure 38).

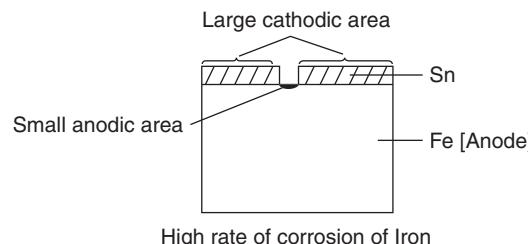


Figure 38 Small ratio of anodic to cathodic region leading to high rate of corrosion.

The ratio of anodic to cathodic region is large, that is, larger anodic region and smaller cathodic region. This causes the corrosion at anodic region to occur very slowly. For example, zinc-coated iron material with some pinholes on the surface where zinc is anodic to iron (Figure 39).

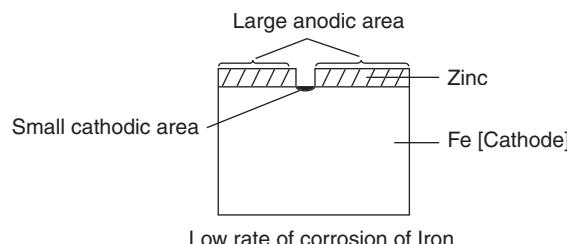


Figure 39 Large ratio of anodic to cathodic region leading to low rate of corrosion.

- 4. Polarization of electrodes:** Polarization is defined as the departure of electrode potentials from their equilibrium values, that is, from the open-circuit potentials causing a decrease in the current density. Polarization at the electrodes is due to concentration changes in the electrode region. It causes the potential of the cathode to become more anodic and that of anode to become more cathodic. The anodic and cathodic reactions must go in-step with one another if corrosion is to be sustained. The overall rate of electrochemical corrosion may be principally governed either by the anodic or by cathodic reaction rate. For metals such as Fe and Zn in aqueous solution, the rate of the cathodic reaction is the rate-determining step and the reaction is said to be under cathodic control (cathode polarization) in which corrosion current is under cathodic control. If the anodic reaction is the rate determining step, then the rate of corrosion is controlled by anodic polarization. Figure 40 shows the polarization curves for corrosion processes proceeding by (a) cathodic control, (b) anodic control and (c) mixed control.

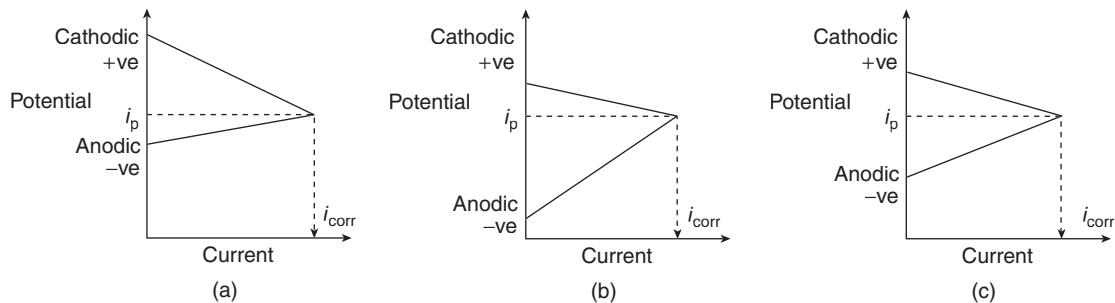


Figure 40 Polarization curves: (a) cathodic control, (b) anodic control and (c) mixed control.

In these diagrams, the polarization curve has a steeper slope for the electrode that is polarized to a greater extent.

- 5. Conductance of the medium:** Corrosion is an electrochemical reaction, which involves electron transfer (conduction). The presence of conducting species in the atmosphere increases the corrosion rate. This rate is more in a wet atmosphere (more conducting) than in the dry atmosphere.
- 6. Humidity:** Rate of corrosion is low at low-relative humidity. It increases with increase in humidity up to a certain value called critical humidity; but corrosion abruptly increases above critical humidity.

Concept Check

- Explain how the following factors influence corrosion rate: (a) nature of the corrosion product and (b) surface state of the metal.
- What is hydrogen overvoltage? How does it affect corrosion rate in materials?
- What is the effect of pH and temperature on the rate of corrosion?
- Write a note on polarization of electrodes in corrosion cell.
- Pin holes on tin-coated iron materials are most disastrous to iron than pin holes on zinc-coated iron materials. Justify the statement.
- Which of the following two conditions favor corrosion rate? Justify your answer.
 - High ratio of anodic to cathodic areas.
 - Low ratio of anodic to cathodic areas.

3.22 Corrosion Control Methods

Corrosion control is more realistic than corrosion prevention, since corrosion of a metal is natural process by which metal is converted into a more stable state. There are varieties of corrosion control techniques as the corrosion depends on the nature of environment. The important corrosion control methods are discussed in the following sections:

1. Design and material selection:

- In any design, the greater the number of angles, corners, edges and internal surface, the more difficult it becomes for efficient surface treatment. Hence, as far as possible, L-, T- and U-shaped profiles in construction should be minimized (Figure 41).
- No corrosion occurs without the presence of moisture. The design of a structure should be such that retention of moisture should be as low as possible.
- Differential metal corrosion can be reduced by the use of a single metal rather than dissimilar metals. If their use is unavoidable, metals closely positioned in the galvanic series should be used. An insulator should be placed between two dissimilar metals.
- The rate of corrosion depends on the relative sizes of anode and cathode. Smaller anode and larger cathode should be avoided as far as possible.

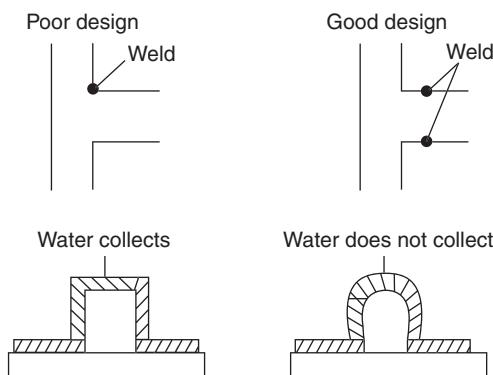


Figure 41 Design selection for corrosion control.

2. Protective coatings: These are used to prevent corrosion at the surfaces of materials. Protective coatings include metallic coatings, chemical conversion coatings, ceramic coatings and organic coatings.

3. Cathodic protection: The corrosion of metal takes place at the anodic region whereas at the cathodic region, metal is unaffected. The principle of cathodic protection involves the elimination of anodic sites and conversion of the entire metal into cathodic site. This can be achieved by providing electrons from an external source so that the specimen always remains cathode. This technique of offering protection to a specimen against corrosion by providing electrons from an external source is called cathodic protection. It can be achieved by the following two methods:

- **Sacrificial anode method:** In this method, the metal structure is converted into a cathode by connecting into a more active metal, which acts as an auxiliary anode. The most commonly used auxiliary anodes are Zn, Mg and Al. These metals being more active, act as anode and undergo

preferential corrosion, thus protecting the metal structure. Since the anodic metals are sacrificed to protect the metal structure, this method is known as sacrificial anode method. New auxiliary anodes replace exhausted sacrificial anodes as and when required. For example,

- (a) Magnesium block connected to underground pipelines.
- (b) Magnesium bars are fixed to the sides of the ships.

- **Impressed current method:** Another method of providing cathodic protection is by applying a direct current larger than the corrosion current. The protected metal is made cathodic by connecting it to the negative terminal of a DC source. Positive terminal is connected to an inert anode like Graphite. The metal structure being cathode, does not undergo corrosion (Figure 42).

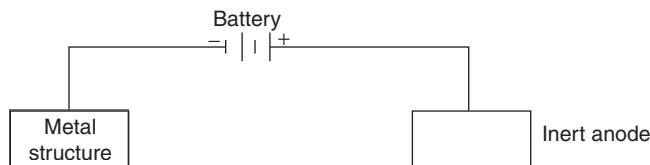


Figure 42 Impressed current method.

4. **Anodic protection:** The prevention of corrosion by **impressed anodic current method** is called **anodic protection**. Few metals like Ti and alloys like steel, when made as anode exhibit passivity by forming their oxide layers. In case of metals, such as Ti, Ni, Cr and their alloys, application of suitable anodic current makes them passive and decreases their rate of dissolution. The potential required to protect the metal can be obtained from potential–current curve as shown in Figure 43.

As the potential is increased, initially the current also increases (line AB), indicating the dissolution of metal. This trend continues until the current reaches a critical value (i_{crit}) and passivation due to the development of oxide layers sets in. This potential is called passivating potential (E_p). Above E_p , the current flow decreases and reaches a minimum value called the passivating current i_p . It is the minimum protective current density to maintain passivation. If the potential is further increased, the metal remains unattacked till a particular potential is reached (line CD). This potential range in which anodic protection can be achieved is called protection range.

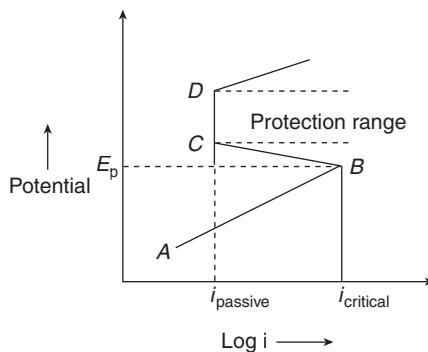


Figure 43 Potential–current curve.

The advantage of the method is that it requires a small current. However, the corrosion rate cannot be reduced to zero as in cathodic protection. A drawback of the method is that it cannot be applied to metals that do not passivate. This method of anodic protection is utilized in the transportation of concentrated acids.

5. **Corrosion inhibitors:** These inhibitors reduce corrosion by retarding either anodic or cathodic reactions.

- **Anodic inhibitors:** Anodic reaction is the oxidation of metal, that is, for example in rusting of iron, Fe^{2+} ions are formed at anode. Anodic inhibitors prevent the formation of Fe^{2+} ions (anodic reaction), and thereby retard the corrosion process. This is achieved by the addition of anions such as chromate, tungstate, molybdate, etc., which combine with metal ions formed at anodic region, forming sparingly soluble salts. These salts are deposited on the anodic sites forming protective films, which act as barriers between metal surface and corrosion medium, prevent further anodic reaction and hence corrosion.
- **Cathodic inhibitors:** These act by inhibiting the cathodic reactions which involve the liberation of hydrogen in acidic solutions and OH^- ions in alkaline solution. These can be of two types:
 - (a) Organic cathodic inhibitors such as amines, mercaptans, thioureas, sulphoxides, form a protective layer on cathodic regions, prevent the evolution of hydrogen; thus decreasing the rate of corrosion.
 - (b) Inorganic cathodic inhibitors such as sulphates of Mg, Mn, Ni and Zn are used in neutral or alkaline medium. These inhibitors react with OH^- ions liberated at cathode, forming insoluble hydroxides, which form protective film over cathode areas and prevent corrosion.

Concept Check

- What are the important preventive measures taken during initial design and material selection for any structure?
- What is the principle of cathodic protection method of corrosion control?
- Explain sacrificial anode protection method.
- Explain anodic protection method of corrosion control.
- Explain impressed current method of corrosion control.
- What are corrosion inhibitors? Explain the action of anodic and cathodic corrosion inhibitors with examples.

3.23 Protective Coatings

Protective coatings are used to prevent corrosion at the surfaces of materials. These include metallic coatings, chemical conversion coatings, ceramic coatings and organic coatings. Underbody structural components are typically coated to provide first line of defence against corrosion. Commonly used coatings include phosphate conversion coating, hot melt wax, electro coating, metallic coating, organic coating, autodeposition and powder coating. Phosphate conversion coatings are employed to enhance paint adhesion, thereby indirectly enhancing corrosion resistance.

1. Inorganic coatings:

- **Anodic metal coatings:** Anodic metal coatings are produced by coating a base metal with more active metals (i.e., metals having low E^0 values), which are anodic to the base metal. For example,

Al, Mg, Zn and Cd coatings on Fe. A characteristic feature of anodic coating is that, even if the coating falls off at some places, the base metal does not undergo corrosion because the base metal is cathodic in nature. These are carried out by four methods such as cladding, hot dipping, spraying and cementation.

- (a) **Cladding:** It is used mainly with metal sheets. The iron sheet to be protected is cladded (sandwiched) between two sheets of the anodic metal and squeezed by rolling under pressure and heat. For example, cladding of aluminium by duralumin (alloy of Al, Mg and Cu). These corrosion-resistant materials are used in the aircraft industry.
- (b) **Hot dipping (galvanization):** Hot dipping involves dipping the base metal in molten anodic metal. For example, galvanizing coating of zinc on iron by hot dipping. Galvanization involves pre-treatment of iron material with organic solvents followed by dilute H_2SO_4 . Iron is then treated with $ZnCl_2$ and NH_4Cl and dipped in molten zinc at $430\text{--}470^\circ C$.
- (c) **Metal spraying:** It is done through flame-spraying technique where metal particles are sprayed by an air blast on the surface to be coated. For example, Al, Zn, Cd and Zn are coated by this technique.
- (d) **Cementation:** It is a process of obtaining a coating by heating the metal object in a powder of the coating metal. For example, coating of Fe by Zn in this way is called sherardizing; coating Al on Fe is called colorizing and coating of Cr and Al on alloys is called chromaluminizing.
- **Cathodic metal coatings:** Cathodic metal coatings are produced by coating a base metal with more noble metals (i.e., metals having high E^0 values) which are cathodic to the base metal. Cathodic coatings are effective only when the coating is continuous, non-porous and free from gap; otherwise rapid corrosion of the base metal takes place as a result of the formation of large cathodic and small anodic areas. Tinning is most commonly used cathodic coating on steel surfaces. It is a process of coating base metal with tin. Tinning involves pre-treatment of iron with organic solvents followed by dilute H_2SO_4 . Iron is then passed through $ZnCl_2$ and NH_4Cl flux and then through tin. Finally, it is dipped in palm oil to prevent the oxidation of tin.

2. Chemical conversion coatings:

- **Anodizing coating:** This coating is generally produced by anodic oxidation process on metals such as Al, Zn, Mg and their alloys. In this process, the base metal acts as anode in an electrolytic bath and by passing direct current. Al exhibits high anodic passivity by developing its oxide layer and thereby prevents corrosion when coated on other metals.

The metal material, after pre-treatment acts as anode; and steel or copper acts as cathode. The electrolyte consists of 5–10% chromic acid. The temperature of bath is maintained at $35^\circ C$. Anodic current density is maintained at $10\text{--}20\text{ mA/cm}^2$. An oxide layer of $2\text{--}8\text{ }\mu m$ thickness is obtained. The anodic oxide film formed on Al in the bath of H_3PO_4 tends to be porous and provides good adherence for paints and dyes. Anodized articles are used as soap boxes, tiffin carriers, window frames, etc.

- **Phosphating:** The phosphate coatings are produced by chemical reaction of aqueous solution of phosphates of Fe, Mn and Zn in dilute H_3PO_4 solution, with the base metal as Fe, steel or Zn. Phosphating involves the following steps:

- (a) Dissolution of metal as metal ions.
- (b) Reaction of metal ions with the phosphate ions to form a metal phosphate.
- (c) Deposition of the metal phosphate on the surface of the metal.

Phosphating offers improved corrosion resistance and also imparts a good adhesion quality to the surface. It is a standard pre-treatment before painting of automotive bodies and other steel sheet fabrications such as refrigerators and washing machines.

3. **Organic coating:** These coatings are of materials that are applied to protect or beautify a surface. These include paints, varnishes, stains, industrial maintenance coatings; and they can be applied to stationary and/or mobile sources. When applied, the solvents in organic coatings can evaporate into the atmosphere and contribute to volatile organic compounds and airborne toxic emissions. Coating of metal surface with organic paints is the most widely used anticorrosion coating. Organic paint is a dispersion of one or more finely divided solids in a medium, which consists of non-volatile, film-forming materials like drying oils and resins in thinners. When a properly treated metal surface is painted, the thinner evaporates leaving behind a film-former and a pigment on the surface.
4. **Ceramic coatings:** For thin-film coatings, hard materials are suitable which include carbides, nitrides, borides and silicides of the Groups 14, 15 and 16 of the periodic table. These coatings are formed by introducing nitrogen, hydrocarbon or silicide during the sputtering process. As it is most energetically favorable, the ceramic compound forms at the surface of the substrate. The most common ceramic coatings available are TiN, CrN, TiCN and TiAlN.

Alloyed elements such as Al, V, Y, Cr, etc., improve oxidation resistance of ceramic coatings. Further, deposition of multilayers and superlattices improve properties of ceramic coatings. These are thin films formed by alternately depositing two different components to form layered structures. Multilayers become superlattices when the distance between different layers is less than 100 Å.

Concept Check

- What is metallic coating? Explain anodic metal coatings with various methods.
- What is galvanizing?
- Write a note on tinning.
- Write a note on anodizing of aluminium.
- Write a note on phosphating.
- Explain briefly ceramic coatings used for corrosion prevention.

3.24 Metal Finishing

Metal finishing involves modification of surface properties of metals by the deposition of layer of another metal/polymer or by the formation of an oxide film. Many industries include metal finishing in their manufacturing processes such as automotive, electronics, aerospace, hardware, appliances, tyres, jewelry, heavy equipment and telecommunications. Without this finishing, the durability of the products made from metals is low and lasts only a fraction of their lifespan owing to corrosion and wear. Sometimes, the finishes are also used for decorative sense depending upon the consumer's demands.

Metal finishing is also used to enhance electrical properties, form and shape components and enhance the bonding of adhesives or organic coatings. Overall, it alters the surface of metal products to enhance corrosion resistance, wear resistance, electrical conductivity, electrical resistance, reflectivity and appearance (e.g., brightness or color), torque tolerance, solderability, tarnish resistance, chemical resistance, ability to bond to rubber (e.g., vulcanizing) and hardness.

For metal finishing, a variety of materials and processes are used to clean, etch and plate metallic and non-metallic surfaces to create a structure that has the desired surface characteristics. The typical processes used in the industry are plating operations, which is categorized into electroplating and electroless plating; and surface treatments, which consist of chemical conversion, electrochemical conversion, case hardening, metallic coating and chemical coating.

Essentials of Metal Finishing

The fundamental principles governing metal finishing are (a) polarization, (b) decomposition voltage and (c) over potential.

Polarization

Polarization is an electrode phenomenon. The electrode potential of an electrode in a cell is determined by the Nernst equation

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

where M^{n+} is the concentration of the metal ion at equilibrium. When there is a passage of current, the metal ion concentration in the vicinity of the electrode surface decreases owing to the reduction of some of the metal ions to metal atoms.



As a result, change in the electrode potential is observed. However, the equilibrium is re-established as the ions from the bulk of the solution diffuse towards the electrode. The diffusion occurs because there exists a concentration gradient between the bulk of the solution and near the electrode surface. If the diffusion is slow, potential of the electrode changes. Thus, polarization is defined as a process where there is a variation of electrode potential due to inadequate supply of species from the bulk of the solution to the electrode. Polarized electrolytic cells lead to the use of a potential more negative than required in order to maintain a given current.

Electrode polarization depends on several factors:

1. Nature, that is, size, shape and the composition of the electrode.
2. Electrolyte concentration and its conductivity.
3. Temperature.
4. Products formed at the electrodes.
5. Rate of stirring of the electrolyte.
6. Large electrode surface, low concentrations and use of highly conducting solutions largely decrease the polarization effects.

Decomposition Potential (Voltage)

An electrolyte undergoes electrolysis on application of potential in an electrolytic cell. A potential at which an electrolyte decomposes and conducts electricity in an electrolytic solution is known as decomposition potential (voltage).

The decomposition voltage can be determined using an electrolytic cell. The cell consists of two platinum electrodes immersed in the electrolyte. The voltage applied to the electrodes A and B is varied by means of variable resistance D, and the current passing through the cell is measured using an ammeter (Figure 44). If a dilute solution of an acid or a base is taken in the cell, at low voltages no reaction is found to occur and there is a very slight increase in the current. On increasing the voltage to slightly above 1.7 V, a sudden evolution of H_2 and O_2 at the electrodes is noticed. This is accompanied by an abrupt increase in the current. The applied voltage of 1.7 V is the decomposition voltage for dilute acids and bases. Similarly, the electrolysis of salt solution occurs above a certain voltage. Hence, the decomposition voltage can be defined as the minimum external voltage that must be applied in order to bring about continuous electrolysis of an electrolyte.

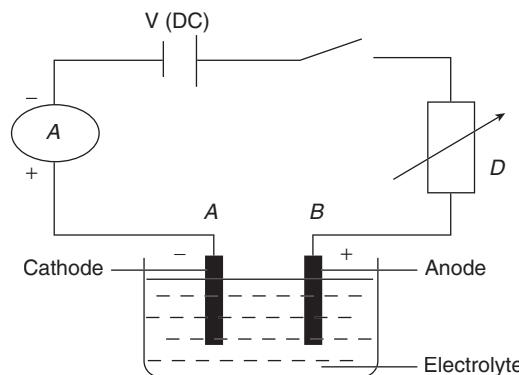


Figure 44 Measurement of decomposition voltage.

A typical plot of the current flowing between the electrodes against the applied voltage is shown in Figure 45. The decomposition voltage may be obtained by extrapolation of the curve as shown. There is a very slight increase in the current at low voltages. Beyond the decomposition voltage, electrolysis begins and thus there is an abrupt increase in the current. Laws of electrolysis are valid only in this region.

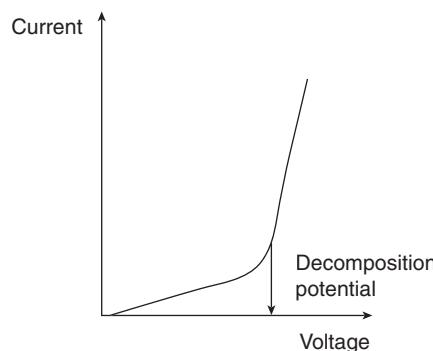
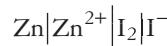


Figure 45 Plot of current flowing between electrodes and applied voltage.

The decomposition voltage of an electrolyte is of the same magnitude as the emf set up by the cell resulting from electrolysis. This is illustrated with the Zn–I₂ system. If a 1 M solution of ZnI₂ is electrolyzed, then zinc and iodine are liberated at the electrodes. For this electrolysis, the decomposition voltage is found to be around 1.30 V. The products formed accumulate on the electrodes the following cell is set up:



This exerts a back emf and offers resistance to the flow of current till the applied voltage overcomes the back emf. In other words, the magnitude of the back emf should be the same as that of E_D . The emf of the above cell is

$$E = E_R - E_L = E_{\text{I}_2} - E_{\text{Zn}} = 0.54 - (-0.76) = 1.3 \text{ V}$$

The cell emf is, therefore, equal to the decomposition voltage E_D which is experimentally found to be 1.3 V for Zn and I₂ cell. In general, E_D of an electrolyte may be equated to the emf of the cell developed due to the products of electrolysis.

$$E_D = E_{\text{back}} = E_{\text{cathode}} - E_{\text{anode}}$$

Overpotential

In general, for continuous electrolysis to take place, the applied voltage should be at least slightly more than the decomposition potential, E_D . However, in a few cases, even when the voltage E_D is reached, electrolysis will not occur and occasionally the applied voltage has to exceed the theoretical value by at least 1 V for the electrolysis to proceed. This is known as overvoltage or overpotential, and is represented by η . It is defined as the excess voltage that has to be applied above the theoretical decomposition potential to start the electrolysis. Mathematically, it is expressed as

$$\eta = \text{Experimental decomposition potential} - \text{Theoretical decomposition potential}$$

Therefore, the decomposition potential E_D for such systems where overpotential is observed is given as

$$E_D = E_{\text{cathode}} - E_{\text{anode}} + \eta$$

Overvoltage for a given electrolyte depends on several factors:

1. Nature and physical state of the metal employed as the electrodes.
2. Nature of the substance deposited.
3. Current density (current per unit area of the electrode surface).
4. Temperature.
5. Rate of stirring of the electrolyte.

The overvoltage of hydrogen on metals is important in electrolysis. Table 7 gives the hydrogen overvoltage of a few metals at a current density of 10 A/m².

Table 7 Hydrogen overvoltage (current density = 10 A/m²)

<i>Electrode</i>	η (V)
Platinum (black)	0.01
Platinum (smooth)	0.09
Nickel	0.33
Iron	0.40
Silver	0.44
Chromium	0.50
Lead	0.67
Mercury	4.04

Concept Check

- What is metal finishing? Write a note on technological importance of metal finishing.
- Explain the term electrode polarization. What are the factors that affect electrode polarization?

- What is decomposition potential? How is it determined? What is its significance in electroplating?
- What is overpotential? How does it affect the electrolysis in an electrolytic cell?

3.25 Electroplating Process

Electroplating is an electrochemical technique by which metal deposits on the substrate when current is passed through the plating bath. Usually there is an anode on which is made of the material to be deposited and cathode is the substrate which is to be coated. The electrochemistry involves the exchange of metal ions and their transfer to the substrate to be coated. The plating bath is usually a non-metallic (usually plastic) tank. This tank is filled with electrolyte containing the ionic form of the metal to be plated. The anode connected to the positive terminal is usually the metal to be plated (assuming that the metal will corrode in the electrolyte); whereas, the cathode connected to the negative terminal is the substrate to be coated. The power supply is well regulated to minimize ripples and deliver a steady predictable current, under varying loads found in plating tanks (Figure 46).

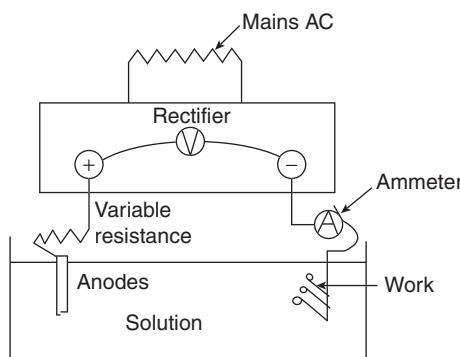
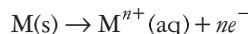


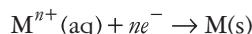
Figure 46 Electroplating process.

When the voltage is applied, positive metal ions from the electrolyte are attracted to the negatively charged cathode and deposit on the cathode. For replenishing the deposited metal ions, the metal from the anode is dissolved, goes into the solution and balances the ionic potential. Hence, plating is an oxidation-reduction reaction, where one material loses electrons (gets oxidized) and the other gains electrons (gets reduced). The oxidation occurs at the anode, and reduction occurs at the cathode.

In the case of materials such as gold, the anode is not sacrificial (i.e., gold does not dissolve easily). However, the anode is made out of material that does not dissolve in the electrolyte, such as titanium. The deposited gold comes out of the solution. The reactions involved in the electroplating process are as follows:
Anode: The metal to be electroplated to the surface is oxidized into cations which enter the plating solution.



Cathode: The cations in the plating solution migrate to the cathode, where they are reduced to metal and deposited on the surface of the metal being plated.



Plating Bath

The cell used in electroplating contains an electrolyte which is usually but not always an aqueous solution containing a reasonably high concentration of a metal ion which is to be electroplated on to the surface. This electrolyte is called by platers as the “bath”. It is practically always an aqueous solution containing a compound of the metal to be deposited (to be electroplated on the surface). The ingredients of a plating bath have one or more of the following functions:

1. Provide a source of the metal or metals being deposited.
2. Form complexes with ions of the deposition metal.
3. Provide conductivity and stabilize the solution against hydrolysis and other reactions.
4. Act as a buffer to stabilize the pH.
5. Modify other properties either of the solution or of the deposit for specific cases.
6. Aid in dissolution of the anode.

Purpose and Applications of Electroplating

Electroplating is frequently used for industrial purposes, either for decoration or to help components function more efficiently. It is a kind of metal finishing. The purposes of electroplating an article are for:

1. Improving appearance.
2. Increasing protection.
3. Special surface properties.
4. Engineering or mechanical properties.

The applications of electroplating are as follows:

1. Steel parts on automobiles are often plated with chrome to help them resist corrosion.
2. Steel and aluminum components in light fixtures are coated with nickel and either chromium or brass to enhance their appearance.
3. Steel bolts are coated with zinc and cadmium to help them last longer, and copper and brass connectors are often plated with silver to prevent tarnishing and increase conductivity.

Concept Check

- Explain briefly the electroplating process.
- Explain the significance of electroplating process.

3.26 Surface Preparation for Coating

The surface pretreatment through chemical and/or mechanical processes is important in the case of preparations for electroplating as well as painting. Before starting the plating process, any dirt, grease, oxides or other materials should be removed as these materials interfere with the metal plating process. Surface preparation involves the following steps:

1. **Degreasing:** This step involves removal of organic impurities (greases) as shown in Figure 47. Solvent degreasing is a cleaning process that uses direct application of solvents for the removal of oil, grease, shop dirt, loose chips and other contaminants. The solvent is sprayed, brushed or wiped on the surface of the material, or the material is immersed in the solvent. The characteristics of this process are as follows:

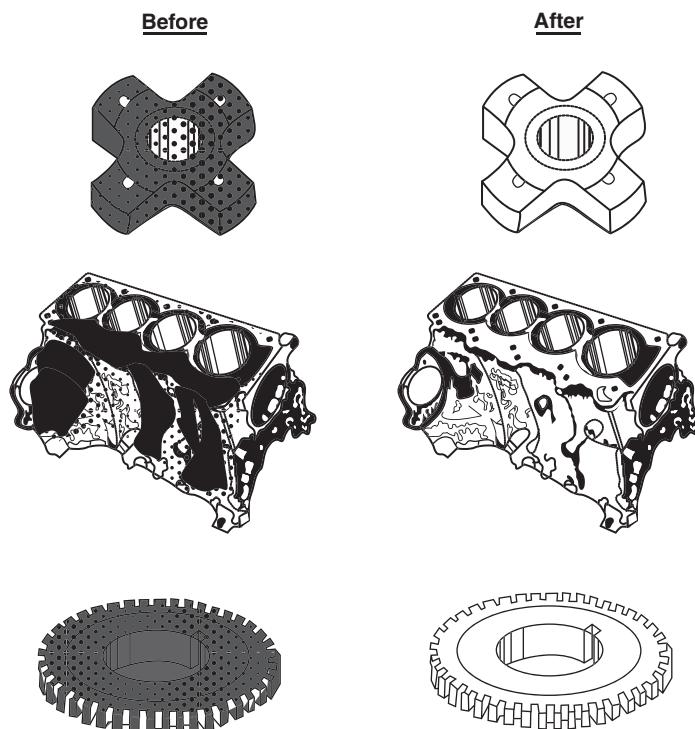


Figure 47 Degreasing step for surface preparation.

1. It removes oil, grease, shop dirt, loose chips and other contaminants.
2. The parts are dried at room or elevated temperatures.
3. It cleans virtually all metals and electrical or electronic assemblies.
4. It can accommodate materials of any size or shape.

Organic solvents such as trichloroethylene and methylene chloride are used to remove organic matter and grease on the surface. A very effective method is the vapor phase degreasing, wherein the vapors of the solvent are allowed to condense on the substrate surface. Trichloroethylene is the solvent of choice for removing varnish or paint films and resins; perchloroethylene is excellent for removing high-melt waxes. For cleaning PCBs and other electronic components, 1,1,1-trichloroethane is used.

Removal of these impurities is also effected by aqueous alkali treatment usually assisted by making the surface cathodic ($30\text{--}80 \text{ mA/cm}^2$) at $60\text{--}80^\circ\text{C}$. This increases the pH and catalyzes the hydrolysis of fats. At the same time, hydrogen liberated on the electrode removes the organic impurities.

2. **Descaling:** This step involves removal of scale and oxide films.
 - **Pickling:** After treatment with alkali, the excess alkali is removed by immersion in 10% sulphuric acid. This also removes any oxide scale or rust on the surface by pickling it in sulphuric acid making the surface anodic (100 mA/cm^2).
 - **Polishing:** Mechanical or electropolishing is given to get a polished surface. Mechanical polishing involves grinding using silicon carbide abrasion wheels. This is followed by sandblasting

and mechanical buffing to create a bright lustrous surface. Electropolishing involves the anodic dissolution of the metal.

- **Sandblasting:** In this method, very finely divided material is propelled at high speed to clean or etch a surface. For this, sand is commonly used, hence the name sandblasting.
- 3. **Rinsing and drying:** The object is finally rinsed with deionized water preferably in hot conditions and dried before it is subjected to electroplating.

Concept Check

- Explain various methods of surface preparation required for electroplating.
- Name two methods adopted for descaling step of surface preparation.

3.27 Electroplating of Chromium and Silver

Electroplating of Chromium

Hard chromium plating is applied as a fairly heavy coating for wear resistance, lubrication, oil retention and other wear purposes. Some examples include hydraulic cylinder rods, rollers, piston rings, mold surfaces, thread guides, gun bores, etc. Note that the “hard chrome” is in fact not harder than other chrome plating, it is called so because it is thick enough to be measured by a hardness test. Whereas thinner plating will break like an eggshell if a hardness test is conducted, so its hardness cannot be measured directly. Hard chrome plating is almost always applied to items that are made of steel, usually hardened steel. It is metallic in appearance, but not particularly reflective or decorative.

Decorative chrome plating or nickel–chrome plating always involves electroplating nickel onto the object before plating the chrome. It sometimes involves electroplating of copper on the object before the nickel. The nickel plating provides smoothness, much of the corrosion resistance and most of the reflectivity. However, the chrome plating is exceptionally thin, and measured in millionths of an inch rather than in thousandths. Table 8 shows the construction requirements of plating cells in hard and decorative chromium plating.

Electroplating of Silver

The electroplating on silver is an old process, but it has steadily evolved in response to changing customer needs, such as in the electronics industry. This continues to be the case even today, when environmental requirements and new potential applications in the photovoltaic (solar) market are evolving and driving these changes. Silver plating baths have been around for more than 100 years and were originally produced from alkaline cyanide electrolytes by dissolving silver cyanide in a solution of sodium cyanide. The silver plating formulations have now switched to “cleaner” baths based on silver potassium cyanide.

As the electronics industry emerged fully during the 1970s, the need for high-speed silver plating has become very apparent. High-cyanide bright silver mechanisms were used quite successfully for barrel plating applications. However, these baths had some limitations when used at high current densities on high-speed reel-to-reel lines, and selective spot lines in particular. Low-cyanide baths have a definite life and need to be replaced regularly. These baths have high production throughputs and build up on the amount of cyanide during their use (Table 9).

Table 8 Plating cell components in hard and decorative chromium plating

<i>Components</i>	<i>Hard Chromium</i>	<i>Decorative Chromium</i>
Anode	Lead with up to 7% Sn or Sb	Lead with up to 7% Sn or Sb
Cathode	Article to be plated	Article to be plated
Bath composition	H_2CrO_4 (250–300 g/l) and H_2SO_4 (2.5–3.0 g/l)	H_2CrO_4 (250–300 g/l) and H_2SO_4 (2.5–3.0 g/l)
Current density (mA/cm ²)	290–580	150–430
Temperature (°C)	45–60	45–60
Current efficiency (%)	17–20	10–15
Applications	Extensively used in industrial and engineering applications, such as hydraulic cylinder rods, rollers, piston rings, mold surfaces, thread guides, gun bores, etc.	Provides durable and good finish on automobiles, surgical instruments, etc.

Table 9 Operating parameters of low-cyanide high-speed silver plating

<i>Electroplating Silver Bath</i>	<i>Low Cyanide Bath</i>	
	<i>Optimum</i>	<i>Working Range</i>
Silver	65 g/l	50–80 g/l
Cyanide	0–20 g/l	0–20 g/l
pH	8.5	8–10
Current density	Phosphate up to 20 A/dm ²	Nitrate up to 80 A/dm ²
Plating rate	15 µm/min	Up to 50 µm/min
Temperature	65°C	40–70°C

Concept Check

- Explain chromium electroplating.
- Write a note on electroplating of silver.

3.28 Electroless Plating

Electroless plating also called autocatalytic plating is a chemical process used for depositing certain metals on a variety of materials including metal and plastics. In contrast to electrolytic plating, no external electrical current is required for the process. The electroless plating process is based on the catalytic reduction of metal ions on the surface of the substrate that is being plated.

In this plating, metal is deposited evenly along edges, inside holes and over irregularly shaped objects that are difficult to plate evenly with electroplating. Electroless plating is also used to deposit a conductive surface on a non-conductive object to improve its electroplating.

Autocatalytic platings are widely used for machine frames, base plates, fixtures, etc. They are also used in machine parts where metal-to-metal wear applications are required which cannot be achieved by using conventional oils and greases. Table 10 shows the difference between electroplating and electroless plating.

Table 10 Distinction between electroplating and electroless plating

Property	Electroplating	Electroless Plating
Source	Electrical energy	Autocatalytic reduction–oxidation reaction (no electrical energy is required)
Site of anodic reaction	Anodic reaction takes place at separate anode used in the electrolytic cell	Article to be plated
Site of cathodic reaction	Article to be plated	Catalytic surface of the article to be plated
Anode	Metal	Reducing agent in solution
Type of cathode used for plating	Plating is carried out on conductors only (metals)	Plating may be carried out on insulators (e.g., plastics) and semiconductors
Reactions	At anode: $M \rightarrow M^{n+} + ne^-$ At cathode: $M^{n+} + ne^- \rightarrow M$	At anode: Reducing agent → Oxidized product + ne^- At cathode: $M^{n+} + ne^- \rightarrow M$

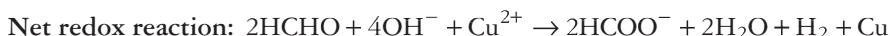
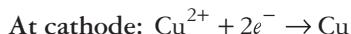
Electroless Copper Plating on Printed Circuit Board

There are two kinds of copper plating in the manufacture of printed circuit boards: electroless copper plating and acid copper electroplating. Acid copper electroplating plates copper only on a conductive surface via electrochemistry method whereby electrons are obtained from a DC power source to reduce metal ions to the metallic state. In electroless plating, the mechanism is similar but the source of electrons is a chemical reducing agent. Hence non-conductive surfaces may be metalized by employing electroless baths, since baths contain their own source of electrons. Electroplating baths cannot be used for non-conductive surfaces because the electrons cannot flow. The hole walls represent the dielectric portion of a circuit board, which are non-conductive. The exposed material may be made of phenolic resin, polyester or epoxy fiberglass. Therefore, electroless copper plating is needed to render the board conductive for subsequent through-hole electroplating.

The electroless plating bath of copper consists of the following components:

1. Copper sulphate as source for copper.
2. Formaldehyde as reducing agent.
3. Caustic–basic medium.
4. Chelating agents (amines, gluconates, glucoheptaonates, various EDTAs, and tartrates). The agents govern the plating rate and have a marked influence on the properties of the deposit and the bath stability.

As shown in the chemical reaction below, with the presence of palladium as a catalyst and under strongly basic medium, electrons are obtained from the reducing agent, formaldehyde, to reduce the cupric ions to metallic copper.



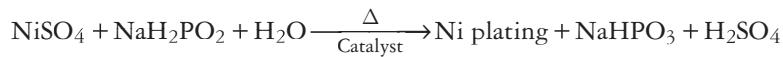
However, the reduction proceeds through a cuprous state. An excess of cuprous oxide formation will cause the reduction reaction to proceed out of control. To inhibit the formation of cuprous oxide, air is bubbled slowly through the electroless copper solution and small complexing agents are added to the solution.

In the manufacturing of printed circuit boards, electroless copper plating is utilized to metalize the entire board with a thin deposit of copper to render the board conductive for subsequent through-hole electroplating. The disadvantages of this electroless plating process are:

1. The chelating agent creates difficulties and interferes with wastewater treatment.
2. The reducing agent, formaldehyde, is a human health hazard.
3. The instability of the electroless copper bath creates difficulties in process control.

Electroless Nickel Plating Process

In autocatalytic platings, the metal ion is reduced to metal only on a specific surface, which must have a catalyst present before the reaction can begin. The electroless plating involving a nickel sulphate bath has the reaction as



The electroless nickel solution consists of the following components

1. Nickel chloride NiCl_2 (20 g/l) which is the source for nickel.
2. Sodium hypophosphite (20 g/l) which is the reducing agent.
3. Sodium acetate buffer (10 g/l), sodium succinate which are the complexing agent and exhaustant, respectively.
4. pH is maintained at about 4.5 and the temperature is about 93°C .

The electrode reactions are:



The H^+ ions are released in the above redox reaction, and decreases the pH of the medium. This affects the quality of the deposit. Therefore, addition of buffer is very essential to maintain the pH. Further, Ni^{2+} ions and sodium hypophosphite are consumed during the redox reaction, and hence it should be replenished periodically.

The advantages of this plating are as follows:

1. The bath possesses excellent throwing power, hence method is suitable for plating the objects having intricate shapes.
2. The deposits are free from pores, hence there is better corrosion resistance.
3. The plating gives harder surface, hence it gives good wear resistance.
4. Ni plating on Al enhances the solderability, also provides a non-magnetic underlay in magnetic components.

The applications of electroless nickel plating are that it is extensively used in electronic appliances, automotive fields, decorative finish on plastic items, hydraulic compressors, pressure vessels, pumps, etc.

Concept Check

- What is electroless plating? Explain the principle involved. Mention its advantages.
- What are the distinguishing features between electroplating and electroless plating?
- Describe the method of electroless plating of copper.
- Explain electroless plating of nickel.

Key Terms

Electrolytic conductance	Standard (normal) hydrogen electrode	Lead–acid battery
Strong and weak electrolytes	Calomel electrode	Nickel–cadmium cell
Specific conductance	Nernst equation	Lithium batteries
Equivalent conductance	Metal–metal ion electrode	Classical and modern batteries
Ionic conductance	Metal–insoluble salt electrode	Fuel cells
Transport (transference) number	Amalgam electrode	Dry corrosion
Electrochemical cells	Gas electrode	Wet corrosion
Electrode potential	Ion-selective electrode	Galvanic cell
Helmholtz electrical double layer	Glass electrode	Electrochemical theory
Oxidation and reduction potentials	Quinhydrone electrode	Crevice corrosion
Standard electrode potential	Liquid junction potential	Pitting corrosion
Electrochemical series	Batteries	Microbial corrosion
Galvanic cell	Primary and secondary cells	Polarization
Salt bridge	Reserve battery	Hydrogen overvoltage
Electromotive force (EMF)	Life cycle and shelf life	Protective coating
Reference electrodes	Dry cell	Ceramic coating
	Alkaline dry cell	Anodic metal coating
		Cladding

Galvanizing	Sacrificial anode	Decomposition potential
Cathodic protection	Anodizing	Electroless plating
Anodic protection	Phosphating	Pilling–Bedworth ratio

Objective-Type Questions

Multiple-Choice Questions

1. The conductivity of a strong electrolyte
 - a. decreases on dilution.
 - b. increases on dilution.
 - c. does not change much with dilution.
 - d. none of the above.
2. Conductance of a weak electrolyte
 - a. increases slowly with concentration.
 - b. increases sharply with concentration.
 - c. decreases slowly with concentration.
 - d. decreases sharply with concentration.
3. The amount of substance deposited at the electrode is directly proportional to
 - a. equivalent weight.
 - b. molecular weight.
 - c. atomic weight.
 - d. none of the above.
4. The electrode potential of hydrogen electrode has been assigned value
 - a. 1 V.
 - b. 10 V.
 - c. 100 V.
 - d. 0 V.
5. The cell in which electrical energy is converted into chemical energy is called
 - a. galvanic cell.
 - b. Daniel cell.
 - c. electrolytic cell.
 - d. electrochemical cell.
6. Which of the following is source of electrical energy in a galvanic cell?
 - a. Endergonic reaction ($\Delta G > 0$)
 - b. Exergonic reaction ($\Delta G < 0$)
 - c. Exothermic reaction ($\Delta H < 0$)
 - d. Endothermic reaction ($\Delta H > 0$)
7. Which of the following cell converts chemical energy of H_2 gas into electrical energy?
 - a. Fuel cell
 - b. Daniel cell
 - c. Electrolytic cell
 - d. Storage cell
8. The relation between ΔG^0 and E^0 is given by
 - a. $\Delta G^0 = nFE^0$
 - b. $\Delta G^0 = -nFE^0$
 - c. $\Delta G^0 = E^0/nF$
 - d. $\Delta G^0 = RT/nE^0$
9. Among Mg, Al, Zn and Fe, which will displace all the other three from their solutions?
 - a. Al
 - b. Zn
 - c. Mg
 - d. Fe
10. In a galvanic cell $E_{Cu^{2+}/Cu}^0 = 0.34\text{ V}$ and $E_{Zn^{2+}/Zn}^0 = -0.76\text{ V}$ is -0.76 V . What is E_{cell}^0 ?
 - a. -0.42 V
 - b. 0.42 V
 - c. -1.10 V
 - d. 1.10 V
11. Which of the following is not true for EMF of a battery?
 - a. It decreases with increase in temperature.
 - b. It increases with increase in value of reaction quotient (Q).
 - c. It increases with increase in difference in standard electrode potential of electrodes.
 - d. It increases with increase in conductivity of electrolyte.

12. Which of the following is a rechargeable cell?
 - a. Nickel–cadmium cell
 - b. Leclanche cell
 - c. H₂–O₂ fuel cell
 - d. Lead storage cell
13. Which of the following is not true for H₂–O₂ fuel cell?
 - a. Hydrogen gas is supplied at the anode.
 - b. Oxygen gas is supplied at the cathode.
 - c. Oxygen is reduced to hydroxyl ions at cathode.
 - d. Water is formed at the cathode.
14. Which of the following is not characteristic of lithium batteries?
 - a. It contains non-aqueous electrolyte.
 - b. It has high cell voltage.
 - c. It is operational over limited temperature range.
 - d. It has high energy density.
15. Iron corrodes faster in
 - a. hard water.
 - b. soft water.
 - c. demineralized water.
 - d. distilled water.
16. Pin holes on zinc-coated iron articles are less corrosive to iron than pin holes on tin-coated iron articles due to
 - a. high ratio of anodic to cathodic areas.
 - b. low reduction potential of tin.
 - c. low ratio of anodic to cathodic areas.
 - d. high rate of corrosion.
17. At low hydrogen overvoltage, rate of corrosion of metals
 - a. decreases.
 - b. increases.
 - c. increases initially and then decreases.
 - d. remains the same.
18. Caustic embrittlement in boilers is an example of
 - a. pitting corrosion.
 - b. waterline corrosion.
19. Which corrosion control technique is most suitable in case of buried iron pipelines?
 - a. Anodic metal coating
 - b. Anodic protection
 - c. Cathodic protection
 - d. Corrosion inhibitors
20. Ships sailing in ocean suffer from
 - a. stress corrosion.
 - b. grain-boundary corrosion.
 - c. pitting corrosion.
 - d. waterline corrosion.
21. Atmospheric corrosion is caused by
 - a. humidity in air.
 - b. frequency of rainfall.
 - c. presence of gases like SO₂.
 - d. presence of O₂ in air.
22. Galvanizing is a process of
 - a. coating tin on zinc.
 - b. coating iron on zinc.
 - c. coating zinc on iron.
 - d. none of the above.
23. Which of the following is an example for anodic coating?
 - a. Tinning
 - b. Galvanizing
 - c. Painting
 - d. Chromaluminizing
24. Which of the following metals protects itself by forming a passive layer of its own oxide?
 - a. Pt
 - b. Au
 - c. Fe
 - d. Al
25. Anodized coatings are generally produced on
 - a. non-ferrous metals.
 - b. ferrous metals.
 - c. alloys.
 - d. non-metals.

26. Which part(s) of corrosion cell undergoes corrosion?
a. Anodic part
b. Cathodic part
c. Both (a) and (b)
d. None of the above
27. During galvanic corrosion, the noblest metal acts as
a. anode.
b. cathode.
c. both (a) and (b).
d. corroding metal.
28. Presence of copper as impurity in zinc causes
a. waterline corrosion.
b. galvanic corrosion.
c. pitting corrosion.
d. crevice corrosion.
29. Cathodic protection corrosion control is most suitable for
a. bimetallic couple.
b. buried iron pipelines.
c. metallic articles completely immersed in water.
d. window grills.
30. Electrochemical corrosion is essentially due to
a. formation of anodic and cathodic areas.
b. electrical contact between anode and cathode for conduction of electrons.
c. electrolyte, usually provided by the presence of moisture.
d. all of the above.
31. Chromate coatings are
a. non-porous.
b. amorphous.
c. more resistant than phosphate coatings.
d. all of the above.
32. Which of the following metals are more corrosion resistant than expected from their position in the electrochemical series?
a. Mg
b. Co
- c. Al
d. Fe
33. Phosphate coatings can be produced by chemical reaction of a base metal with aqueous solution of
a. chromic acid and chromite.
b. phosphoric acid and phosphate.
c. sulphuric acid and sulphate.
d. Stannic acid and stannate.
34. In anodized aluminum, the corrosion protection is due to
a. passive oxide coating.
b. phosphate coating.
c. chromate coating.
d. organic coating.
35. Which of the following factor accounts for higher corrosion rate?
a. Large anodic area and small cathodic area.
b. Small anodic and large cathodic area.
c. High temperature.
d. High humidity.
36. Sacrificial anode method of protecting a metal is an example of
a. anodic protection.
b. cathodic protection.
c. metal coating.
d. organic coating.
37. Differential metal corrosion is an example of
a. galvanic corrosion.
b. crevice corrosion.
c. stress corrosion.
d. water line corrosion.
38. Anodized coatings have good resistance to corrosion because
a. they are thicker than neutral oxide films.
b. they are thinner than neutral oxide films.
c. both (a) and (b).
d. none of the above.

39. Polarization of anode results in
a. increase in the rate of corrosion.
b. decrease in the rate of corrosion.
c. increase in the rate of cathodic reaction.
d. increase in the rate of anodic reaction.
40. Pitting corrosion can be explained on the basis of
a. differential aeration.
b. size of anode and cathode.
c. localized corrosion.
d. All of the above.
41. Anodic protection can be applied to
a. all the metals.
b. metals which undergo active-passive transition.
c. more electropositive metals.
d. less electropositive metals.
42. The flux used in galvanizing is
a. NH_4Cl
b. BaCl_2
c. NaCl
d. palm oil
43. The main objective of metal finishing is to modify
a. chemical properties of materials.
b. surface properties of materials.
c. physical properties of materials.
d. electrical properties of materials.
44. Polarization of electrodes is reduced by
a. increasing the ionic concentration.
b. increasing the electrode surface area.
c. decreasing the ionic concentration.
d. both (c) and (d).
45. The process of electroplating involves
a. electrolysis.
b. discharge of metal ions at cathode.
c. redox reaction.
d. all of the above.
46. The electrode with lowest hydrogen overvoltage is
a. Zn
b. Ni
- c. Hg
d. Pt
47. For an electrolytic mixture containing Zn^{2+} , Cu^{2+} , Ag^+ , Au^{3+} the ion which is discharged first is
a. Zn^{2+}
b. Cu^{2+}
c. Ag^+
d. Au^{3+}
48. In electroplating, the article to be plated is subjected to pickling. This is to
a. remove grease.
b. increase the rate of plating.
c. remove oxide scale.
d. get a bright deposit.
49. Electroless plating can be used for plating of
a. metals.
b. semiconductors.
c. insulators.
d. all of the above.
50. In chromium plating, anode is
a. soluble chromium anodes.
b. insoluble anodes.
c. inert anodes.
d. both (b) and (c).
51. During plating, favorable condition for having brighter and smooth deposits is
a. low temperature.
b. low metal ion concentration.
c. both (a) and (b).
d. none of the above.
52. If metal A has high hydrogen over voltage compared to metal B, then
a. hydrogen evolution occurs very easily at metal A than at metal B.
b. hydrogen evolution occurs very easily at metal B than at metal A.
c. both metals A and B exhibit similar tendency to liberate hydrogen.
d. none of the above.
53. When the metal structure to be plated is irregular, the process employed is

- a. electroplating.
b. electroless plating.
c. electropolishing.
d. none of the above.
54. The practical decomposition potential is greater than the theoretical decomposition potential because of
a. ionization.
b. dissociation.
c. polarization of electrodes.
d. none of the above.
55. Which of the following is not essential in electroless plating?
a. Metal ions
b. Reducing agent
c. Substrate for plating
d. Electrical contacts
56. Formation of rust on iron is an example of
a. oxidation.
b. liquid metal corrosion.
c. electrochemical corrosion.
d. chemical corrosion.
57. Which of the following is not true for dry corrosion?
a. It takes place in dry conditions.
b. It takes place on heterogeneous metal surfaces only.
c. It takes place uniformly.
d. It takes place by direct chemical attack on metal.
58. The corrosion of buried pipelines in passing from one soil type to another is caused by
a. differential aeration.
b. stress.
c. erosion.
d. presence of microbes.
59. Welding is a better joining technique than using mechanical fasteners because it prevents
a. stress corrosion.
b. pitting corrosion.
c. galvanic corrosion.
d. crevice corrosion.
60. During rusting of iron
a. corrosion occurs at cathode.
b. corrosion product is deposited at anode.
c. corrosion occurs at anode and rust is deposited at cathode
d. corrosion occurs at anode and rust is deposited at anode
61. The protection of ship hull from marine corrosion by using magnesium sheets or blocks is an example of
a. cathodic protection.
b. impressed voltage protection.
c. sacrificial cathodic protection.
d. sacrificial anodic protection.
62. Which of the following types of corrosion does not occur due to formation of oxygen concentration cell?
a. Crevice corrosion
b. Waterline corrosion
c. Erosion corrosion
d. Soil corrosion
63. Wire mesh corrodes faster at the joints due to
a. galvanic corrosion.
b. stress corrosion.
c. crevice corrosion.
d. pitting corrosion.
64. Which among the following cannot be used for sacrificial anodic protection of steel?
a. Pb
b. Mg
c. Al
d. Zn
65. The process of coating iron and steel with powdered zinc and zinc oxide is called
a. Sherardizing
b. Metal cladding
c. Colorizing
d. Chromizing

66. Zinc can be electrodeposited from acidic solutions, even though the standard electrode potential of zinc is less than that of hydrogen because of
 a. polarization.
 b. decomposition potential.
 c. hydrogen overvoltage.
 d. none of the above.
67. Which of the following factors does not affect the polarization of electrodes?
 a. Stirring
 b. Nature of electrode
 c. Concentration and conductivity of electrolyte
 d. None of the above
68. In electrodeposition of copper from CuCN, NaCN is added to the electrolyte bath
 a. as brightener.
 b. as structure modifier.
 c. to reduce metal ion concentration.
 d. to enhance electrolyte concentration.
7. The EMF of a cell consisting of calomel electrode and standard hydrogen electrode is equal to the EMF of _____ electrode.
8. In the cell represented by $\text{Cd}|\text{Cd}^{2+}||\text{Cu}^{2+}|\text{Cu}$, oxidation occurs at the _____ electrode.
9. The cell representation $\text{Ag}|\text{Ag}^+(0.1\text{M})||\text{Ag}^+(1.0\text{M})|\text{Ag}$ constitutes a _____ cell.
10. The Nernst equation relates _____ to the concentration of reactants and products in half cells.
11. In electrolysis of an aqueous solution of silver nitrate between two silver electrodes, reduction of _____ takes place at cathode and oxidation of _____ occurs at anode.
12. In alkaline version of Leclanche cell, _____ is replaced by _____ or _____.
13. _____ batteries use oxygen directly from the atmosphere to produce electrochemical energy.
14. Nickel- _____ battery is a conventional battery where as nickel- _____ battery is a modern battery.
15. Iron undergoes severe corrosion in _____ water.
16. The rate of corrosion decreases with _____ in hydrogen overpotential.
17. _____ corrosion control technique is most suitable in case of buried iron pipelines.
18. Galvanizing is a process of coating _____ on iron.
19. _____ metal protects itself by forming a passive layer of its own oxide.
20. Phosphate coatings can be produced by chemical reaction of a base metal with aqueous solution of _____.
21. The metal with lowest hydrogen overvoltage is _____.

Fill in the Blanks

- The conductance of an electrolyte solution containing 1 g equiv. of solute placed between two parallel electrodes 1 cm apart is called _____ conductance.
 - According to _____ law, at infinite dilution, the cations and anions move independently of each other in the solution of electrolyte.
 - In a Daniel cell, the potential difference causes electrons to migrate from _____ through external circuit to _____.
 - In electrochemical series, tendency to gain electron _____ from top to bottom.
 - The liquid junction potential between two electrolytes in a cell is eliminated by use of a _____.
 - A platinum wire in contact with solution containing ferric and ferrous salt is an example of _____ electrode.
- Iron undergoes severe corrosion in _____ water.
 - The rate of corrosion decreases with _____ in hydrogen overpotential.
 - _____ corrosion control technique is most suitable in case of buried iron pipelines.
 - Galvanizing is a process of coating _____ on iron.
 - _____ metal protects itself by forming a passive layer of its own oxide.
 - Phosphate coatings can be produced by chemical reaction of a base metal with aqueous solution of _____.
 - The metal with lowest hydrogen overvoltage is _____.

22. Insulators can be plated with metal by _____ technique.
23. During electrolytic plating process, reduction of metal ions occur at _____.
24. In chromium plating, anode acts as _____.
25. In an electrochemical cell formed by two metals, corrosion takes place at the _____.
26. The use of copper pipes in conjunction with iron pipes in water distribution system leads to _____.
27. A pure metal rod half-immersed vertically in water starts corroding at the bottom due to _____.
28. During galvanic corrosion, the more noble metal acts as _____.
29. When the ratio of anodic to cathodic area increases, the rate of corrosion _____.
30. _____ is the property by which a metal or an alloy develops corrosion resistance due to formation of highly protective but thin film on the surface of the metal.
31. Presence of suspended particles in atmosphere _____ the rate of corrosion.
32. _____ corrosion is also known as galvanic corrosion.
33. Inhibitors which readily vaporize and form a protective layer over the metal are called _____.
34. Nuts and bolts should be made of same material to prevent _____ corrosion.
35. Chemical cleaning of the surface to be coated for removal of scales is called _____.
36. The protection of base metal sheet against corrosion by sandwiching it between thin sheets of corrosion resistant material is known as _____.
37. Chromizing of low carbon steel is carried out by heating it with a mixture of _____ and _____.
38. _____ coating is formed on base metal by combined action of sodium chromate and dilute sulphuric acid.
39. The minimum voltage that must be applied to bring about continuous electrolysis of an electrolyte is called _____.
40. Concentration polarization can be eliminated by _____ of the solution.
41. Electroless plating of copper is used in making _____.
42. In electroplating, the driving force is _____ and in electroless plating it is _____.

Review Questions

Short-Answer Questions

1. Distinguish between metallic and electrolytic conductors.
2. Explain why electrolytic conductance:
 - a. increases with increase in temperature.
 - b. decreases with dilution of solution.
3. What is specific conductance? How specific conductance measured and what is its unit?
4. Distinguish between equivalent and molar conductivities.
5. What is the effect of dilution on:
 - a. specific conductance;
 - b. equivalent conductance of weak electrolytes;
 - c. equivalent conductance of strong electrolytes.
6. State and explain Kohlrausch's law of independent migration of ions.

7. Explain why the ionic conductance of the cation of alkali chloride increases with atomic weight from lithium to cesium.
8. What is standard electrode potential?
9. What is EMF of a cell? How is it determined?
10. Define oxidation and reduction potential and explain why reduction potential is always taken for calculating voltage of cell.
11. What is a galvanic cell? Distinguish between a half cell and galvanic cell.
12. What is a salt bridge? Why is it used in the construction of a Daniel cell?
13. With the example of Daniel cell, write the following:
 - a. reactions occurring at the electrodes
 - b. electrical charges at the electrodes.
14. What are reference electrodes? Mention the limitations of primary reference electrode and advantages of secondary reference electrodes.
15. What are electrochemical cells? Distinguish primary cells from secondary cells with examples.
16. Why do electrochemical cells stop working after sometime?
17. Why is electrode potential of zinc assigned a negative value and that of copper assigned a positive value?
18. How is single electrode potential determined using standard hydrogen electrode?
19. Why is calomel electrode called a secondary reference electrode?
20. What are ion selective electrode? Illustrate their principle.
21. List different kinds of ion selective electrodes. Explain the use of ion selective electrode in determination of CO_2 in blood sample.
22. Write the electrode reactions and calculate the EMF of the following cell at 298 K given $E_{\text{cell}}^0 = 1.3 \text{ V}$.

$$\text{Cu(s)} | \text{Cu}^{2+}(0.01\text{M}) || \text{Ag}^+(0.01\text{M}) | \text{Ag(s)}$$
23. A cell consists of following electrodes:
 - (a) copper rod dipped in copper nitrate solution (1 M) and (b) silver rod dipped in silver nitrate solution (1 M). Give the following:
 - a. cell notation to represent the cell;
 - b. half cell and net cell reaction;
 - c. direction of spontaneous reaction;
 - d. direction of flow of electrons in external circuit.
24. Write down the reaction taking place at the separate electrodes and in the complete reversible cell given by:

$$\text{Pt, H}_2(\text{g}) | \text{HCl(aq)} | \text{KCl(aq)} | \text{AgCl(s)} | \text{Ag}$$
25. How does electrochemical series predict the feasibility of a reaction?
26. Explain why:
 - a. Nickel spatula cannot be used to stir copper sulphate solution.
 - b. Blue color of copper sulphate fades when electrolyzed using platinum electrode.
27. Write the Nernst equation for the following electrode reaction, giving significance of terms:

$$\text{M}^{n+}(\text{aq}) + ne^- \rightarrow \text{M(s)}$$
28. Write the cell reaction, if the Nernst equation is given by

$$E_{\text{cell}} = E^0 - \frac{RT}{2F} \ln \frac{[\text{Pb}^{2+}]}{[\text{H}^+]^2}$$
29. Write the Nernst equation for the following cell:

$$\text{Zn} || \text{Zn}^{2+}(0.01\text{M}) || \text{H}^+(0.1\text{M}) | \text{H}_2, \text{Pt}$$
30. Give reasons:
 - a. EMF of a cell is always positive.

- b. Reactivity of metal varies inversely with its electrode potential.
31. Discuss any three important characteristics of a battery.
32. What are the special properties of lithium that make it advantageous to use as an electrode material? Write the electrode reactions that occur in the Li–MnO₂ cell.
33. Why does dry cell become dead after sometime even if it has not been used?
34. What are reserve batteries? Give examples.
35. Give example of an alkaline storage battery, along with half cell and net cell reactions.
36. A lead storage cell can act both as galvanic cell and electrolytic cell. Explain.
37. Explain the following:
- The EMF of a lead storage battery is dependent on concentration of sulphuric acid.
 - In primary alkaline cells, the electrolyte KOH is invariant.
38. Give the half cell and net cell reactions in the following batteries:
- nickel–cadmium cell;
 - nickel–metal hydride battery;
 - lithium–manganese dioxide cell.
39. What is a fuel cell? How does a fuel cell differ from a conventional cell?
40. How are fuel cells classified on the basis of: (a) temperature range and (b) type of electrolyte.
41. Write a note on hydrogen oxygen fuel cell.
42. Explain dry corrosion with an example.
43. What is meant by wet corrosion?
44. Explain corrosion of steel screws in contact with copper plumbing.
45. What do you mean by differential aeration corrosion? Give example.
46. What is pitting corrosion?
47. Explain waterline corrosion with an example.
48. Explain the mechanism of crevice corrosion.
49. Write a note on microbial corrosion.
50. What is soil corrosion?
51. Explain the role of pH on the rate of corrosion.
52. Explain the effect of relative sizes of anode and cathode on the corrosion rate.
53. Explain sacrificial anode method of corrosion control.
54. What are anodic corrosion inhibitors?
55. Give few examples for cathodic corrosion inhibitors
56. Explain hot dipping method of anodic coating.
57. Mention few examples for organic and ceramic coatings.
58. What is meant by decomposition potential?
59. Write short notes on (a) pickling and (b) polishing.
60. What is electroless plating?
61. Distinguish between electroplating and electroless plating.
62. Write the reactions involved in the electroless plating of copper.
63. The oxide film formed by alkali and alkaline earth metals develops cracks and pores leading to excessive corrosion, whereas oxide film formed by Al, Cr and W is protective in nature. Explain.
64. What are the conditions necessary for electrochemical corrosion to take place?
65. Give reasons for formation of cathodic and anodic regions on the surface of the metal.

66. The nature of oxide film decides the rate of corrosion. Explain.
67. Give brief description of galvanic corrosion.
68. If a drop of an electrolyte is placed on iron surface, rusting occurs in the central region beneath the drop. Explain.
69. What is intergranular corrosion?
70. Why is galvanic series preferred to electrochemical series for predicting corrosion of metals?
71. What do you understand by passivity? What is its significance?
72. Explain why:
 - a. Impure metals corrode faster than pure metals.
 - b. Corrosion is more rapid if area of cathode is larger than the anode.
73. Copper rivets can be used on steel sheets but steel rivets cannot be used on copper sheets. Explain.
74. Account for the following:
 - a. Rusting of iron nail is faster in saline solution than in water.
 - b. Part of the nail inside the wood undergoes corrosion easily.
75. What is meant by stress corrosion?
76. Why does brass develop fissures and cracks in presence of atmosphere containing traces of ammonia?
77. What is the type of corrosion that may occur in following cases?
 - a. Riveted joints
 - b. Iron tank for strong water
 - c. Steel pipe connected to copper plumbing
 - d. Buried pipelines
 - e. Caustic embrittlement of steel
78. Explain why:
 - a. Plastic washers are preferred over metallic washers.
66. Chromium is used as an alloying metal for iron and steel.
79. What is the method of anodic protection for control of corrosion?
80. What is cathodic protection? How is it achieved by use of sacrificial anode?
81. What is impressed current cathodic protection?
82. What are protective coatings? How are they classified?
83. Iron does not rust if the zinc coating is broken in galvanized iron pipe but rusting occurs if tin coating covering iron is broken. Explain.
84. Acidic foods should not be stored in galvanized containers. Explain
85. Why should nickel-plated steel be free from pores and pin holes?
86. What are chemical or surface conversion coatings?
87. Explain the terms: (a) Colorizing and (b) chromizing.
88. What is metal finishing? Enumerate five objectives of metal finishing.
89. Explain the term polarization? What are the factors affecting polarization?
90. Explain the term overvoltage? What are the factors affecting overvoltage?
91. What is the principle involved in electroplating process?
92. What are the advantages of electroless plating over electroplating?
93. What are the reactions involved in electroless plating of nickel?
94. Explain why chromium anodes are not used in electroplating.

95. Explain why chromium coatings are given copper or nickel undercoats.
96. Explain the methods employed to clean the surface of metal, to be electroplated.
97. Explain how cathodic polarization affects the rate of corrosion.
98. Explain what type of corrosion occurs when
 - a. Screw and washer are made of different metals.
 - b. Presence of NaOH in mild steel boiler under stress.
99. Discuss the electroplating of gold and mention its application.
100. Discuss electroless plating of copper and its application to printed circuit boards.
101. What is electroplating? Give the technological importance of metal finishing.
102. Write down the equation for the hydrogen evolution in an electrochemical corrosion reaction.
103. Explain how nature of corroding environment influences the rate of corrosion.
104. Explain how heterogeneity of metal increases the rate of corrosion.
105. What is sherardizing? Explain and discuss its applications.
106. Differentiate between dry corrosion and wet corrosion.
107. Describe how electrochemical properties are used in protecting submerged metals from being corroded.
108. Justify the statement by giving suitable examples “Design and material selection help to control metallic corrosion”.
109. Explain why stainless steel is resistant to atmospheric conversion.
110. Explain why iron in contact with copper corrodes more readily than in contact with lead.
111. Explain sandblasting method of surface preparation.
112. Distinguish between anodizing and electroplating.
113. What is anodizing? Why is anodizing best suited to aluminium?
114. How are metals protected from corrosion by anodic coatings?
115. How does zinc coated on iron prevents corrosion?
116. What are the criteria for a good electrolyte chosen for electroplating?
117. Compare sherardizing and chromizing.
118. Distinguish between galvanizing and sherardizing.
119. What are electrochemical series? How are they useful in determining the rate of corrosion?
120. What is the significance of Pilling–Bedworth ratio. What happens if it is (a) less than 1, (b) greater than 1 and (c) equal to 1?

Long-Answer Questions

1. What are the changes that occur when direct current is passed through an electrolyte solution? What are the factors that affect the conductivity of electrolytes?
2. Explain the terms cell potential (EMF of cell) and single electrode potential and describe the method for determination of electrode potential.
3. Show how chemical energy is converted into electrical energy in a galvanic cell, using the example of a Daniel cell. Also

- explain the terms cathode, anode, half cell reaction with respect to galvanic cell.
4. Write notes on (a) electrochemical conventions and (b) functions of a salt bridge.
 5. Derive Nernst equation for the potential of a single electrode from thermodynamic principle.
 6. What is a primary references electrode? Describe the working and construction of hydrogen electrode.
 7. Explain the construction and working of the calomel electrode. Mention its advantages.
 8. Explain the construction of Ag/AgCl electrode. Give the half cell reaction.
 9. What are 2°ary references electrodes? Give the construction, cell reaction and electrode reaction of:
 - a. Calomel electrode;
 - b. silver–silver chloride electrode.
 10. a. What are ion selective electrodes? What are the types of membranes used in ion selective electrodes?
b. Explain the method of determining concentration of metal ions using ion selective electrodes.
 11. a. Describe the principle and construction of a glass electrode.
b. Explain the method of determining the pH of a given solution using glass electrode.
 12. Explain the working of quinhydrone electrode for determination of pH of a solution, what are its advantages and disadvantages over the glass electrode?
 13. Explain the principles of a membrane electrode. Mention the different types of membranes available.
 14. Construct the cell for the following cell reactions:
- $\text{Fe} + \text{CuSO}_4 \rightarrow \text{FeSO}_4 + \text{Cu}$
- $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$
- $\text{Fe} + \text{SnCl}_2 \rightarrow \text{FeCl}_2 + \text{Sn}$
15. What is an electrochemical series? Discuss its important applications.
 16. Represent the cell formed by the coupling of two copper electrodes immersed in cupric sulphate solutions. Concentration of cupric ions in one electrode system is 100 times more concentrated than the other. Write the cell reaction and calculate the potential at 300 K.
 17. Explain the principle components in a battery and their characteristics.
 18. Describe the following with respect to a battery: (a) voltage, (b) current, (c) capacity, (d) energy density and efficiency, (e) life cycle and shelf life.
 19. Describe the working of a dry cell using the example of Leclanche cell. How does alkaline battery differ from Leclanche cell?
 20. How are batteries classified? What are the factors that affect the EMF of a battery?
 21. Describe the construction and working of lead storage battery. Explain the process of recharging in the battery.
 22. Explain the construction and working of nickel–cadmium battery along with relevant reactions taking place. What are its advantages and applications?
 23. Describe the construction, working, cell reaction and uses of nickel – metal hydride battery.
 24. Discuss on capacity and shelf life a battery. Explain the construction and working of $\text{Li}-\text{MnO}_2$ cell.
 25. Explain the construction, working and application of lead-acid battery along with reactions involved during discharging and charging.

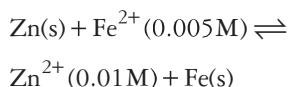
26. What are fuel cells? How do they differ from conventional galvanic cells? How are they classified?
27. Explain the construction and working of hydrogen–oxygen fuel cells. Give the half cell reaction and advantages of these cells.
28. What is meant by corrosion? Explain the electrochemical theory of corrosion.
29. Explain differential aeration corrosion, waterline corrosion and pitting corrosion.
30. Write an informative note on stress corrosion. Explain caustic embrittlement in boilers.
31. Explain how the following primary factors affect the rate of corrosion:
 - a. Nature of the metal
 - b. Hydrogen overvoltage
 - c. Tendency to form protective film
32. Explain how the following secondary factors affect the rate of corrosion: (a) pH, (b) temperature, (c) anodic to cathodic area effect and (d) polarization.
33. Explain anodizing of aluminium and give its applications.
34. Write a note on anodic metal coating. Explain galvanization.
35. Write a note on tinning and phosphating.
36. Explain cathodic protection techniques of corrosion control.
37. How do you control corrosion by anodic protection technique?
38. Explain corrosion inhibitor method of corrosion control.
39. What are the types of protective coatings? How do protective coatings help corrosion prevention.
40. Differentiate the following with suitable examples,
 - a. Galvanic series and electrochemical series
 - b. Pitting corrosion and stress corrosion
41. What type of corrosion occurs in the following cases? Mention corrosion control methods.
 - a. Bolt joints and rivets.
 - b. Buried iron pipelines.
 - c. Metallic articles completely immersed in water.
 - d. Window grills
42. Explain the term electrode polarization. What are the factors affecting it?
43. What is decomposition potential? How is it determined experimentally?
44. In a Haring–Blum cell if the distances C_1 and C_2 are the two cathodes from the anode are different show that throwing power is 100% if the weights of the metal deposited w_1 and w_2 respectively on the two cathodes is the same.
45. Explain the methods of pretreatment of the electrode surface for plating.
46. What is electroless plating? Explain the principle involved. Mention its advantages.
47. Describe the method of electroless plating of nickel.
48. What do you understand by dry and wet corrosion? State their distinguishing features.
49. Discuss the mechanism of dry corrosion. What are its three main types?
50. Explain the rusting of iron on the basis of electrochemical theory of corrosion. Discuss the mechanism of hydrogen evolution and oxygen absorption.
51. What is stress corrosion? Explain its role in season cracking and caustic embrittlement of steel.
52. Describe the properties of metal that affect the rate of corrosion.
53. Discuss the importance of design and material selection in controlling corrosion.

54. What is cathodic protection for controlling corrosion? Explain the two methods by which cathodic protection is achieved.
55. What are corrosion inhibitors? Briefly describe three types of corrosion inhibitors and their functions with examples.
56. What are metallic coatings? Write notes on following methods of their application:
 - a. Hot dipping
 - b. Metal cladding
 - c. Metal spraying
 - d. Cementation
57. What are the two types of metallic coatings? Describe briefly the process of galvanizing and tinning.
58. What are chemical conversion coatings? Give brief description of the following:
 - a. phosphate coating
 - b. oxide coating
 - c. chromate coating
59. What are organic coatings? Briefly describe various components of paint and their functions.
60. What are the various components involved in the process of electroplating? Discuss the process and mechanism of electroplating.
61. Give brief description of process and reactions involved in the electroplating of (a) chromium and (b) gold.
62. Describe the steps involved in pretreatment of surface and process of electroless plating of copper.
63. Explain the following terms and their significance in electrolysis: (a) polarization and (b) decomposition potential.
64. What is metallic corrosion? Explain the electrochemical theory of corrosion taking iron as an example.
65. What are the main objectives of metal finishing? Explain the electroplating of nickel.
66. What are the types of protective coatings? How do they help in controlling corrosion?
67. What are the main objectives of metal finishing? Explain the electroplating of nickel.
68. Explain the following factors influencing the nature of deposit: (a) complexing agents, (b) brighteners, (c) levelers and (d) wetting agents.
69. Define polarization, decomposition potential and overvoltage. Mention their significance with reference to electrode position and factors influencing them.
70. How do the following affect the nature of electroplating: (a) current density, (b) temperature, (c) pH and (d) organic additives.
71. What is oxidation corrosion and how does it take place? Describe the mechanism of oxidation corrosion.
72. Explain the process of wet corrosion by evolution of hydrogen and absorption of oxygen.
73. Give an account of any eight factors that influence the rates of corrosion.
74. Explain how corrosion control can be brought about by the following methods: (a) modifying the environment and (b) cathodic protection.
75. Justify the statement by giving suitable examples "Electrochemical series gives a basis for the prediction of the process of corrosion".
76. Differentiate the following with suitable examples,
 - a. Galvanic series and electrochemical series
 - b. Pitting corrosion and stress corrosion.
77. Explain impressed current method of corrosion control with a neat diagram.

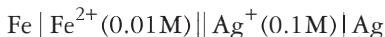
78. Discuss the following methods used for surface cleaning of articles and give their significance.
- Solvent cleaning
 - Pickling
 - Sand blasting.
79. What are the main objectives of electroplating? Give an account of the method used in electroplating of nickel on steel.
80. Write short note on the following:
- Concentration cell corrosion with examples.
 - Conditions for wet corrosion to occur.

Numerical Problems

1. Construct the cell and calculate the EMF for the reaction:

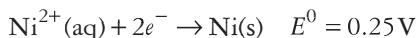


2. For the cell:



write the cell reaction and calculate the EMF of the cell at 298 K, if standard electrode potentials of Fe and Ag electrodes are -0.44 V and 0.8 V , respectively.

3. Calculate the EMF of the cell from the following data



$$[\text{Ni}^{2+}] = 1 \times 10^{-4}\text{ M} \text{ and } [\text{Cr}^{3+}] = 2 \times 10^{-3}\text{ M}.$$

4. What voltage will be generated by cell constituted by iron rod immersed in 0.1 M FeSO_4 and manganese rod dipped in 0.01 M MnSO_4 solution at 25°C . Given $E_{\text{Fe}}^0 = -0.44\text{ V}$ and $E_{\text{Mn}}^0 = -1.18\text{ V}$.

5. The EMF of the cell $\text{Mg} | \text{Mg}^{2+}(0.01\text{M}) | \text{Cu}^{2+}(x\text{M}) | \text{Cu}$ is measured to be 2.78 V at 298 K . Standard electrode potential of magnesium electrode is -2.371 V . Calculate the electrode potential of copper electrode and concentration of copper ions ($E_{\text{cell}}^0 = 2.711\text{ V}$).

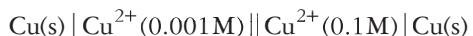
6. The EMF of the cell represented as



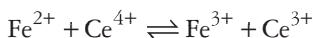
is 0.535 V at 298 K and increases with temperature by $1.45 \times 10^{-4}\text{ V/K}$. Write the electrode and overall cell reactions and calculate the enthalpy of the reaction taking place in the cell.

7. Find the potential of a Daniel cell containing 100 l each of 1.0 M Cu^{2+} M ion and 1 M Zn^{2+} ion after passage of 0.1×10^6 coulombs of charge ($E_{\text{cell}}^0 = 1.1\text{ V}$).

8. Calculate the EMF of following concentration cell at 298 K



9. Calculate the equilibrium constant for the reaction at 298 K



Given that $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.68\text{ V}$ and $E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 = 1.44\text{ V}$.

10. Calculate the EMF of a Cd–Cu cell in which Cd is in contact with 0.002 M CdSO_4 and copper is in contact with 0.02 M CuSO_4 solution. The standard EMF of the cell is 0.74 V at 298 K .

11. The E^0 values of Li^+/Li , Zn^{2+}/Zn , Cu^{2+}/Cu and Ag^+/Ag are -3.0 V , -0.77 V , $+0.33\text{ V}$ and $+0.80\text{ V}$, respectively. Which combination of electrodes would you use to con-

- struct a cell of highest potential, if ionic concentrations are 1.0 M, 0.1 M, 0.001 M, 0.01 M, respectively.
12. Calculate the equilibrium constant at 25°C for the cell reaction:
- $$\text{Ni(s)}|\text{Ni}^{2+}(\text{aq})||\text{Ag}^+(\text{aq})|\text{Ag(s)}$$
- Given that $E_{\text{Ni}}^0 = -0.25 \text{ V}$ and $E_{\text{Ag}}^0 = 0.80 \text{ V}$.
13. Calculate the EMF of the cell $\text{Fe}|\text{Fe}^{2+}(0.01\text{M})||\text{Ag}^+(0.1\text{M})|\text{Ag}$ at 298 K if standard electrode potentials of Fe and Ag electrodes are -0.42 V and 0.68 V , respectively.
14. Calculate the potential of Ag-Zn cell at 298 K if the concentration of Ag^+ and Zn^{2+} are $5.2 \times 10^{-6} \text{ M}$ and $1.3 \times 10^{-3} \text{ M}$, respectively. E^0 of the cell at 298 K is 1.5 V . Calculate the change in free energy ΔG for the reduction of 1 mol of Ag^+ (1 Faraday = 96.5 kJ/V-mol.).
15. Calculate the potential of Daniel cell at 25°C given that the electrode potentials of Cu and Zn are 0.34 V and -0.76 V , respectively.
16. Write the electrode reactions and calculate the EMF of the following cell at 298 K. Given that $E_{\text{Cu}}^0 = 1.3 \text{ V}$.
- $$\text{Cu(s)}|\text{Cu}^{2+}(0.01\text{M})||\text{Ag}^+(0.1\text{M})|\text{Ag(s)}$$
17. Calculate the standard electrode potential of Cu^{2+}/Cu if its electrode potential at 25°C is 0.296 V when $[\text{Cu}^{2+}]$ is 0.015 M .
18. Calculate the cell potential for the cell containing 0.10 M Ag^+ and 4.0 M Cu^{2+} at 298 K. Given that $E_{\text{Ag}^+/\text{Ag}}^0 = 0.80 \text{ V}$ and $E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34 \text{ V}$.
19. Calculate the EMF of the following cell at 25°C:
- $$\text{Ni}|\text{Ni}^{2+}(1\text{M})||\text{Pb}^{2+}(1\text{M})|\text{Pb}$$
- Given that standard electrode potentials of Ni and Pb are -0.24 V and -0.13 V , respectively, at 25°C.

Answers

Multiple-Choice Questions

- | | | |
|---------|---------|---------|
| 1. (c) | 13. (d) | 25. (a) |
| 2. (b) | 14. (c) | 26. (a) |
| 3. (a) | 15. (a) | 27. (b) |
| 4. (d) | 16. (a) | 28. (b) |
| 5. (c) | 17. (b) | 29. (d) |
| 6. (b) | 18. (c) | 30. (d) |
| 7. (a) | 19. (c) | 31. (d) |
| 8. (b) | 20. (d) | 32. (c) |
| 9. (c) | 21. (a) | 33. (b) |
| 10. (d) | 22. (c) | 34. (a) |
| 11. (b) | 23. (b) | 35. (b) |
| 12. (a) | 24. (d) | 36. (b) |

- | | | |
|---------|---------|---------|
| 37. (a) | 48. (c) | 59. (d) |
| 38. (a) | 49. (d) | 60. (c) |
| 39. (b) | 50. (d) | 61. (d) |
| 40. (d) | 51. (b) | 62. (c) |
| 41. (b) | 52. (b) | 63. (b) |
| 42. (a) | 53. (b) | 64. (a) |
| 43. (b) | 54. (c) | 65. (a) |
| 44. (d) | 55. (d) | 66. (c) |
| 45. (d) | 56. (c) | 67. (d) |
| 46. (d) | 57. (b) | 68. (c) |
| 47. (d) | 58. (a) | |

Fill in the Blanks

- | | | |
|--|-----------------------------------|---|
| 1. equivalent | 15. hard water | 29. decreases |
| 2. Kohlrausch's | 16. decrease | 30. Passivity |
| 3. zinc, copper | 17. Cathodic protection | 31. increases |
| 4. increases | 18. zinc | 32. Differential metal |
| 5. salt bridge | 19. Aluminium | 33. vapor phase inhibitors |
| 6. oxidation-reduction | 20. phosphoric acid and phosphate | 34. galvanic |
| 7. calomel | 21. platinum | 35. pickling |
| 8. cadmium | 22. electroless plating | 36. metal cladding |
| 9. concentration | 23. cathode | 37. chromium, alumina |
| 10. electrode potential | 24. anode | 38. Chromate |
| 11. silver, silver | 25. anode | 39. decomposition potential |
| 12. NH_4Cl , KOH, NaOH | 26. galvanic corrosion | 40. stirring |
| 13. Metal-air (zinc-air) | 27. differential aeration | 41. printing circuit boards |
| 14. cadmium, metal hydride | 28. cathode | 42. current; autocatalytic redox reaction |

Numerical Problems

- $\text{Zn}|\text{Zn}^{2+}(0.01)\parallel\text{Fe}^{2+}(0.005)|\text{Fe}; 0.231 \text{ V}$
 - at anode $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$
 - at cathode $\text{Ag}^+ + e^- \rightarrow \text{Ag}$
 - $\text{Fe} + 2\text{Ag}^+ \rightarrow \text{Fe}^{2+} + 2\text{Ag}$
- 1.24 V
3. 0.925 V
 4. 0.7695 V
 5. $0.34 \text{ V}; 0.234 \times 10^3 \text{ M}$

6. at anode $\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$
- at cathode $\text{Hg}^+ + e^- \rightarrow \text{Hg}$
- $\underline{\text{Pb} + 2\text{Hg}^+ \rightarrow \text{Pb}^{2+} + 2\text{Hg}}$
- 8236.275 J
7. 1.10 V
8. 5.076
9. 7.079×10^{12}
10. 0.7695 V
11. Li^+/Li and Ag^+/Ag
12. 3.388×10^{35}
13. 1.10 V
14. 1.27 V; 122555 J/mol
15. 1.10 V
16. 1.182 V
17. 0.379 V
18. 0.3832 V
19. 0.38 V

4

Stereochemistry, Reaction Mechanism and Synthesis of Drug Molecules

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Phenomenon of stereoisomerism and classification of stereoisomers into configurational and conformational isomers.
- Concept of chirality and various elements of symmetry.
- Optical activity and methods for its measurement.
- Characteristics of enantiomers, diastereomers, *meso* compounds and racemic mixtures.
- Relation between number of chiral carbons and number of optical isomers.
- Relative and absolute configuration.
- Geometrical isomerism, its cause and systems of nomenclature for geometric isomers.
- Conformational isomerism, analysis and relative stability of various conformers of ethane, butane, cyclohexane, etc.
- Nature of bonding in organic molecules.
- Various electronic displacement effects in organic molecules that explain their reactivity.
- Different kinds of reactive intermediates and attacking agents involved in organic reactions.
- Types of reactions that organic molecules undergo such as addition, substitution and elimination and the mechanism of these reactions.
- Oxidation and reduction reactions of organic compounds.
- Structure, synthesis and pharmaceutical applications of drug molecules

STEREOCHEMISTRY

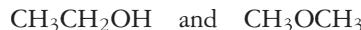
Based on many experimental observations, Van't Hoff and Le Bel in early 1900s concluded that the spatial orientation of groups around carbon atoms is tetrahedral when a carbon atom is bonded to four other atoms. Over the years, the structural arrangement of atoms around carbon in three dimensions has gained much significance and developed into a separate branch of study called *Stereochemistry*. Stereoisomerism, stereogenicity (chirality), optical activity are some essential components of stereochemistry which will be discussed in this chapter.

4.1 Isomerism

Isomerism was first recognised by J.J. Berzelius in 1847. In 1848 Louis Pasteur separated racemic mixture of acid into its components by crystallization.

Isomerism is a distinctive property of organic compounds by virtue of which two or more compounds with same molecular formula exhibit different physical and chemical properties. The compounds are known as isomers and may be of two types:

- 1. Structural (constitutional) isomers:** These are compounds having same molecular formula but differing the way atoms are connected within the same molecule. For example, a compound with molecular formula C_2H_6O , can have the following structural isomers:

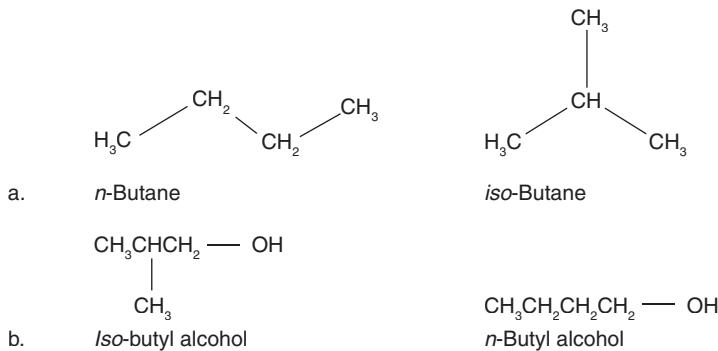


- 2. Stereoisomers:** These are compounds having same molecular formula in which the atoms are connected in the same sequence but differ in the arrangement of atoms in space. Stereoisomerism is the isomerism exhibited by two or more compounds which have the same molecular and structural formulae, but different spatial arrangement of atoms or groups.

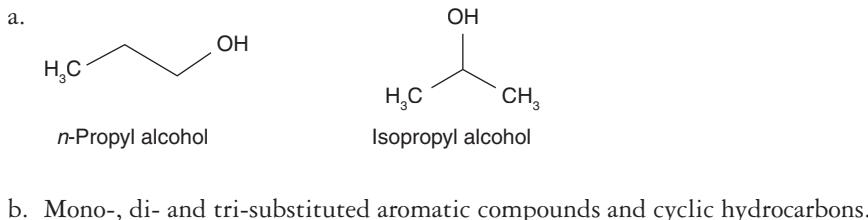
Types of Structural Isomers

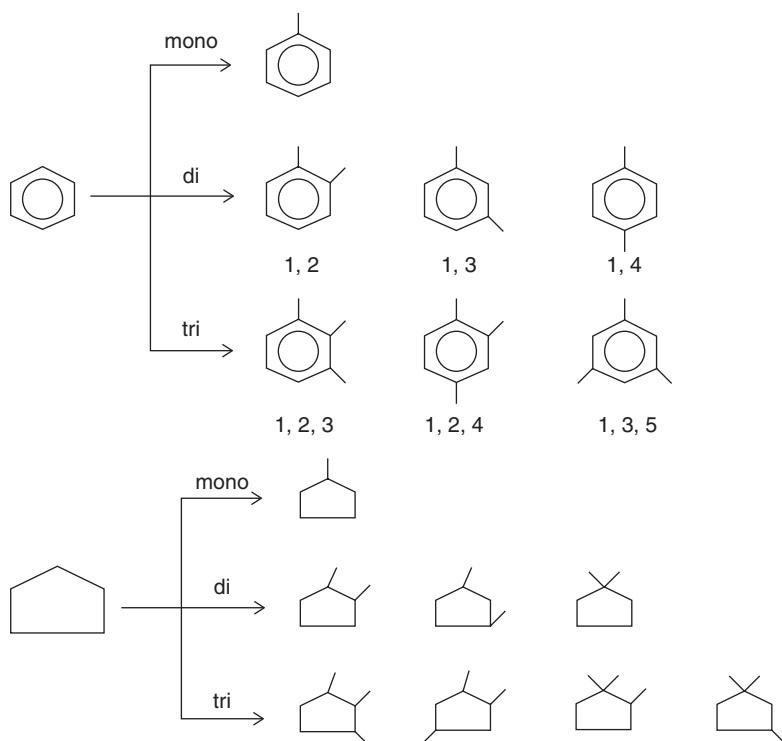
Structural isomers can be classified into the following categories:

- 1. Chain isomers:** These are compounds with the same molecular formula but differ in the carbon chain length. For example,



- 2. Positional isomers:** These are compounds which have the same molecular formula but differ in position of the functional group. For example,



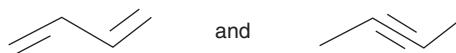


3. **Functional isomers:** These are compounds that have the same molecular formulas but different functional groups. For example,

a. Alcohols and ethers



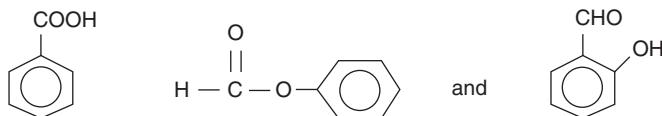
b. Alkadienes and alkynes



c. Aldehydes, ketones, unsaturated alcohols and unsaturated ethers



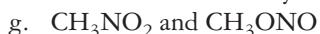
d. Carboxylic acids, esters and hydroxy aldehydes



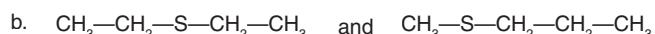
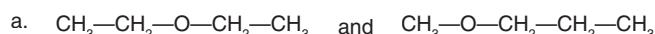
- ### e. Cyanides and isocyanides



- #### f. Nitro alkanes and alkyl nitrites



4. **Metamers:** These are compounds which have the same molecular formula but different alkyl groups attached to the functional group. Ethers, thioether and ketones exhibit metamerism. For example,

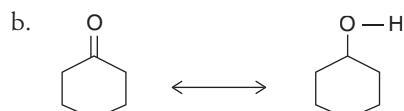


5. **Tautomers:** These are structural isomers that are mutually interconvertible and exist in a dynamic equilibrium with each other. For example,



Keto form

Enol form



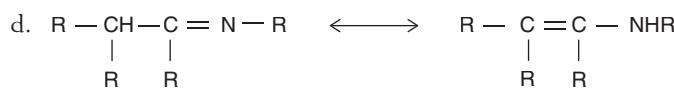
Keto form

Enol form



Amid

Imidol



Imine

Enamine

Types of Stereoisomers

Stereoisomers can be classified into two categories as follows:

1. **Conformational isomers:** If we consider an ethane molecule, $\text{H}_3\text{C}-\text{CH}_3$ and allow one CH_3 group to rotate and other to remain stationary through the C–C axis, we see that an infinite number of atomic arrangements resulting from this rotation are possible depending upon the angle through which we rotate the CH_3 group. This angle of rotation is called the *dihedral* angle and the different arrangements that result are called *conformations* or *conformers*. Thus, the stereoisomers that result from rotation of a group about carbon–carbon single bond are called *conformational isomers*.

2. **Configurational isomers:** The stereoisomers which cannot be converted into one another by rotation around a single bond are called *configurational isomers*. The two major type of stereoisomers are:

- **Enantiomers:** These are stereoisomers that are mirror images of each other.
- **Diastereomers:** These are stereoisomers that are not mirror images of each other.

There are two important types of stereoisomerism exhibited by configurational isomers: optical and geometrical isomerism.

Concept Check

- Define isomerism and distinguish between structural isomers and stereoisomers.
- What are the two types of stereoisomers?
- How are configurational isomers further classified?
- What are different type of structural isomerism?
- Differentiate between metamers and tautomers.

4.2 Three-Dimensional Representation of Structures

It is very difficult to represent three-dimensional structures on two-dimensional paper. Therefore, various two-dimensional projection formulae have been developed to represent three-dimensional structures. There are four kinds of projection formulae used, namely, Fischer, Newman, sawhorse and flying wedge. Of these, Fischer projections are mainly used to represent configurational isomers and are discussed in this section. Newman projections are also mainly to represent conformational isomers and are also discussed under Section 4.7.

Wedge Projections

Wedge projections of molecules help in visualization of the group of atoms around central carbon atom. In this representation three types of lines are used to draw the three-dimensional structure. Solid lines represent bonds which are in the plane of the paper, dashed lines represent bonds that project away from the observer or below the plane of the paper and wedge-shaped lines to represent bonds which are nearer to the observer or bonds which project above the plane of the paper (Figure 1).

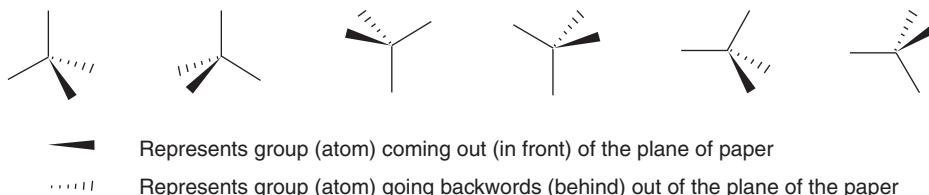
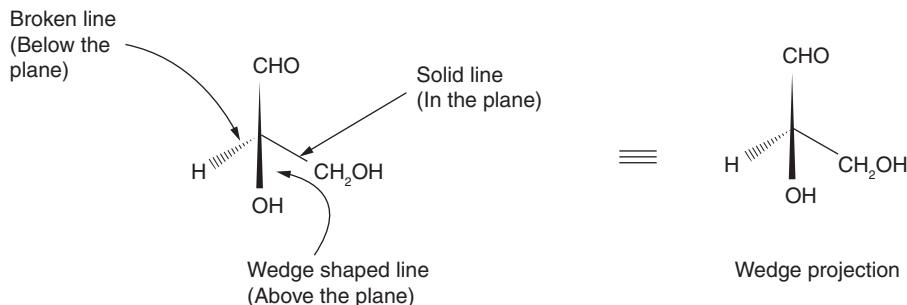


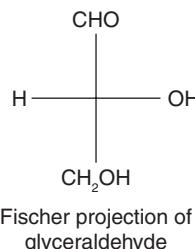
Figure 1 Wedge-dash projection.

Hence in wedge formula two bonds of the chiral carbon atom are shown in the plane of the paper by solid lines, whereas one bond is shown above the plane of the paper by a wedge-shaped line, and another one is shown below the plane of the paper by a broken line. For example, the wedge projection of glyceraldehyde is represented as:

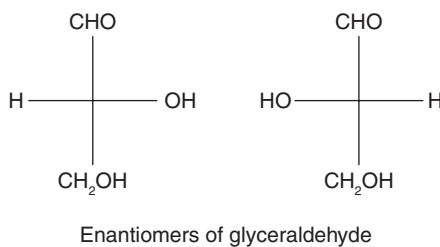


Fischer Projection Formula

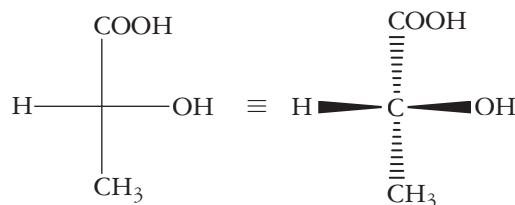
Fischer projection formula was devised by Emil Fischer in 1891. In writing this representation, in the longest carbon chain, the most oxidized carbon should be placed on the top or closer to the top. The tetrahedral carbon atom is visualized as a cross, where the point of intersection of two perpendicular straight lines is designated as the chiral carbon atom. The vertical lines are considered to be away from the observer or project below the plane of the paper, whereas the horizontal lines are nearer to the observer or project above the plane. In the example of glyceraldehyde given below, the horizontal groups $-H$ and $-OH$ are above the plane of paper whereas vertical groups $-CHO$ and $-CH_2OH$ project below the plane.



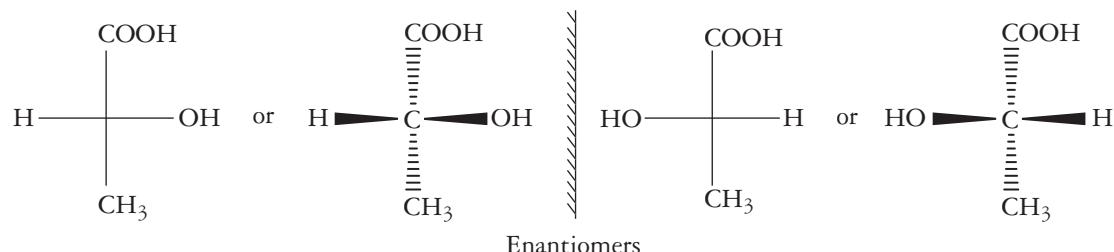
In the tetrahedral model of the molecule, if the chiral C-atom is in the plane, the two vertical groups $-CHO$ and $-CH_2OH$ project below the plane, and the other two horizontal groups $-OH$ and $-H$ project above the plane. It is to be noted that interchange of two groups in the Fischer's formula by odd number of times gives the same enantiomer. But interchange of two groups by even number of times does not change the configuration.



Consider the example of lactic acid (2-hydroxypropanoic acid) $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$:



The non-superimposable mirror images or the enantiomers of lactic acid are represented as:



The following points need to be kept in mind while manipulating the Fischer projection:

1. Fischer projection of a molecule can be converted into another identical Fischer projection by interchanging any *two pairs* of substituents bonded to the chiral carbon (Figure 2).

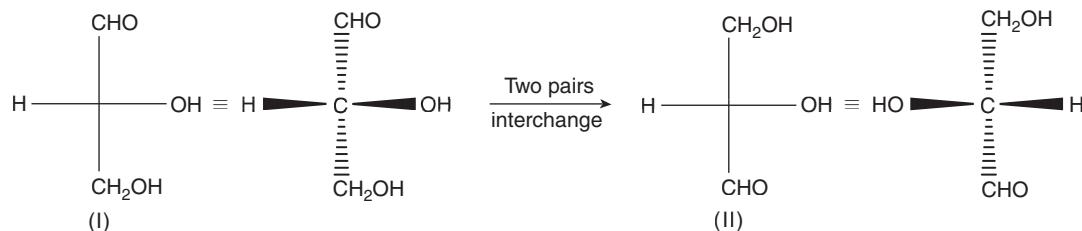


Figure 2 Same molecule obtained by interchanging two pairs of substituents.

From Figure 2, we find that Structure II is identical with Structure I.

2. If only one pair of substituents in a Fischer projection is interchanged, a projection of its enantiomer is obtained (Figure 3).

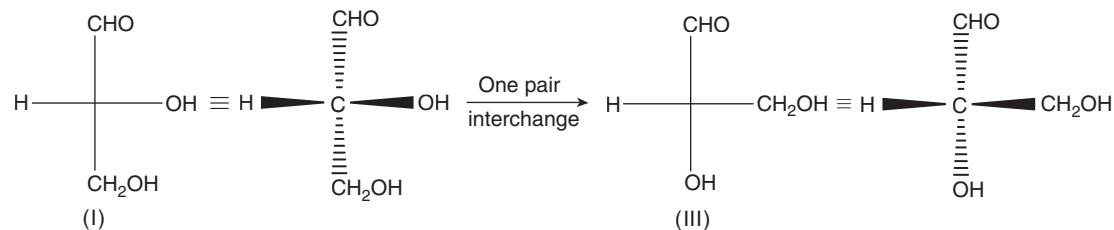


Figure 3 Enantiomers obtained by interchanging one pair of substituent.

From Figure 3, we find that Structures I and III are enantiomers.

3. If the Fischer projection of a molecule is rotated through 180° within the plane of the paper about an axis perpendicular to the plane of the paper, an identical structure is obtained (Figure 4).

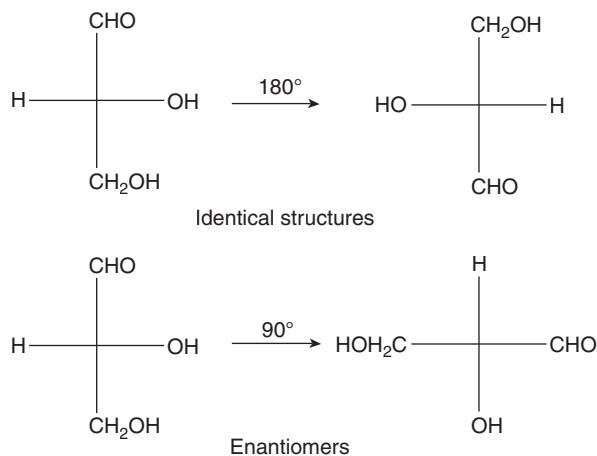
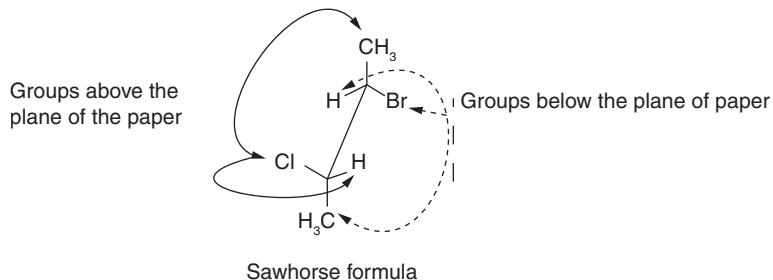


Figure 4 Effect of rotation by angles 180° and 90° on Fischer projection formula.

Sawhorse Projections

The sawhorse representation is quite convenient to know the spatial relation and chirality. In this projection, the two chiral carbon atoms are joined by a diagonal line in the plane of the paper. The remaining bonds are shown by smaller lines projected above and below the plane of the paper. As the two chiral carbon atoms are joined by a single bond, free rotation either clockwise or anticlockwise around the diagonal line is possible. For example, in the molecule $\text{CH}_3\text{CHClCHBrCH}_3$, the two key atoms are C2 and C3 joined by a diagonal line in the plane of the paper. The sawhorse formula of the compound can be drawn as:



The sawhorse conformation of the compound in which the bulky atoms or groups (Br atoms) make a dihedral angle $\theta = 180^\circ$, is called the *staggered conformation*. Since the free rotation along the diagonal C2-C3 bond is allowed, other conformations of the compound are also possible. The conformation in which the dihedral groups of sawhorse formula, make an angle equal to 120° , the representation is known as the *partially eclipsed* sawhorse formula. The *totally eclipsed* sawhorse formula is the one which contain $\theta = 0^\circ$ between the groups. These are depicted in Figure 2.

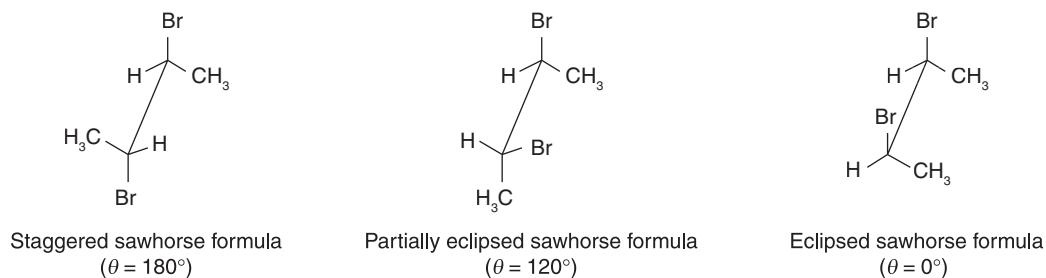
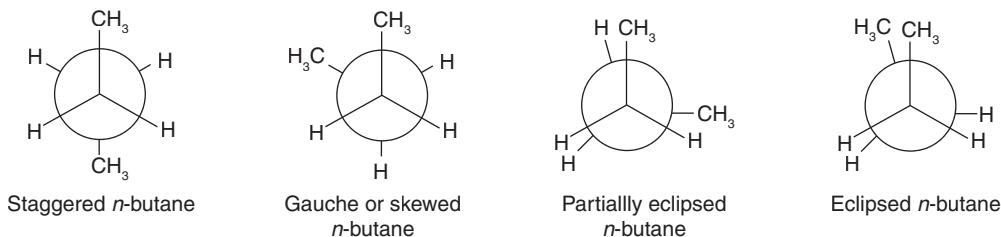


Figure 5 Sawhorse confirmations.

4.3 Newman Projections

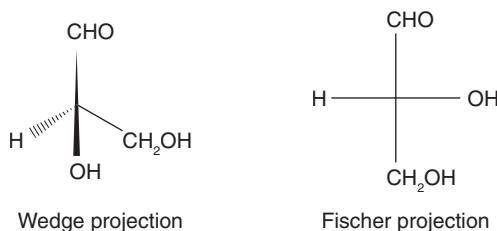
In this representation, the molecule is viewed along the bond that binds the two key carbon atoms of the molecule, as superimposed circles. Only one circle is drawn (visible) the center of which represents the front carbon atom, and it is understood that another key carbon atom is present at the rear side of the circle. The three σ -bonds of the front carbon atom are shown by three small lines drawn from the center of the circle, making an angle of 120° with one another. The three σ -bonds of the rear carbon atom are drawn from the circumference of the circle. In this notation the staggered, eclipsed, gauche, and partially eclipsed conformations of *n*-butane are represented in Figure 6.

Figure 6 Newman projections of *n*-butane.

Interconversion of Projection Formulas

Different projection formulas may be interconverted by following simple steps.

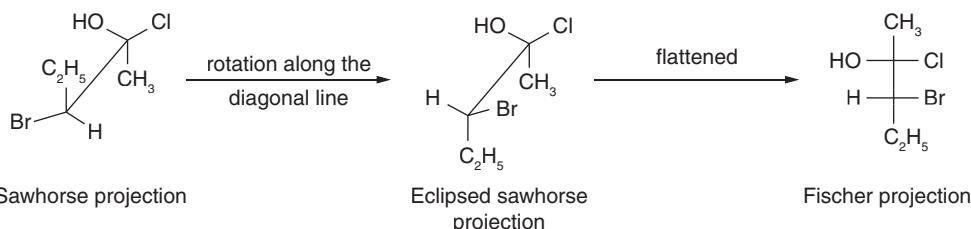
- Wedge to Fischer projection:** While converting the wedge formula to Fischer projection formula, the two solid lines of the wedge formula are shown as the vertical lines in the Fischer's formula. The other two groups held by broken line and wedge-shaped line are placed in the horizontal line.



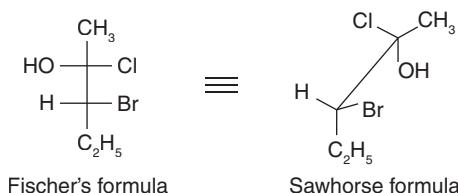
2. **Sawhorse to Fischer projection:** For converting sawhorse projection to Fischer projection, the front carbon atom of sawhorse formula is considered as the lowest chiral carbon atom in the Fischer formula. Then:

- (i) The given sawhorse conformation is converted to an eclipsed sawhorse conformation by rotation along the diagonal line by the minimum number of degrees.
 - (ii) The eclipsed sawhorse conformation so obtained is now flattened to get the Fischer's projection formula.

For example,



3. **Fischer to sawhorse projection:** A Fischer's formula can also be converted to a sawhorse formula. Here, lowest chiral carbon atom of the Fischer's formula becomes the front carbon atom of the sawhorse formula. Then, the groups in Fischer's formula that are drawn in anti or trans orientation with respect to each other are drawn on the same side of the diagonal line in the sawhorse formula. For example,



4.3 Chirality and Optical Activity

Concept of Chirality

The word chiral comes from the Greek word “chier” that means hand. Just like a right hand is a non-superimposable mirror image of the left hand, an object which is not superimposable on its mirror image is called *chiral* (Figure 7). It can be visualized that only non-planar molecules can be chiral.

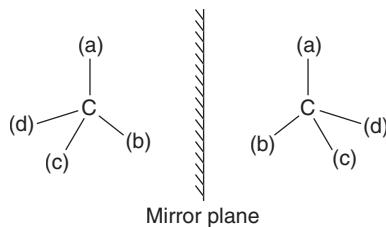
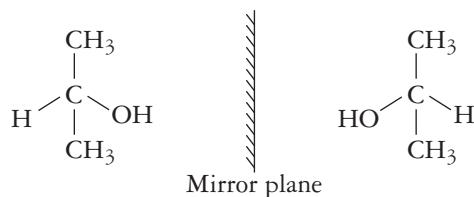


Figure 7 Chirality.

The origin of chirality in organic molecules can be attributed to the tetrahedral nature of the carbon atom. The tetrahedral carbon atom attached to four different atoms or groups is known as a chiral center or an asymmetric carbon atom. A pair of enantiomers is always possible for molecules that contain at least one chiral center. If the tetrahedral atom in the molecule has two or more groups attached that are identical, the molecule is superimposable on its mirror image and is achiral (e.g., 2-propanol).



A chiral molecule and its mirror image are called a *pair of enantiomers* and the relationship between them is enantiomeric. In case of enantiomers, by interchanging any two groups at the chiral carbon atom, one enantiomer can be converted into the other. A carbon atom, where an interchange of groups leads to the other stereoisomer is known as a *stereogenic center*.

Chirality and Symmetry Elements

The simple chiral molecule can be recognized by the presence of a chiral or stereogenic carbon. Another way to identify a chiral molecule is to look for the presence of certain symmetry elements. A molecule will not be considered chiral if it possesses symmetry elements such as a plane of symmetry (σ), a center of symmetry (i) and an n -fold alternating axis of symmetry (S_n).

- 1. Plane of symmetry:** The plane that divides an object into two identical halves is called a *plane of symmetry*. An orange can be divided by a plane into two identical halves so it is achiral. Our hand cannot be divided into two identical halves, that is, the hand does not have a plane of symmetry and hence it is chiral. Some compounds showing plane of symmetry are shown in Figure 8:

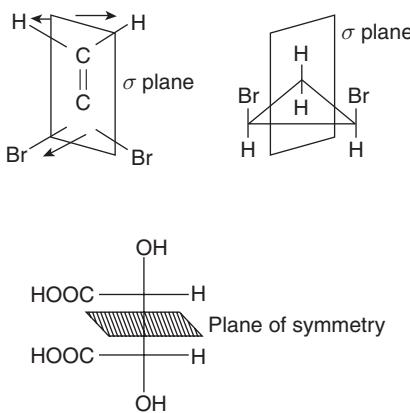


Figure 8 Compounds having plane of symmetry.

2. **Center of symmetry:** It is a point in a molecule, such that if a line is drawn from any atom or group to the opposite end through this point, the identical group or atom is found at the opposite end. Some compounds showing center of symmetry are given in Figure 9.

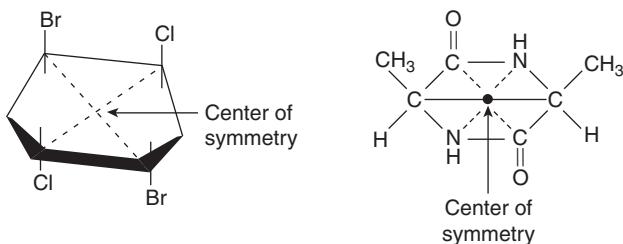


Figure 9 Compounds having center of symmetry.

3. ***n*-Fold alternating axis of symmetry:** If a molecule is rotated by an angle of $(2\pi)/n$ through an axis and then reflected across a plane perpendicular to this axis, and this results in an identical structure, then the molecule is said to possess an *n*-fold axis of symmetry. For example, if a molecule is rotated through an imaginary axis by an angle of 60° , and then reflected across a plane perpendicular to this axis resulting in an identical structure, it is said to possess a six-fold alternating axis of symmetry or S_6 .

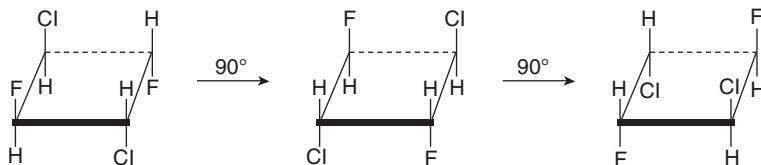


Figure 10 Compound having two-fold alternating axis of symmetry.

The foldedness or multiplicity of the alternating axis is given by the extent of rotation. For example, in the Figure 10,

$$\text{Multiplicity} = \frac{360^\circ}{180^\circ} = 2$$

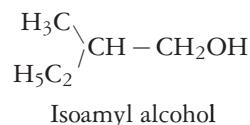
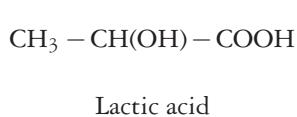
A plane of symmetry is equivalent to a one-fold alternating axis of symmetry and a center of symmetry is equivalent to a two-fold axis of symmetry.

Concept of Optical Activity

Light is a form of electromagnetic radiation that comprises waves vibrating in all directions perpendicular to the direction of propagation of light. When this light is passed through a Nicole prism, or a polarizing lens, it is found to vibrate in only one plane. Such a light that vibrates only in a single direction is known as plane polarized light, and the phenomenon is known as *polarization*.

When a plane polarized light is passed through a solution containing a single enantiomer, the plane of polarized light is rotated either to the right or to the left. The rotation of plane polarized light is called *optical rotation* and the compound that rotates the plane polarized light is called *optically active*.

If the optically active isomer rotates the plane of polarized light to the right, it is known as *dextrorotatory* (Latin term *dexter*, meaning right), designated by (+) or *d*, and if the optically active isomer rotates the plane of polarized light to the left, it is known as *laevorotatory* (Latin term *laevo*, meaning left), designated by (−) or *l*. Some simple organic compounds that show optical activity are:



Measurement of Optical Activity

Optical rotation is measured in terms of *specific rotation* $[\alpha]$. It is constant for a compound and is its characteristic property just like melting and boiling points. It is defined as the number of degrees of rotation based on unit concentration (1 g/ml) and unit sample tube length (1 dm).

Specific rotation is the angle of rotation (α) produced by 1 dm length of solution having 1 g of the sample per 1 ml of the solution at specified temperature and wavelength. The specific rotation of a given substance may be calculated by using the following expression:

$$[\alpha]_D^{20} = \frac{\alpha_{\text{obs}}}{lc}$$

where $[\alpha]_D^{20}$ is the specific rotation of sodium D line at 20°C , α_{obs} is the observed rotation at 20°C , l is the cell length in dm (1 dm = 10 cm) and c is the concentration of sample solution in g/ml. Molecular rotation is the product of specific rotation and molecular mass of the molecule.

The instrument used for the measurement of optical activity is called *polarimeter* and is shown schematically in Figure 11.

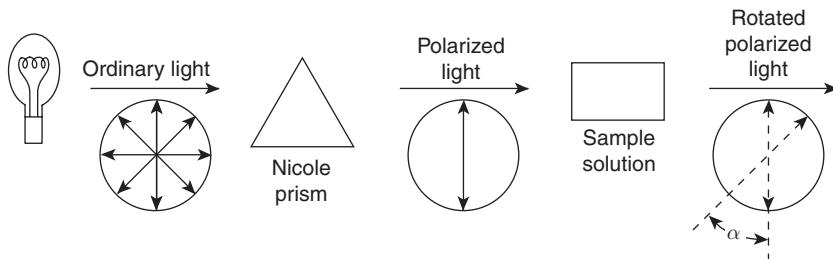


Figure 11 Schematic representation of polarimeter.

Relation between Chirality and Optical Activity

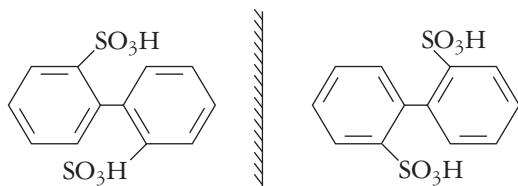
Optical activity is measured by the degree of rotation of plane-polarized light upon passage through a chiral medium. Molecules having one or more asymmetric or chiral carbon atoms are said to be optically active. To understand the relation between chirality and optical rotation, a beam of plane polarized light can be considered to be composed of two counter-rotating in-phase, circularly polarized beams of light. The optical activity results from the fact these two counter-rotating, circularly polarized beams travel with different velocities through the chiral medium. As they propagate through the sample, their vector

sum describes a progressively rotating plane. When it emerges from the sample, a net rotation of plane-polarized light arising due to differences in velocity of circularly polarized components is observed. Molecules that are not chiral do not cause the difference in velocity of circularly polarized beams, therefore, achiral compounds are optically inactive.

However, the presence of one or more asymmetric or chiral carbon atom in a molecule is not a necessary and sufficient condition for a compound to be optically active. There are examples of compounds which are optically active even without the presence of a chiral carbon and of compounds which are optically inactive even when chiral carbon is present.

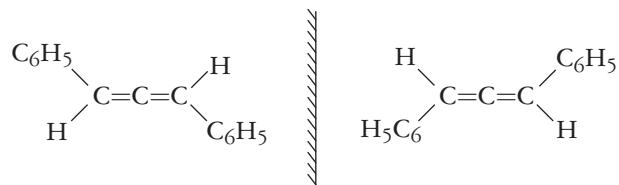
Optical Activity without Chiral Carbon Center

There are compounds which show optical activity even though they do not possess any asymmetric carbon. In these compounds, the rotation about carbon–carbon single bond is hindered due to the presence of bulky substituents. These compounds are also not planar due to steric repulsion between the bulky groups. For example,



From the above figure, we can see that the two isomers of bisphenyl-2,2-disulphonic acid are mirror images of each other.

Compounds in which the central carbon atom is hybridized in a manner such that the substituents at one end are in a plane perpendicular to the substituents at the other end, can also exist as non-superimposable mirror images and exhibit optical activity. For example,



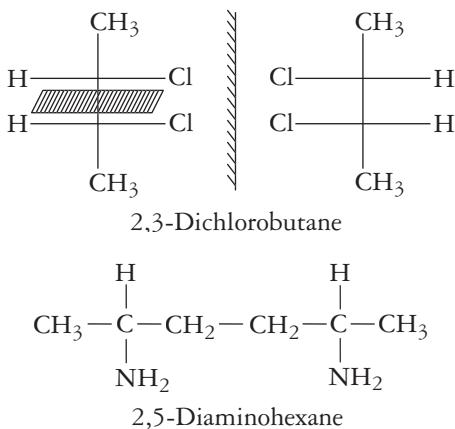
From the above figure, we can see that the two isomers of 1,3-diphenyl propadiene are mirror images of each other.

Optical Inactivity with Chiral Carbon Center

1. **Meso compounds:** These compounds contain two or more chiral centers and a plane of symmetry which bisects the compound into two equal parts that are mirror images of each other.

Meso compounds are optically inactive. This optical inactivity is due to the equal and opposite rotation by two identical parts of the same molecule. The dextro rotation of one half of the molecule is compensated by the laevo rotation of the other half. Since this compensation arises from within the molecule itself, the molecule is said to be inactive due to internal compensation and is known as a *meso* isomer.

For example, in 2,3-dichlorobutane the plane of symmetry lies between C-2 and C-3 and bisects the molecule into two equal halves. Similarly in 2,5-diaminohexane, the plane of symmetry lies between C-3 and C-4.



Hence it can be stated that molecular dissymmetry is the necessary and sufficient condition for a molecule to be optically active

2. **Racemic mixture (racemate):** A racemic mixture (or racemic form) is an equimolar mixture of two enantiomers and hence is optically inactive. A racemic mixture is optically inactive by external compensation. It can be resolved into its active constituents by various methods such as mechanical separation, biochemical resolution and chemical methods. These methods are termed as resolution of the racemic mixture.

Problem 1

An optical pure compound A has $\{\alpha\}^{25} = +20^\circ$. A mixture of A and its enantiomer B have $\{\alpha\}^{25} = +10^\circ$. Calculate the ratio of A to B in the mixture.

Solution

Optical purity or the enantiomeric excess of a mixture of enantiomers can be determined as

$$\text{Optical purity} = (\text{Percentage of one enantiomer}) - (\text{Percentage of the other isomer}) = \frac{100[\alpha]_{\text{mixture}}}{[\alpha]_{\text{pure}}}$$

Given that $[\alpha] = +10^\circ$ and $[\alpha]_{\text{pure compound A}} = +20^\circ$. Therefore, optical purity is calculated as

$$\text{Optical purity} = 100 \times \frac{10}{20} = 50$$

The pure compound A is present in 50% excess over its enantiomer B. The remaining 50% which is optically inactive will contain equal amounts of A and B. The excess 50% is all A, therefore the amount of A in the mixture will be 75% and B will be 25%. The ratio of A to B in the mixture is thus 3:1.

Problem 2

Calculate the specific rotation of a pure enantiomer of a given molecule, given that it has an optical rotation of $+0.52^\circ$ when measured in a 1 dm tube at a concentration of 0.5 g per 10 ml.

Solution

Specific rotation is given by

$$[\alpha] = \frac{\alpha_{\text{obs}}}{lc}$$

where α_{obs} is the observed rotation, l is length of the cell in decimeter and c is the concentration in grams per milliliter.

Given that concentration = 0.5 g/10 ml = 0.05 g/ml; length of tube = 1 dm and observed rotation = $+0.52^\circ$.

Therefore, the specific rotation is given by

$$[\alpha] = \frac{0.52^\circ}{0.05 \times 1} = 10.4 \text{ deg} \cdot \text{ml/g} \cdot \text{dm}$$

Problem 3

A compound is dissolved in chloroform at concentration of 3.25 g per 100 ml.

- (a) The solution placed in 5 cm polarimeter tube shows a rotation of -1.5° . Calculate the specific rotation of the compound.
- (b) What would be the observed rotation when the sample is placed in a 10 cm tube?
- (c) What would be the observed rotation of 10 ml of this solution if further diluted to 20 ml and placed in 10 cm tube?

Solution

The specific rotation is given by

$$[\alpha] = \frac{\alpha_{\text{obs}}}{lc}$$

where α_{obs} is the observed rotation, l is the length of cell in decimeter and c is the concentration in grams per milliliter.

- (a) Given that concentration = 3.25 g per 100 ml = 0.0325 g/ml; length of the tube = 5 cm = 0.5 dm and specific rotation $\alpha_{\text{obs}} = -1.5^\circ$.

The specific rotation is given by

$$[\alpha] = \frac{-1.5}{0.0325 \times 0.5} = -92.3^\circ$$

- (b) The observed rotation is given by

$$\alpha_{\text{obs}} = [\alpha] \times l \times c$$

Given that $[\alpha] = -92.3^\circ$; $l = 10 \text{ cm} = 1 \text{ dm}$; $c = 3.25 \text{ g per } 100 \text{ ml} = 0.0325 \text{ g/ml}$. Therefore, the observed rotation is calculated as

$$\alpha_{\text{obs}} = -92.3 \times 1 \times 0.0325 = -2.9^\circ$$

- (c) Given that $c = 3.25 \text{ g per } 100 \text{ ml} = 0.325 \text{ g per } 10 \text{ ml}$

On further dilution, $c = 0.325 \text{ g per } 20 \text{ ml} = 0.01625 \text{ g/ml}$.

Substituting the value of c , the observed rotation is obtained as

$$\alpha_{\text{obs}} = [\alpha] \times l \times c = -92.3^\circ \times 1 \times 0.01625 = -1.49^\circ$$

Problem 4

A sample of pure 2-butanol has specific rotation of $+129^\circ$. A solution of 2-butanol placed in 5 cm polarimeter tube shows a rotation of $+85^\circ$. Calculate the concentration of 2-butanol in the solution.

Solution

The specific rotation is given by

$$[\alpha] = \frac{\alpha_{\text{obs}}}{l \times c}$$

where α_{obs} is the observed rotation, l is the length of cell in decimeter and c is the concentration in grams per milliliter.

Given that specific rotation, $[\alpha] = +129^\circ$; length of the tube, $l = 5 \text{ cm} = 0.5 \text{ dm}$; observed rotation, $\alpha_{\text{obs}} = +85^\circ$.

Substituting these values, we obtain concentration as

$$c = \frac{\alpha_{\text{obs}}}{[\alpha] \times l} = \frac{85}{129 \times 0.5} = 1.32 \text{ g/ml}$$

Concept Check

- What is optical activity? What are compounds that differ only in their optical activities called?
- Optical activity is measured and expressed in terms of specific rotation. What is the mathematical relation between observed and specific rotations?
- An optically active molecule should have a chiral carbon and should lack molecular symmetry. Explain.
- A plane of symmetry is equivalent to one-fold alternating axis of symmetry. Explain.
- Tartaric acid (2,3-dihydroxybutanoic acid) HOOC(CHOH)₂COOH has two asymmetric carbons. How many stereoisomers are possible?
- How is a racemic mixture different from a *meso* compound?

4.4 Optical Isomerism

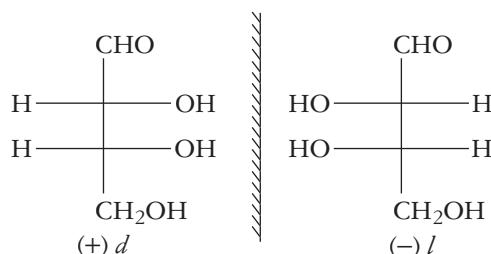
Optical isomerism is the type of stereoisomerism in which the isomeric compounds differ only in the direction in which they rotate the plane of polarized light. Compounds possessing identical molecular

and structural formulae and identical physical and chemical properties, but differing only in their behaviour towards plane polarized light are called *optical isomers*. The stereoisomers that exhibit optical isomerism can either be enantiomers or diastereomers. These are discussed as follows.

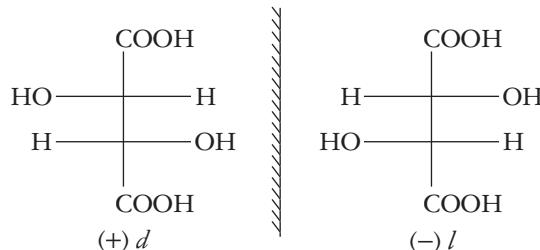
Enantiomers and Optical Activity

Enantiomers are compounds represented by non-superimposable mirror images of each other and the phenomenon is known as enantiomerism. A pair of enantiomers has the same physical and chemical properties except for their interaction with other chiral molecules and with the plane-polarized light. For example, erythrose (2,3,4-trihydroxybutanal) and tartaric acid:

Erythrose:



Tartaric acid:



The physical and chemical properties of enantiomers are as follows:

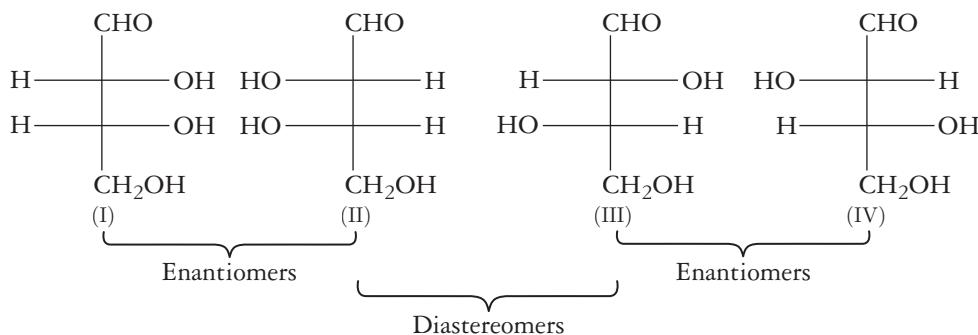
1. Enantiomers have identical physical properties such as melting and boiling points, density and refractive index, except their optical rotations which are of equal magnitude but opposite sign.
2. Their odors may be different, for example, (+)-limonene has a smell of oranges and (-)-limonene smells like lemons.
3. They have identical chemical properties except in their behavior towards chiral reagents and chiral solvents, where their rate of reactions and nature of product formed is different.
4. They can be separated only by the use of a chiral column agent.
5. They may display different physiological properties, for example, (-)-nicotine is more poisonous than (+)-nicotine and (+)-ascorbic acid is more efficient than (-)-ascorbic acid. Sometimes, one enantiomer of a drug is more effective and safer than the other.

Diastereomers and Optical Activity

The stereoisomers that are not enantiomers are called diastereomers. These molecules are not mirror images of each other. Diastereomers containing atleast two dissimilar chiral carbon atoms exhibit optical isomerism. The physical and chemical properties of diastereomers are as follows:

- Unlike enantiomers, diastereomers usually have different physical properties such as melting point, boiling point, density, refractive index, solubility, etc.
- They have similar but not identical chemical properties. The rate of reaction of diastereomers differs with chiral and achiral reagents and solvents.
- They can be separated using fractional crystallization, fractional distillation etc. because of the difference in their physical properties.

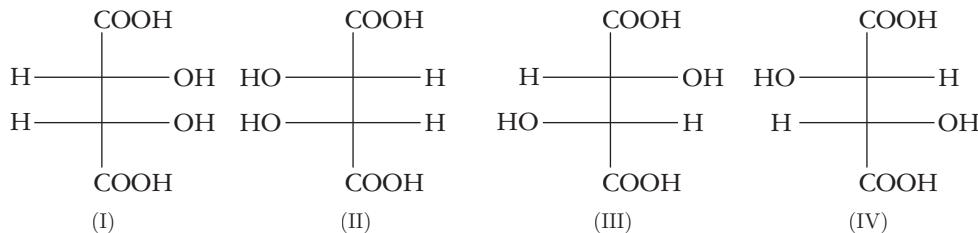
The number of optically active forms of a compound depends on the number of chiral carbon atoms. If there are n chiral carbons, the number of optically active forms will be 2^n , provided the chiral atoms are not identically substituted. All the optical isomers are not enantiomers, the enantiomers occur in pairs, the rest of the isomers are diastereomers. For example, consider a 2,3,4-trihydroxy butanal molecule with two chiral carbon atoms. It can have four (2^2) optically active isomers as follows:



(I) and (II); (III) and (IV) are enantiomers.

(I) and (III); (II) and (III); (I) and (IV); (II) and (IV) are diastereomers.

Similarly, let us take an example of tartaric acid, which has two chiral carbons. The number of possible stereoisomers are $2^2 = 4$ as shown below.



(I) and (II) are identical and *meso* compounds.

(I) and (III); (II) and (III) are diastereomers.

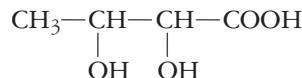
(III) and (IV) are enantiomers.

However, the actual number of stereoisomers is three because two structures (I and II) are identical due to presence of plane of symmetry.

Relation between Number of Optical Isomers and Chiral Carbons

In compounds with stereoisomerism arising due to tetrahedral stereogenic carbon atoms, the total number of stereoisomers will be less than or equal to 2^n , where n is the number of tetrahedral stereogenic carbons. The number of stereoisomers, optical isomers and *meso* forms for a given formula can be derived as follows:

When the molecule is unsymmetrical: Number of *d* and *l* isomers (α) = 2^n , number of *meso* forms (m) = 0; total number of stereoisomers = ($\alpha + m$) = 2^n where n is the number of chiral atoms. For example, in 2,3-dihydroxybutanoic acid.

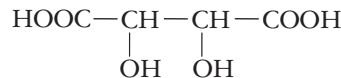


Number of optical isomers (α) = 2^n = 4;

Number of *meso* forms (m) = 0;

Total number of stereoisomers = 4.

When the molecule is symmetrical and has even number of chiral carbon atoms: Number of *d*, *l* isomers (α) = $2^{(n-1)}$; number of *meso* forms (m) = $2^{(n/2-1)}$; and the total number of optical isomers = ($\alpha + m$). For example, in tartaric acid:



Number of optical isomers (α) = $2^{(2-1)}$ = 2;

Number of *meso* forms (m) = $2^{(2/2-1)}$ = 1;

Total number of stereoisomers = $\alpha + m$ = 3.

When the molecule is symmetrical and has odd number of chiral carbon atoms: Number of *d*, *l* forms (α) = $2^{(n-1)} = 2^{(n/2-1/2)}$; number of *meso* forms (m) = $2^{(n/2-1/2)}$ and the total number of stereoisomers = ($\alpha + m$) = $2^{(n-1)}$. For example, in 2,3,4-trihydroxy-1,5-pentan-dioic acid:



Number of optical isomers = $2^{3-1} - 2^{(3/2-1/2)} = 2$;

Number of *meso* isomers = $(2^{3/2-1/2}) = 2$;

Total number of stereoisomers = 2 + 2 = 4.

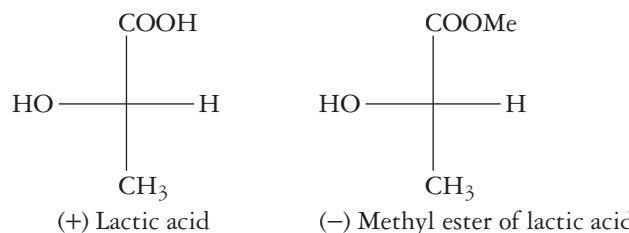
Concept Check

- What is the necessary condition for existence of enantiomers?
- Enantiomers have identical physical and chemical properties. What is the one property with respect to which they differ?
- For the compound, $\text{CH}_3-(\text{CHOH})_2-\text{COOH}$, write the structure of two enantiomers.
- How do diastereomers differ from each other?
- How are diastereomers related in terms of their physical and chemical properties?
- For the compound $\text{CH}_3-(\text{CHOH})_2-\text{COOH}$, write the structure of two diastereomers.
- How many configurational isomers are possible with the compound 2-bromo, 3-chlorobutane?
- What is the number of optically active isomers possible for a compound with unlike chiral centers with $n = 3$?
- In a compound containing two like chiral centers, how many optically active and inactive isomers are possible?

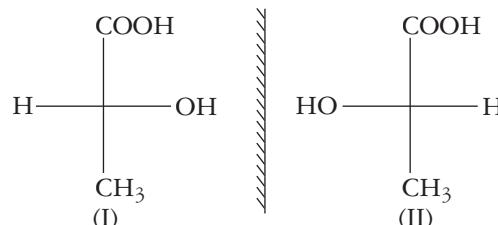
4.5 Configuration

A stereoisomer is characterized by the arrangement of atoms or groups. This arrangement is called its configuration. A stereoisomer is best recognized by its configuration and not by whether it is dextrorotatory (+) or laevorotatory (-), as the sign of rotation of a stereoisomer is an experimentally observed fact and is not related to its configuration. A compound and its derivatives may have the same configuration but different signs of rotations.

For example, lactic acid and its ester having the same configuration possess opposite sign of rotation.



Lactic acid has one chiral center and therefore has $2^1 = 2$ stereoisomers.

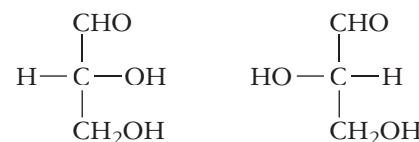


Both the isomers have different configurations about the chiral center, but how do we characterize them? There are two conventions used for assigning the configuration of stereoisomers.

Relative Configuration (D and L System)

Till about 1950, there was no standard method of studying the absolute configuration of stereoisomers, that is, the actual arrangement of atoms in space. Then glyceraldehyde was chosen as an arbitrary standard and configuration of various stereoisomers was relative to that of glyceraldehydes. Hence the name relative configuration, because it is always studied relative to some compound.

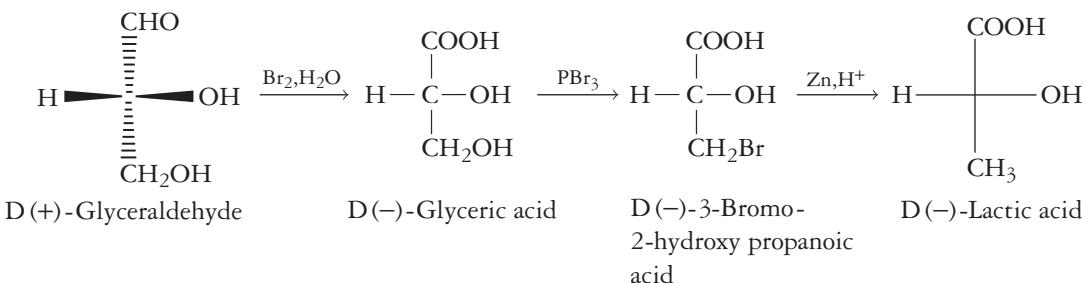
Glyceraldehyde structure with the -OH group on the right and hydrogen atom on the left, -CHO at the top and -CH₂OH at the bottom was arbitrarily given the configurational symbol D. The mirror image compound, with -OH group on the left and H atom on the right was given the configurational symbol L.



D(+)-Glyceraldehyde L(-)-Glyceraldehyde

However, it must be kept in mind that D and L are distinct from *d* and *l* forms which indicate dextro-rotatory and laevo-rotatory property, respectively.

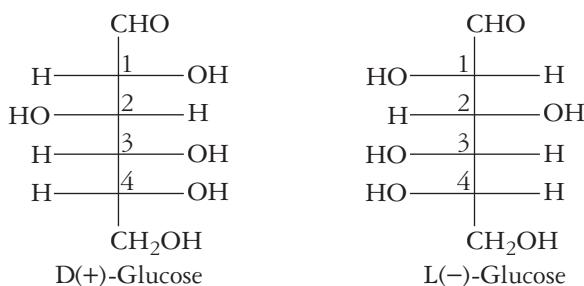
Any stereoisomer that could be obtained from or converted to D-glyceraldehyde would be assigned configuration D. That is, the compounds obtained from glyceraldehyde by means of the reactions that did not involve breaking of bonds to a chiral center could be configurationally related to it. On the basis of the configuration assigned to the glyceraldehyde, these related compounds could also be assigned configurations.



The (+) or (−) sign added after D and L letter indicates the direction of optical rotation. An optically active substance having D-configuration can be dextro (+) or laevo (−). Similarly, a substance having L-configuration can be dextro (+) or laevo (−).

The D and L system is commonly used to assign stereochemistry to carbohydrates and amino acids.

- Carbohydrates:** The D, L nomenclature of carbohydrates depends on configurational arrangement of the highest number symmetric carbon in a Fischer projection. The longest carbon chain is vertical with the most oxidized carbon at C-1. If the OH group at the highest numbered asymmetric carbon lies towards right as in D-glyceraldehyde, then the given compound belongs to the D-series and if it is towards the left, then it belongs to L-series.



- α -Amino acids:** The configurational arrangement of $-\text{NH}_2$, $-\text{COOH}$, $-\text{R}$ and H at C_α correspond to $-\text{OH}$, $-\text{CHO}$, $-\text{CH}_2\text{OH}$ and H of glyceraldehyde. Hence, looking at the relative positions of the $-\text{NH}_2$ group we can also characterize the amino acid as part of D or L series (Figure 12).

Absolute Configuration (R and S System)

Absolute configuration is the three-dimensional arrangement of groups or atoms in an asymmetrical molecule. A scheme of representation of optical isomers on paper was proposed by Cahn, Ingold and Prelog. This assignment of the configuration to an optically active compound is based upon the nature of groups attached to the asymmetric center and the priority assigned to them. The absolute configuration is defined by a prefix *R* (Greek term *rectus*) or prefix *S* (Greek term *sinister*) depending upon the sequence

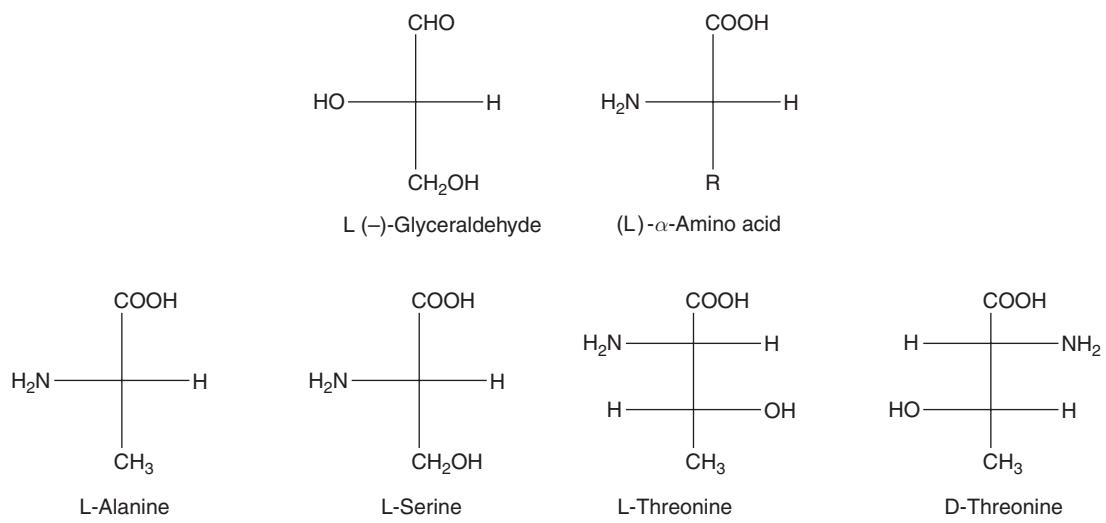


Figure 12 D- and L-series of amino acids.

of the groups. The steps involved in assigning absolute configuration and the sequence rules to determine the order of priority of groups are as follows:

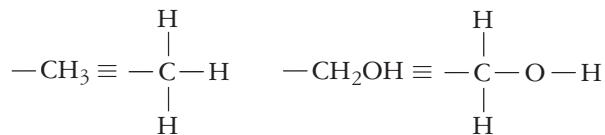
Cahn, Ingold and Prelog Rules:

Step 1: Various groups attached to the chiral carbon are assigned priority based on the following sequence rules:

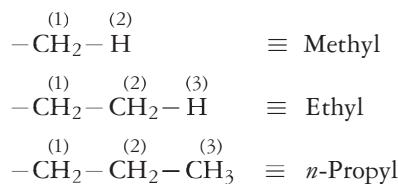
Rule 1: The order of priority is determined on the basis of atomic numbers of the atoms attached directly to the chiral carbon. The greater the atomic number, higher is the priority. For example, if –H, –OH, CH₃ and Br are the groups attached to the chiral carbon then Br (atomic number = 35) will have the highest priority, followed by –OH group (atomic number of O = 12) then CH₃ (atomic number of carbon = 6) and finally hydrogen (atomic number = 1). The order of priority will be Br > OH > CH₃ > H.

Rule 2: If two isotopes of the same element are present, the heavier isotope has higher priority, that is, D > H and C¹³ > C¹².

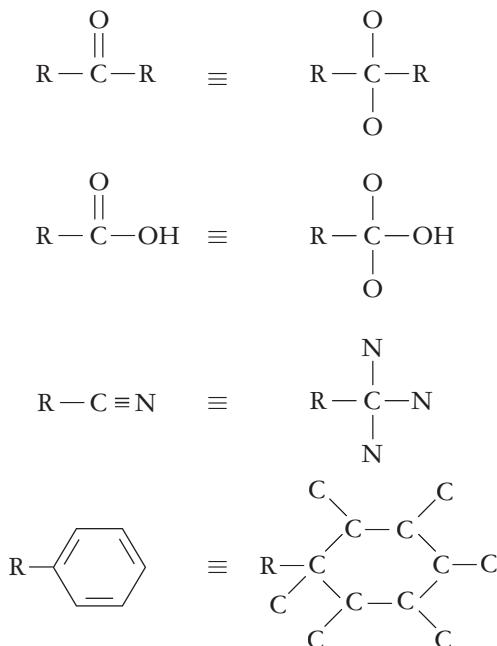
Rule 3: If two atoms directly linked to the chiral carbon are identical, then atomic numbers of the next atoms are used for the assignment of priority. If these atoms also have identical atoms attached to them, the priority is determined at the first point of difference along the chain. For example, between –CH₃ and –CH₂OH, the latter has a higher priority.



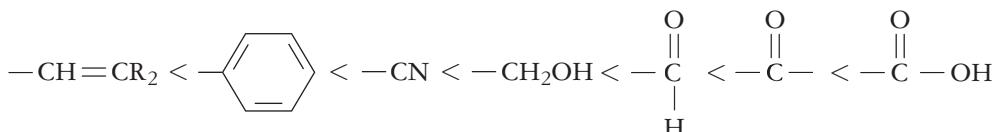
Similarly for methyl, ethyl and *n*-propyl groups, the priority may be assigned as follows. The first carbon atom in methyl and ethyl is carbon and therefore atomic numbers of the second atoms H (atomic number = 1) and C (atomic number = 6) decide the priority order, that is, ethyl > methyl. While considering ethyl and *n*-propyl, the second carbon is also identical and hence the third atoms (H, C) give the priority order as *n*-propyl > ethyl.



Rule 4: A doubly or triply bonded atom present in a group attached to the chiral carbon, is considered equivalent to two or three singly bonded atoms in determining priority. For example, the following groups,



can be arranged in the increasing order of priority as follows:



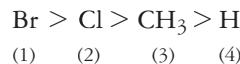
Step 2: The molecule is oriented in such a fashion that the group of the lowest priority is directed away from the viewer. It should be placed at the vertical bond as it lies behind the plane of paper and is the furthest from the eye.

Step 3: If in moving from first, second and third priority groups, the eye travels in clockwise or right-handed direction, the configuration is assigned as *R*. If in going from first, to second and then to third priority groups, the eye moves in counter clockwise or left-handed direction, the configuration assigned is *S*. Consider the following examples illustrating assigning of *R/S* configuration:

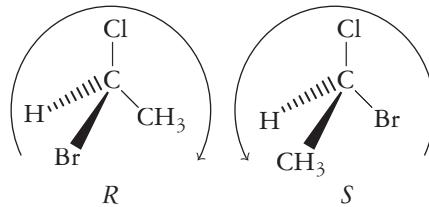
EXAMPLE 5

1,1-Chlorobromoethane $\text{CH}(\text{Cl})(\text{Br}) \cdot \text{CH}_3$

The four atoms directly bonded to the asymmetric carbon are Br (atomic number = 35), Cl (atomic number = 17), C (atomic number = 6), and H (atomic number = 1). Hence, the priority order is

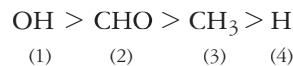


The configurations of two enantiomers are assigned as

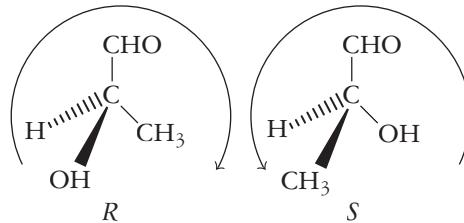
**EXAMPLE 6**

Glyceraldehyde [$\text{CHO} \cdot ^*\text{CHOH} \cdot \text{CH}_2\text{OH}$]

The groups bonded to asymmetric carbon in glyceraldehyde have the priority order:

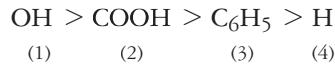


The configurations of the two isomers are assigned as

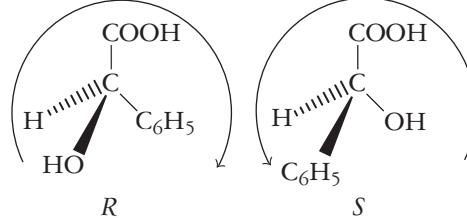
**EXAMPLE 7**

Mandelic acid [$\text{C}_6\text{H}_5 \cdot ^*\text{CH}(\text{OH}) \cdot \text{COOH}$]

The priorities of the four groups attached to the asymmetric carbon atom are:



The configurations of the two isomers are:



Assigning Configuration using Fischer Projections

If an atom or group of lowest priority occupies vertical position in the Fischer projection then the configuration obtained gives the actual configuration of the molecule. If however, the atom or group of lowest priority occupies horizontal position in the Fischer projection, then interchange to place the least priority group at the vertical position. This should be done in pairs to avoid a configuration change, since single interchange leads to an enantiomer of the compound and hence inverts configuration (Figure 13).

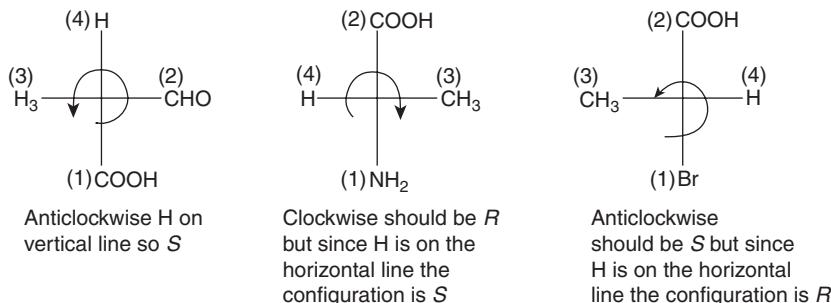


Figure 13 Assigning configuration using Fischer projections.

Concept Check

- Write the structures of glyceraldehyde representing D and L configurations.
- How are D and L configurations assigned?
- Cahn, Ingold and Prelog devised sequence rules to determine the priority of groups on asymmetric carbon. According to these rules, which among the following will have highest priority:
 - CHO, -CH₂OH, -CH₃
 - CH₃, -CH₂Cl, -CHCl₂
- The groups attached on central carbon (a, b, l, m) are assigned relative priority a > b > l > m. How will you designate R and S configuration when the group m is farthest from the eye?
- The groups bonded to asymmetric carbon in glyceraldehyde are -H, -CH₂OH, -OH, -CHO. Arrange them in proper sequence or priority.

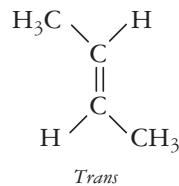
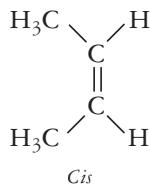
4.6 Geometrical Isomerism

The isomers which have the same structural formulae but differ in the relative spatial arrangement of atoms or groups around the double bond or ring systems are called *geometrical isomers*, and the phenomenon is called *geometrical isomerism*.

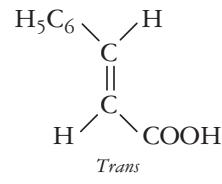
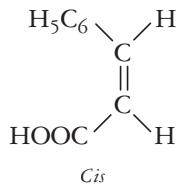
Cis and Trans Nomenclature

When two similar groups lie on the same side of a double bond, the arrangement is called a *cis* isomer. When two similar groups lie on the opposite side of a double bond, the arrangement is called a *trans* isomer. Some examples of compounds showing geometrical isomerism are as follows:

Cis-2-butene and *trans*-2-butene:

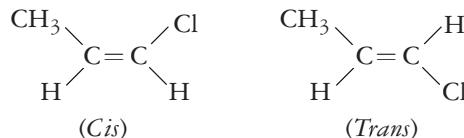
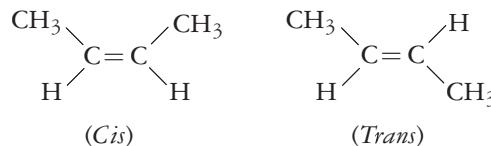


Cis- and *trans*-cinnamic acid:



The cause of geometrical isomerism is the restricted or hindered rotation about carbon–carbon double bond. The two important and necessary conditions for a molecule to exhibit geometrical isomerism are:

1. The molecule must contain a carbon–carbon double bond.
2. Each carbon atom of the double bond must have different atoms or groups attached to it. For example, compounds of the type abC=Cab, abC=Cdc, abC=Cad show this type of isomerism. The following show the case where abC=Cab and abC=Cad.

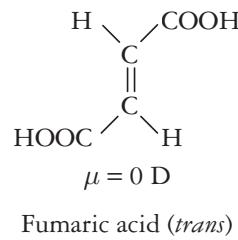
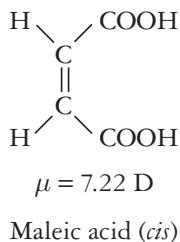


The *cis* and *trans* isomers may be distinguished on the basis of their physical and chemical properties as follows.

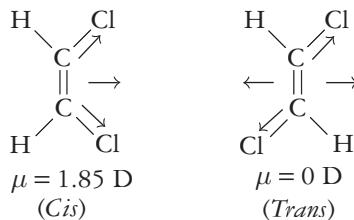
1. From their physical properties:

- The boiling point of the *cis* isomer is higher than the *trans* isomer. The boiling point of isomeric compounds depends upon the dipole–dipole interactions. Since *cis* isomers usually have a higher value of dipole moment than the corresponding *trans* isomer, therefore their boiling point is more.
- The melting point and density of a *trans* isomer is higher than the *cis* isomer due to the symmetrical nature and more close packing in *trans* isomer.

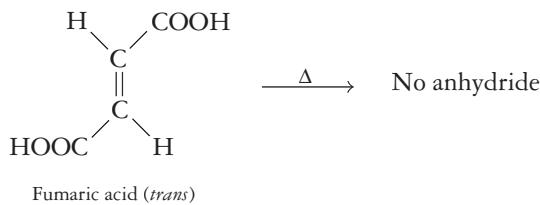
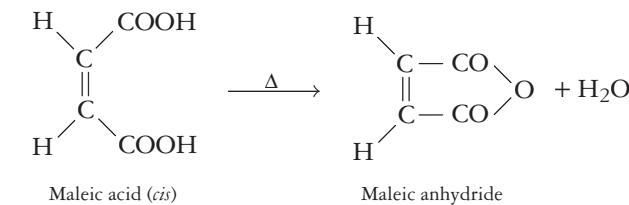
2. **From their dipole moments:** *Cis* isomers have higher dipole moments than *trans* isomers which may have zero dipole moments. For example, the dipole moment of *cis*-maleic acid is quite high while that of fumaric acid is zero because dipole moments of C—COOH bonds cancel out the effects of each other as these are in opposite directions.



Similarly in 1,2-dichloroethene, the dipole moment of C—Cl bond is cancelled out in the *trans* isomer.

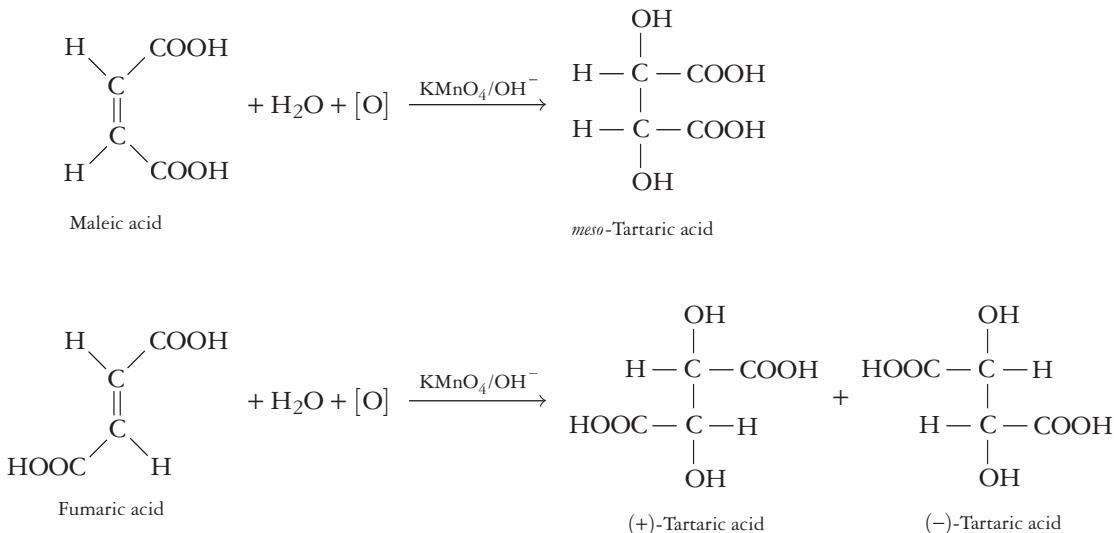


3. **From their cyclization reactions:** The *cis* isomers react more readily to form a cyclic compound because in the *cis* forms, the reacting groups are in close proximity to each other. In *trans* isomers, the reacting groups are situated quite apart from each other, so they do not react to form cyclic compounds. For example, *cis*-maleic acid on heating readily loses a molecule of water because of the close proximity of two carboxylic acid groups and a cyclic maleic anhydride is formed. Fumaric acid, on the other hand, does not form a cyclic anhydride.



4. **From the nature of the optical isomers formed:** Both forms of ethylene dicarboxylic acid, that is, maleic acid and fumaric acid, on hydroxylation give optically inactive variety of tartaric acid.

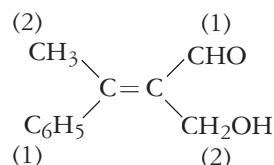
The one obtained from maleic acid (*cis* isomer) is *meso* while the other obtained from fumaric acid (*trans* isomer) is racemic.



E and Z Nomenclature

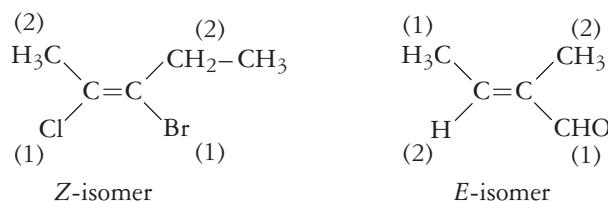
In compounds where all four atoms or groups attached to carbon atoms of double bond are different, the *cis* and *trans* nomenclature cannot be followed. Such geometrical isomers are designated by *E* and *Z* nomenclature. In this system, each of the groups on the two carbon atoms of the double bond are assigned priority number (1) and (2) on the basis of the *sequence rules* proposed by Cahn, Ingold and Prelog and discussed in Section 10.4.

For example, in the following compound



Now on the basis of relative priorities and position of groups/atoms the *E-Z* designation is assigned as follows:

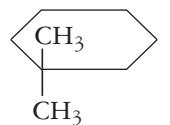
1. If the atoms or groups of higher priority on each carbon atom of the double bond, are on the opposite side, the configuration is designated as *E* (German term *entgegen*, meaning opposite).
2. If the atoms or groups of higher priority on each carbon atom are on the same side of the double bond, the configuration is designated as *Z* (German term *zusammen*, meaning together). For example,



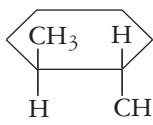
Geometrical Isomerism in Cyclic Structures

In cyclic compounds, presence of ring systems restricts the rotation about carbon–carbon single bond. These compounds can thus exist as geometrical isomers, provided there are at least two other groups besides hydrogen on the ring. These groups are present on different carbon atoms of the ring.

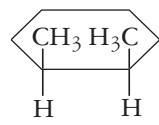
Some examples:



1,1-Dimethyl
cyclohexane
(no geometrical
isomers possible)



Trans-1,2-dimethyl
cyclohexane



Cis-1,2-dimethyl
cyclohexane

Concept Check

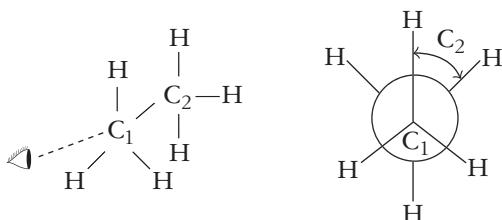
- What causes geometrical isomerism to occur?
- What is the system of nomenclature followed for geometric isomers when all four groups on carbon–carbon double bond are different?

4.7 Conformational Isomerism

The different spatial arrangements that a molecule can have due to free rotation about carbon–carbon single bond are known as conformations. The isomers that differ in their conformations are called conformational isomers or conformers, and the phenomena is known as conformational isomerism. This type of isomerism mostly occurs in alkanes and cycloalkanes and their substituted derivatives.

Newman Projections

Newman projections are structural formulae used for representing molecules on a planar surface that are particularly useful in representing conformational isomers. In this projection, the molecule is viewed along the bond joining the carbon atoms. For example, in ethane molecule, the carbon atoms C₁ and C₂ are represented as superimposed circles, only one circle being drawn.

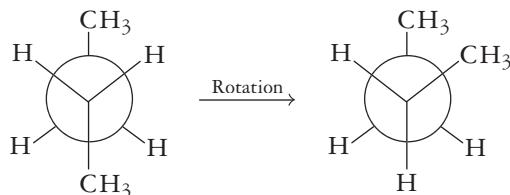


The center of the circle represents the front carbon C₁ while the circumference represents the back carbon atom C₂, the line joining the two carbon atoms is not visible. The remaining bonds on each carbon atom are shown by small straight lines at angles of 120° joined to the center and to the circumference.

The different conformations are characterized by the angles formed between the bonds on the front carbon atom and the bonds on the rear carbon atom, which are called *dihedral angles*.

Conformations

Conformations of a molecule are three-dimensional arrangements that differ only by rotation around a single bond. Each increment of rotation, however small, produces a change of conformation. In particular, the atoms remain connected in the same order during conformational change, with bonds being neither formed nor broken. For example, in *n*-butane,



Thus, a molecule can assume an infinite number of conformations because of rotation around its sigma bonds. However, certain conformations are more stable than others. Isolation of conformers in non-rigid systems is not feasible because the potential energy barrier for the inter-conversion is too low.

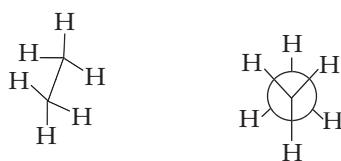
Conformations of Ethane

The energy required to rotate the molecule about the carbon–carbon bond is called torsional energy. In case, of ethane (or other alkanes), this energy is small and easily available at room temperature resulting from molecular collisions. As a result, there are infinite numbers of conformations possible about the carbon–carbon σ bond. Two extreme kinds of rearrangements are represented by

- Eclipsed conformation:** In which the C–H bonds of the front and back carbons are aligned with each other with dihedral angle of 0° .



- Staggered conformation:** In which the C–H bonds of the rear carbon lie between those of the front carbon with dihedral angle of 60° .



The infinite numbers of intermediate conformations are referred to as skew conformations.

Energy Diagram for Rotation about C–C in Ethane

The potential energy for all the conformations is different. For ethane molecule, it is the minimum for staggered conformation, increases with rotation and becomes maximum for eclipsed conformation (Figure 14). The relative instability of eclipsed or intermediate skew conformations as compared to

staggered conformation is due to torsional strain or strain due to steric hindrance. This instability of eclipsed form arises due to repulsive interactions arising from close proximity of electron densities on C–H bond.

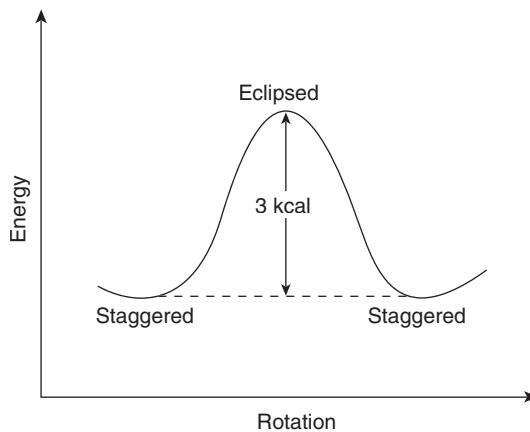
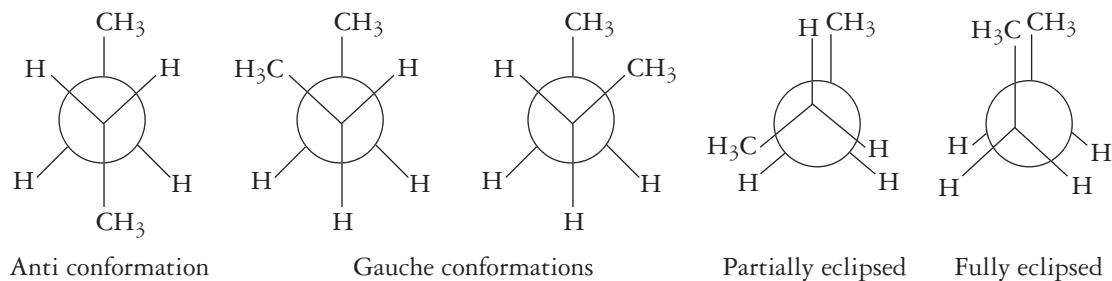


Figure 14 Energy diagram for rotation about carbon–carbon single bond in ethane.

Conformations of *n*-Butane

In *n*-butane, the C₂–C₃ bond can be considered similar to ethane in which one of the hydrogen is replaced by a methyl group. It has not only one staggered and eclipsed conformations but a number of other conformations arising due to relative orientation of the two methyl groups. These include

- Fully eclipsed (*syn*):** Here both the methyl groups are aligned, so that the dihedral angle between two methyl groups is 0°.
- Gauche:** This is a staggered form in which the methyl groups are in close proximity with dihedral angle equal to 60°. There are two gauche conformations possible.
- Partially eclipsed:** This arises due to further rotation of gauche conformation by 60°, such that the dihedral angle between two methyl groups becomes 120°.
- Anti:** This is a staggered conformation in which the two methyl groups are farthest from each other with dihedral angle 180°.



Energy Diagram for Rotation about C₂–C₃ in Butane

The eclipsed conformations are of higher energy than the staggered form due to close proximity of methyl groups. Both *anti* and *gauche* conformations are free from torsional strain, but there is steric hindrance

between the methyl groups in *gauche* conformation and it is less stable than *anti* form. The *anti* conformation with two methyl groups farthest apart (180°) is the lowest energy arrangement (Figure 15).

The increasing order of stability of these conformations is



Conformations of Cyclohexane

Cyclohexane has many conformations such as chair form, boat form, twist boat form and half chair form. Among these, the two extreme conformations are boat and chair form.

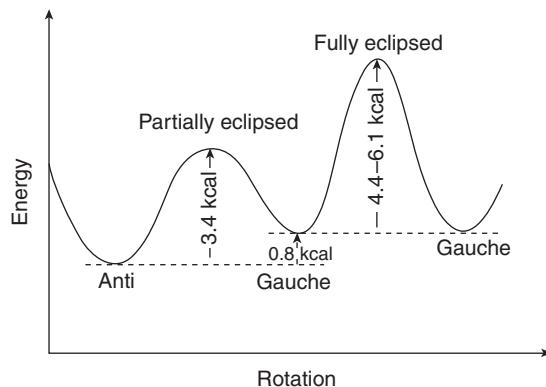
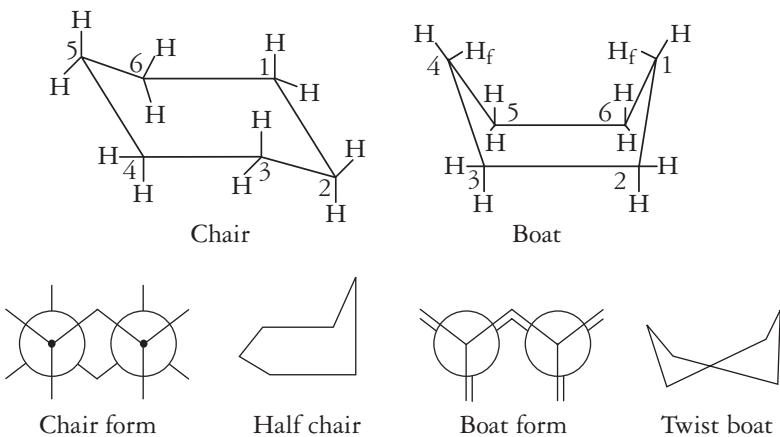


Figure 15 Energy diagram for rotation about C_2-C_3 in *n*-butane.



The relative energies of the different conformations of cyclohexane can be explained as follows:

1. The chair conformation is more stable than the boat conformation because of the following two reasons:
 - In chair conformation, all the hydrogen atoms on C_1-C_2 , C_2-C_3 , C_3-C_4 , C_4-C_5 , C_5-C_6 and C_6-C_1 are in more stable staggered orientations and hence there is no torsional strain.

On the other hand, in boat conformation, the adjacent hydrogen atoms on $C_2 - C_3$ and $C_5 - C_6$ are in the less stable eclipsed orientation. These eclipsing interactions raise the energy of boat form relative to the chair form.

- The two hydrogen atoms (marked as H_β) are called *flagpole hydrogens*. In boat form these are quite close to each other (1.83 Å) as compared to chair form (2.29 Å). These hydrogen atoms strongly repel each other and introduce steric strain in the boat conformation.
- 2. The boat conformation is stabilized by moving apart the flagpole hydrogens to give twist boat confirmation. This is a lower energy conformation due to reduced repulsion between flagpole hydrogens and reduced torsional strain between pair of side carbons.
- 3. Higher energy is associated with the transition conformation called the half chair. It is obtained by moving carbon C_1, C_2, C_3, C_4 of the chair conformation into one plane, while C_5 lies below and C_6 above the plane.

The relation between energies of different conformations is given in Figure 16.

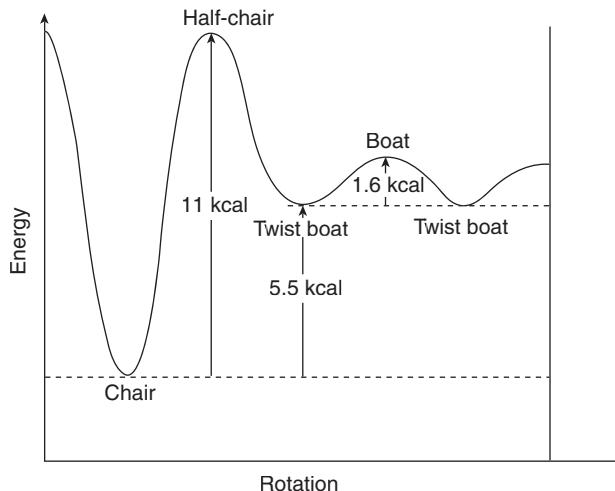


Figure 16 Potential energy relationship between different conformations of cyclohexane.

Concept Check

- How do different conformations arise in alkane molecules?
- Dihedral angle is the angle formed between the bonds on front carbon and bonds on rear carbon atom. What is the dihedral angle in staggered and eclipsed conformations in ethane molecule?
- How do you account for the following in conformation of *n*-butane:
- a. Higher energy of eclipsed conformation than staggered.
- b. Lower stability of *gauche* conformation as compared to *anti*.
- In cyclohexane, chair conformation is more stable than boat conformation. Explain.

ORGANIC REACTION MECHANISMS

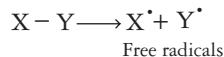
The common characteristic of organic compounds is the presence of the element carbon; and so organic chemistry can easily be defined as study of carbon compounds obtained from living sources. Organic chemistry is treated as a separate branch because of the existence of large number of organic compounds. These result from the unique ability of carbon to bond with itself to form long chain or ring compounds. Organic molecules are formed by covalent bonding between atoms, resulting from sharing of electrons. The reactions of organic compounds and their pathways are determined by the nature of this covalent bond. Since organic reactions are slow and occur through well-defined steps, it is possible to study organic reaction mechanism in detail.

4.8 Bonding in Organic Molecules

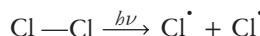
Organic molecules are mainly composed of covalent bonds, and organic reactions proceed by the cleavage of these bonds and formation of new bonds. The covalent bond is made up of two electrons known as the bonding pair, and this pair can be broken by homolytic or heterolytic fission.

Homolytic Fission

In homolytic fission, the covalent bond is cleaved in such a manner that one electron of the bonding pair remains with each of the originally bonded atoms. For example, in the molecule X—Y where two electrons are shared between atoms X and Y, homolytic cleavage leads to the formation of X[·] and Y[·] free radicals (free radicals will be discussed in detail, later in this chapter).



For example, when chlorine gas is exposed to sunlight, two chlorine free radicals are formed.

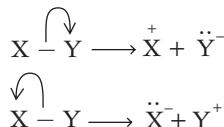


The shift of a single electron is represented by a single barbed fish-hook arrow (↖).

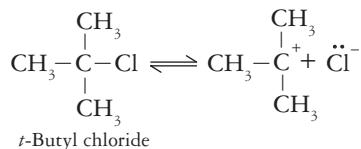
Heterolytic Fission

In heterolytic fission, the covalent bond is cleaved in such a manner that both the electrons of the bonding pair remain attached with only one of the two originally bonded atoms resulting in the formation of negative and positive ions.

For example, in the molecule X—Y, the bond cleavage may occur in either of the two ways:



For example,



The shift of an electron pair is represented by a double banded fish hook (\curvearrowright). In general heterolytic fission occurs when X and Y are not identical and homolytic fission occurs when X and Y are identical.

Concept Check

- Homolytic fission occurs when both the bonded atoms are the same. Explain.
- Heterolytic fission leads to the formation of positive and negative ions. Explain.

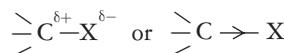
4.9

Electronic Displacement Effects in Organic Molecules

The bonding pairs of the covalent bond in organic compounds undergo electronic displacements on their own or under the influence of an attacking agent. These displacements may be temporary or permanent in nature and are described as follows.

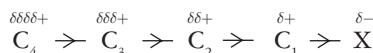
Inductive Effect

In a covalent single bond between non-identical atoms, the bonding pair (electron pair) forming the bond is not shared absolutely evenly between the two atoms. It is always attracted towards the more electronegative atom of the two. For example, in an alkyl halide $\text{C}-\text{X}$ when $\text{X} = \text{Cl}$, the electron density is greater near Cl than C because Cl is more electronegative than C. This is represented as:



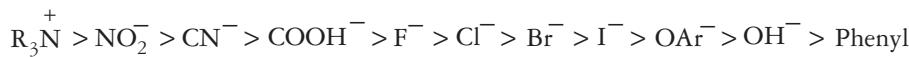
Although the bonding pair is permanently displaced towards the more electronegative atom, yet it remains in the same valence shell.

If the carbon atom that is bonded to the halogen is itself further bonded to carbon atoms, the effect is transmitted further down the chain as shown:



Here, X leaves C_1 slightly electron deficient, therefore C_1 pulls more than its share of electrons from the σ bond joining it to C_2 , and this continues down the chain. The effect of Cl on C_2 is less than the effect of Cl on C_1 and the extent of partial charge keeps on decreasing away from the polar bond. This effect is known as inductive effect. It decreases with the increase in distance and is not noticeable beyond C_2 .

1. The effect is said to be $-I$ if a group pulls the electrons away from the carbon atom. Such a group is called an electron withdrawing group. Electron withdrawing groups in the order of decreasing $-I$ effect are shown

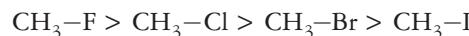


2. The effect is said to be $+I$ if a group pushes the electrons towards the carbon atom. Such a group is called electron releasing group. Electron releasing groups in order of decreasing $+I$ effect are shown



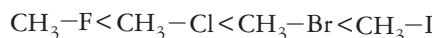
Applications of Inductive Effect

1. **Dipole moment:** Inductive effect causes development of a dipole moment in the molecule, which increases with increase in inductive effect. For example



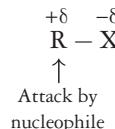
as the order of inductive effect is F > Cl > Br > I.

2. **Bond length:** The bond length of the organic molecules decreases with increase in inductive effect. For example

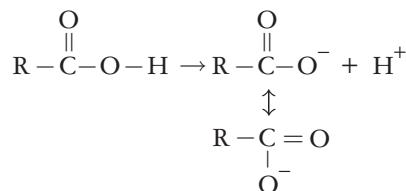


as the inductive effect increases in the order F > Cl > Br > I.

3. **Reactivity of alkyl halides:** The alkyl halide bond is polar in nature due to inductive effect ($-I$) of the halide ion. As a result, the carbon atom attached to halide acquires a partial positive charge and is easily attacked by a nucleophile. Alkyl halides thus undergo nucleophilic substitution reactions more readily than corresponding alkanes.

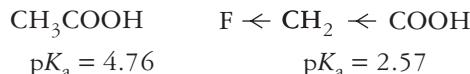


4. **Relative acidic strength of carboxylic acids:** The strength of the carboxylic acids is determined by the ease with which they lose a proton and form a carboxylate ion.



The nature of group R and the substituent present on it will affect the stability of carboxylate ion and hence the strength of the acid. Introduction of electron withdrawing substituent on to simple aliphatic acids increases the strength of the acid, because it stabilizes the carboxylate ion formed.

For example



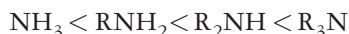
Fluorine being highly electronegative produces an increase in the strength of fluoroethanoic acid as compared to ethanoic acid itself.

Similarly on increasing the number of Cl atoms on the α -C atom, the acidity of the carboxylic acid increases. On introduction of electron donating substituents like alkyl groups on the acid, the

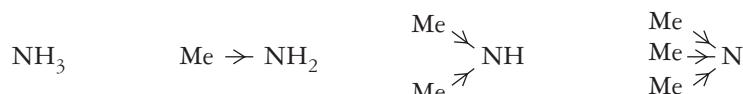
acidity decreases; however, this effect is not as large as compared to the effect produced by electron withdrawing substituents.

5. **Relative basic strength of amines:** Amines ($\text{R}-\text{NH}_2$) are basic organic compounds because there is an unshared electron pair on nitrogen and hence they can take up protons. On introduction of an alkyl group on to the amines, we might think that the basicity will increase because alkyl group is an electron donating group which will donate electrons and hence enhance the availability of the unshared electron pair on N.

Thus theoretically the basic strength of amines should increase in the following order due to increasing inductive effect of successive alkyl groups added, which make the N atom more negative.



However, the actual order of basicity of amines is



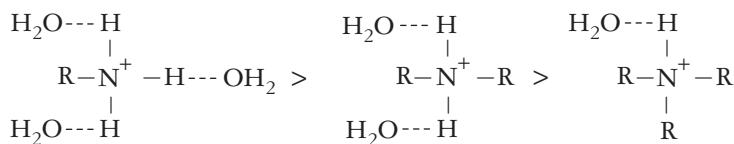
$$\text{p}K_a = 9.25$$

$$\text{p}K_a = 10.64$$

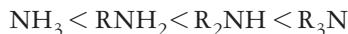
$$\text{p}K_a = 10.74$$

$$\text{p}K_a = 9.80$$

It is seen that introduction of a methyl group to ammonia significantly increases the basic strength as expected. The introduction of the second methyl group further increases the basic strength, but the net effect of introducing the second methyl group is much less significant than the first. The introduction of a third methyl group to yield a tertiary (3°) amine, however, decreases the basic strength. The reason for this decrease is that the basic strength of an amine in water is determined not only by the electron availability on the N atom, but also by the extent to which the cation formed by uptake of an H^+ ion undergoes solvation and becomes stabilized. More the number of H atoms attached to N in the cation, greater is the solvolysis via hydrogen bonding between these hydrogens and water molecules. Stability by solvation varies in the following order:



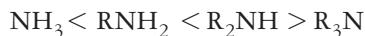
Thus the inductive effect will increase the basicity in the following order:



However, the solvation effect will reverse the order to



Thus, the net effect is



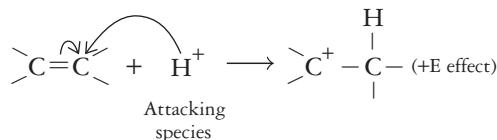
Inductomeric Effect

The inductive effect present in a molecule may be temporarily increased in the presence of an attacking species, which is generally a charged ion. This temporary increase aids the reaction and is known as inductomeric effect.

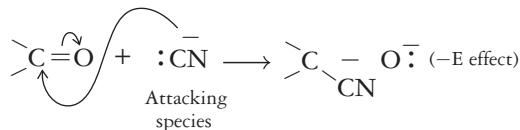
Electromeric Effect

This effect involves the displacement of π -electrons in a multiple bond towards one of the bonded atoms at the demand of an attacking species. It is a temporary displacement and a time-variable effect.

If the transference of π -electrons occurs towards the atom where attacking species attaches, it is called +E effect.



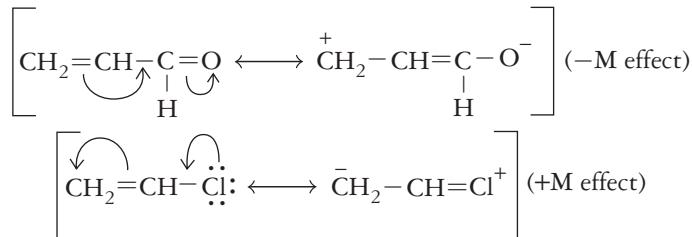
If the transference of π -electrons occurs away from the atom where the attacking group attaches, it is called -E effect.



Mesomeric or Resonance Effect

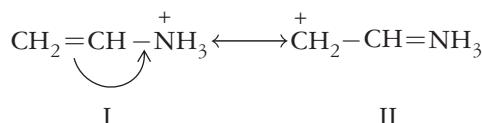
Electron redistributions take place in unsaturated, especially in conjugated systems via their π orbitals. This generates centers of high- and low-electron densities. This phenomenon is called resonance or mesomeric effect (R or M effect). It is a permanent effect.

- Groups which tend to withdraw electrons from the conjugated system possess -R or -M effect, for example, $-\text{NO}_2$, $\text{C}\equiv\text{N}$, $-\text{C}=\text{O}$, etc.
- Groups which tend to donate electrons to the conjugated system possess +R or +M effect, for example, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{NH}_2$, $-\text{OH}$, $-\text{OCH}_3$, etc.



Conditions for Resonance

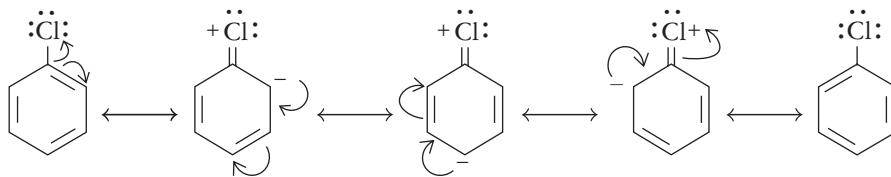
1. The resonance structures should differ only in the position of electrons and not in the position of atoms or nuclei.
2. All the resonance structures should have the same number of unpaired electrons.
3. In case of atoms present in the second period of the periodic table, those resonance structures which violate the octet rule should not be considered. For example,



Structure (II) cannot be considered as a resonance structure of (I) since it violates the octet rule because N in this structure has 10 electrons which is not feasible in absence of d orbitals.

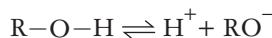
Applications of Resonance Effect

1. **Low reactivity of aryl and vinyl halides:** Aryl and vinyl halides do not undergo nucleophilic substitution because of delocalization of electrons by resonance. Consider halobenzene and its various resonance structures:

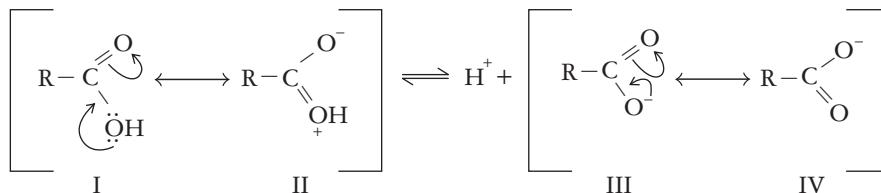


The C–Cl bond thus attains a double-bond character and is difficult to break.

2. **Carboxylic acids are more acidic than alcohols:** The OH of a carboxylic acid releases an H^+ ion more easily than OH of an alcohol. In ionization of alcohol, both alcohol and alkoxide ion are represented satisfactorily by a single structure:

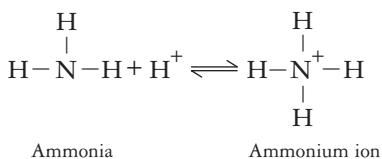


However, carboxylic acid and carboxylate ion may be represented by the following resonance structures:

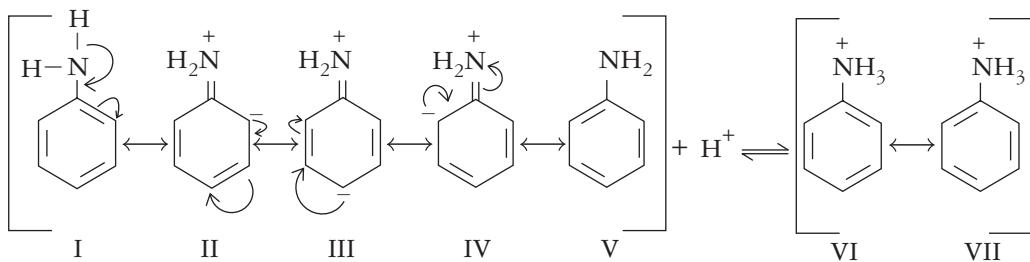


In case of carboxylic acid, two canonical structures (I and II) can be drawn; and for the carboxylate anion, two canonical structures (III and IV) can be drawn. The resonance is more significant between the exactly equivalent structures III and IV than between the non-equivalent structures I and II. Therefore, although both acid and anion are stabilized by resonance, stabilization is much more for the anion than for the acid. Equilibrium is, therefore, shifted in the forward direction and hence K_a is increased.

- Aromatic amines are less basic than ammonia:** In ionization of ammonia, both ammonia and ammonium ion are represented satisfactorily by a single structure.

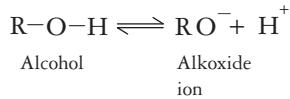


Aniline and anilinium ion contain a benzene ring and, therefore, are resonance hybrids of structures I–V and VI and VII, respectively.

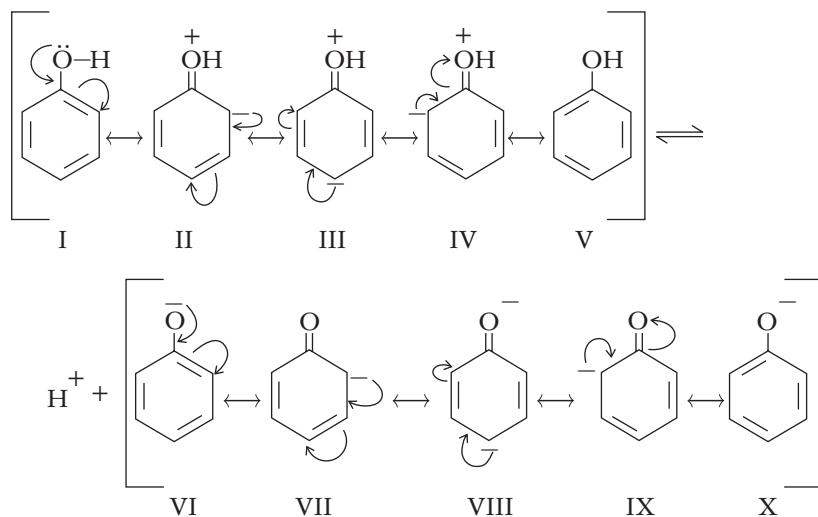


Aniline is stabilized by five resonating structures whereas anilinium ion is stabilized only by two. So the reaction prefers backward direction, and hence aniline is a weaker base than ammonia.

- Phenols are stronger acids than alcohols:** In the ionization of an alcohol, both the alcohol and alkoxide ion are each represented satisfactorily by a single structure.

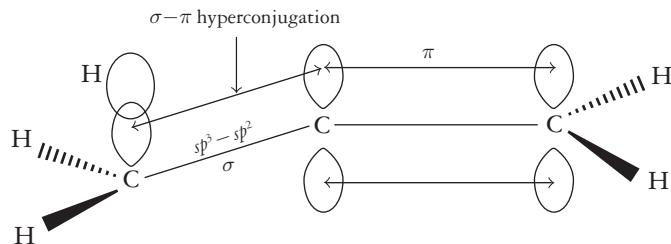


In ionization of phenol, both phenol and phenoxide ions contain a benzene ring and therefore are hybrid structures of I–V and VI–X, respectively. This resonance, presumably, stabilizes both the molecule and ion to the same extent. However, the structures II–IV contain both positive and negative charges, whereas structures VI–X contain only a negative charge. Since energy is required to separate the opposite charges, structures for phenol contain more energy and hence are less stable than those of phenoxide ion. Therefore, the net effect of resonance stabilizes the phenoxide ion to larger extent than phenol; and thus shifts the equilibrium in forward direction, thereby increasing K_a .



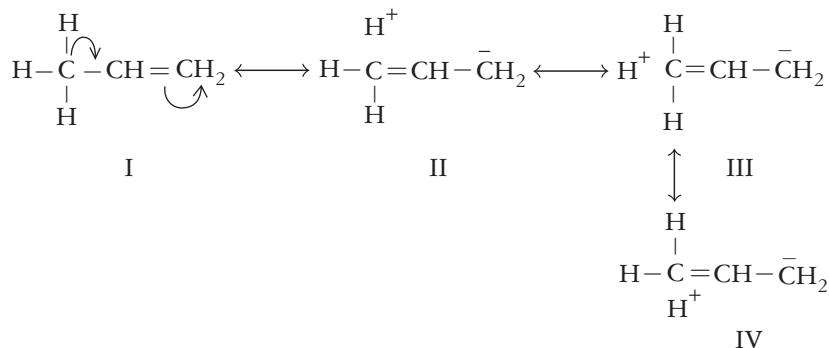
Hyperconjugative Effect: Baker–Nathan Effect

Hyperconjugation is the conjugation of σ electrons of a single C–H bond and the π electrons of the adjacent multiple bond. It is also called $\sigma-\pi$ conjugation or no-bond resonance because in the various canonical forms, no bond exists between C and H atom of the alkyl group directly attached to the multiple-bonded C atoms. This may be depicted diagrammatically as



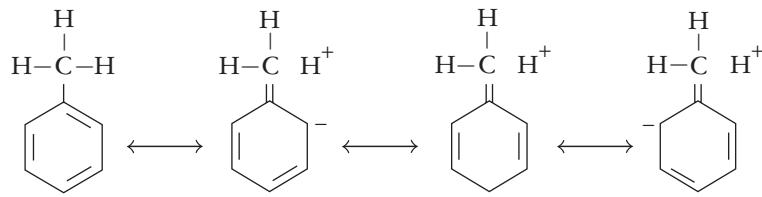
π electrons or adjacent non-bonding p -orbitals may also be involved in hyperconjugation. An example of stability of tert-butyl carbocation radical is discussed in Section 9.3.

For example in $\text{CH}_3-\text{CH}=\text{CH}_2$, the hyperconjugation may exist as



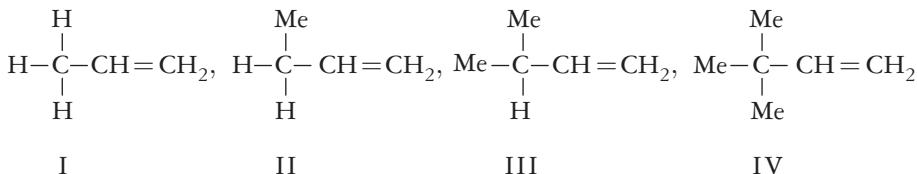
Applications of Hyperconjugation

1. *Ortho* and *para* directing influence of methyl or alkyl group:



We can see that electron density at *ortho* and *para* positions with respect to methyl groups increases due to hyperconjugation; and, therefore, electrophilic substitution in toluene will occur at *ortho* and *para* positions.

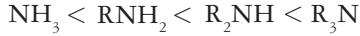
2. Relative stability of alkenes: Consider the following structures



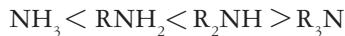
Since the maximum number of hyperconjugated structures is possible in I, so it is the most stable.

Concept Check

- Distinguish between inductive and electromeric effects with suitable examples.
- Introduction of electron-withdrawing substituents increases the strength of carboxylic acid. Explain why?
- Alkyl halides undergo nucleophilic reactions more readily than corresponding alkanes. Explain why?
- The order of basicity of amines expected on the basis of inductive effect is



However, the observed order of basicity is



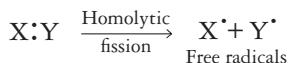
How will you account for the difference?

4.10 Reactive Intermediates

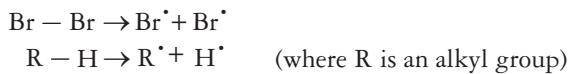
Reactive intermediates are short-lived and highly reactive chemical species formed by homolytic or heterolytic cleavage of a covalent bond. These include free radicals, carbocations, carbanions and carbenes.

Free Radicals

When homolytic fission occurs in a covalent bond, free radicals are generated. Free radicals possess an unpaired electron (single non-bonding electron). These radicals are highly reactive because they possess an odd electron which has a tendency to pair up with another available electron.



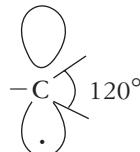
For example,



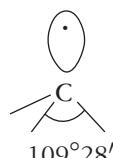
Free radicals are electrically neutral species and are paramagnetic due to the presence of an odd electron. They are generated in reactions either carried out at high temperatures or in presence of high energy radiation.

Structure

Free radical is a planar species in which the C atom bearing the odd electron is sp^2 hybridized. The carbon atom lies in the center of the triangle and the three bonds are directed towards the three corners of planar trigonal geometry. The odd electron lies in the unhybridized p orbital, perpendicular to the plane.

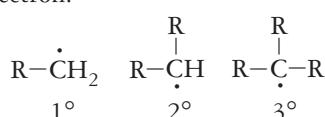


In some free radicals, the central carbon atom may be sp^3 hybridized with trigonal pyramidal geometry. The odd electron lies in the sp^3 hybrid orbital.

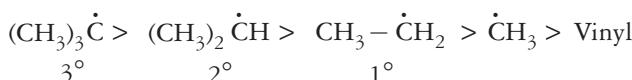


Stability

The free radicals are classified as primary (1°), secondary (2°) and tertiary (3°) depending on the nature of the carbon atom carrying the free electron.

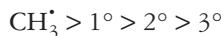


The relative stability of alkyl free radicals follows the order:

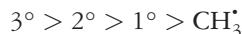


The relative stability can be explained on the basis of ease of formation and hyperconjugation.

1. Lower the homolytic bond dissociation energy, greater is the ease of formation of free radicals. The bond dissociation energy decreases in the order:



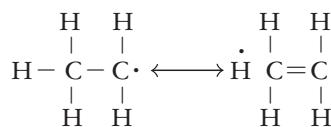
Therefore ease of formation is of the order:



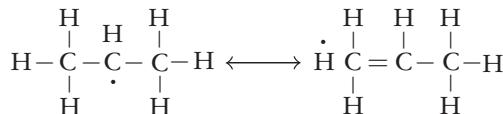
Greater the stability of the radical, more rapidly or easily it will be formed. Therefore, stability of free radicals also follows same order.

The relative stability of free radicals can also be explained on the basis of hyperconjugation. More the number of hyperconjugative structures, more will be the resonance energy and greater will be the stability of the free radical. Primary free radical has three hyperconjugative structures, secondary has six and tertiary has nine. Hence tertiary free radical is most stable. For example,

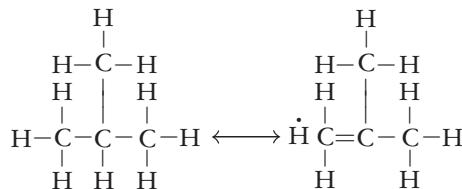
- Ethyl free radical may have three hyperconjugative structures, the one shown below and two more similar structures with other two hydrogen atoms.



- Isopropyl free radical may have six hyperconjugative structures, the one shown below and five more similar structures due to five other hydrogen atoms.

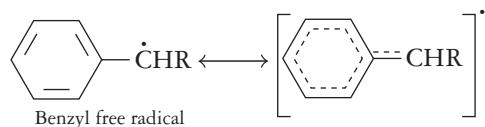
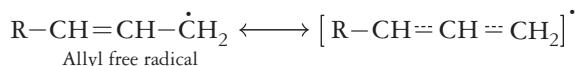


- Tertiary butyl free radical may have nine hyperconjugative structures, the one shown below and eight more similar structures due to eight other hydrogen atoms.



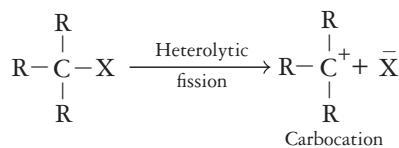
The stability of radical increases as the extent of potential delocalization increases, and due to nine hyperconjugative structures maximum delocalization is on the 3° free radical.

The greater stability of allyl and benzyl free radicals as compared to alkyl free radical can be explained on the basis of resonance. Due to resonance the delocalization of electrons increases, thereby increasing the stability.

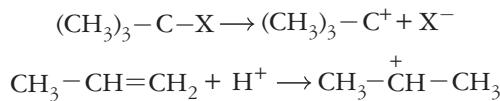


Carbocations

Heterolytic fission of covalent bond results in the formation of a carbocation, in which the carbon atom bears a positive charge and has six electrons in the valence shell.

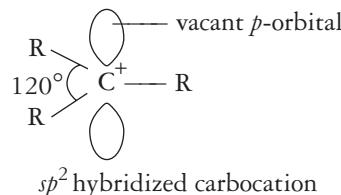


Carbocations were earlier referred to as carbonium ions. Carbocations may either be produced by direct ionization (e.g., in organic halides) or by protonation of multiple bonds.



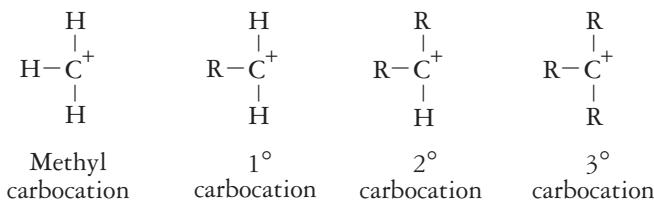
Structure

A carbocation has a planar structure. The carbon atom carrying the positive charge is sp^2 hybridized and bonded to three other atoms with bond angle of 120° . There is a vacant unhybridized p -orbital, lying perpendicular to plane of hybridized orbitals.

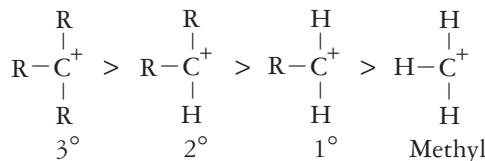


Stability

Alkyl carbocations can be classified as primary, secondary and tertiary.



The stability of these carbocations follows the order:

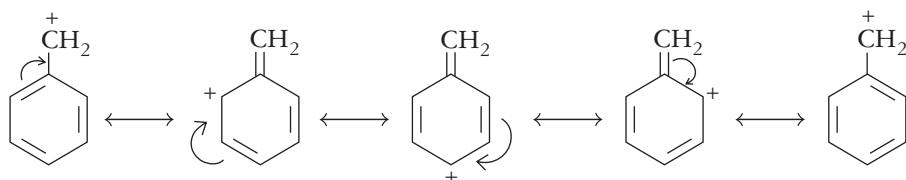


The stability order can be explained on the basis of the following:

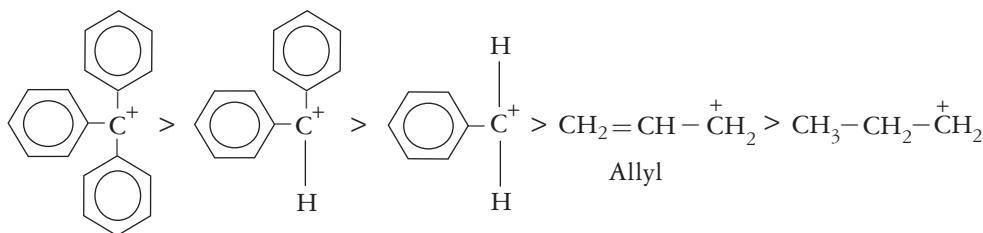
1. **Electron donating inductive effect of the alkyl group:** Greater the number of alkyl groups attached to the carbon bearing positive charge, greater will be the electron donation and hence

greater will be the positive charge dispersal. Therefore, the tertiary carbocation carrying three alkyl groups is the most stable.

2. **Hyperconjugation:** The relative order of stability of alkyl carbocations can be explained on the basis of hyperconjugation in a manner similar to the stability of alkyl free radicals. Tertiary carbocation with nine hyperconjugated structures is the most stable followed by secondary and primary carbocations.
3. **Resonance:** Stability of aryl carbocations can be explained on the basis of resonance.



Due to resonance, the positive charge on the central carbon atom gets dispersed over the other C atoms and hence this carbocation gains a lot of stability. More the number of canonical structures more will be the positive charge dispersal and greater will be the stability. Therefore,



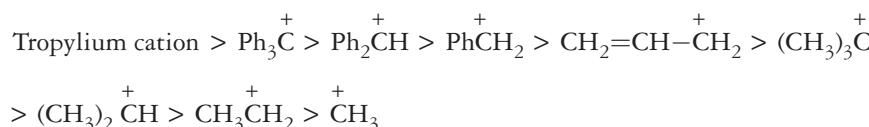
The reason for the stability of allyl carbocation is again resonance:



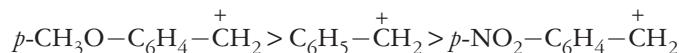
- The basic requirement for a carbocation to be stable is that it should be planar, because it is only in this configuration that effective delocalization can occur. For example, tropylium cation is planar, has 6π electrons and is stabilized by aromatization.



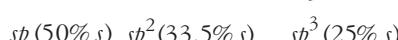
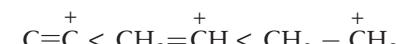
Hence, the order of stability is



- If there is an electron donating substituent in the benzene ring, it stabilizes the carbocation by dispersing the positive charge, whereas if an electron withdrawing substituent is attached to the benzene ring, it destabilizes the carbocation by intensifying the positive charge. Hence, the order of stability is

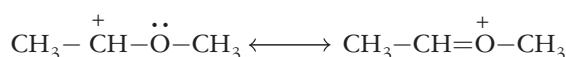


- If we compare the carbocations of an alkane, alkene and alkyne, we see that the stability of the carbocation having maximum *s* character is the least; and as the *s* character decreases, the stability increases.



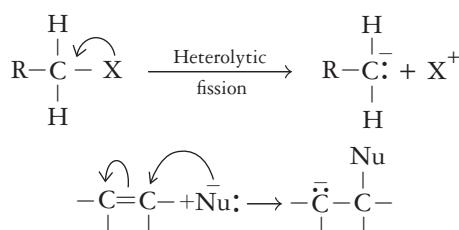
This is because more the *s* character more will be the electronegativity of that carbon; and hence it will be difficult for it to carry a positive charge.

- If the carbocation contains a hetero atom (O, N, Cl, etc.) having a lone pair of electrons, the stability of carbocation increases due to resonance. For example,



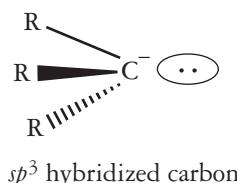
Carbanions

Carbanions are also formed by the heterolytic fission of a covalent bond. The central carbon atom has a negative charge and possesses an unshared pair of electrons. It is generated when carbon is attached to a less electronegative element or by nucleophilic attack on a carbon–carbon multiple bond.



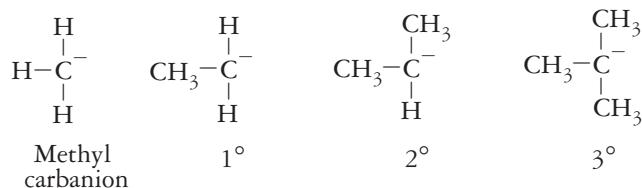
Structure

The carbon atom bearing the negative charge in the carbanion is in sp^3 hybridized state. It is bonded to three other atoms and the unshared electron pair occupies the apex of the tetrahedron.

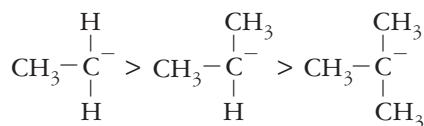


Stability

Alkyl carbanions can be classified as primary, secondary and tertiary.

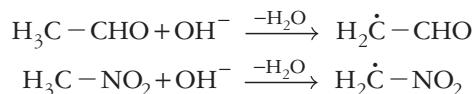


The relative order of stability of carbanions is

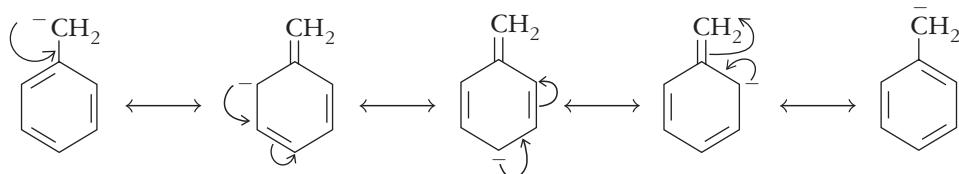


The stability order can be explained with the help of +I effect of the alkyl groups. Greater the number of alkyl groups attached to the C bearing the negative charge, greater will be the electron donating effect and hence the negative charge will be intensified. Therefore, tertiary carbanion carrying three alkyl groups is least stable.

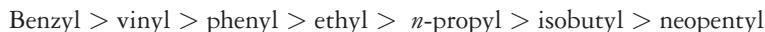
The carbanions are stabilized by the presence of electron withdrawing groups. Few examples of carbanions that are readily formed under experimental conditions are as follows:



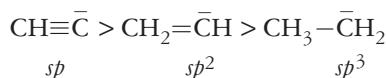
The stability of aryl carbanions can be explained on the basis of resonance.



Due to resonance, the negative charge on the central carbon atom gets dispersed over the other C atoms of the ring, and hence this carbanion gains a lot of stability. Hence the stability follows the following order:



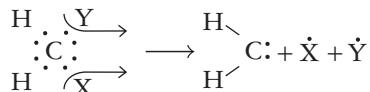
If we compare the carbanions of an alkane, alkene and alkyne, the stability of the carbanion having maximum s character is the maximum. As the s character decreases, the stability decreases.



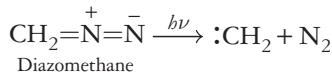
This is because more the s character more will be the electronegativity of that C; and hence it will be easier for it to carry a negative charge.

Carbene

These are highly reactive species containing divalent carbon having no charge and surrounded by a sextet of electrons. For example, :CH_2 is called methylene carbene and :CCl_2 is known as dichlorocarbene. There are two non-bonded electrons on the carbon in carbenes. These non-bonding electrons are derived by the homolytic fission of bonds.



They are generated by photolytic cleavage, for example, methylene carbene is generated by photolysis of diazomethane.

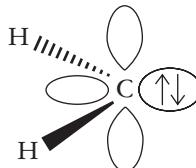


Since the C atom in carbenes has six electrons, it is an electron deficient species.

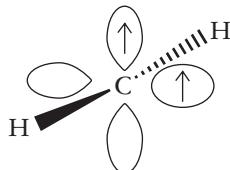
Structure

Carbenes exist in two forms: singlet or triplet.

- Singlet:** If both non-bonding electrons are in one orbital (antiparallel spin) then the carbene is said to be in a singlet state. This is a diamagnetic state. It has a trigonal geometry with carbon undergoing sp^2 hybridization.



- Triplet:** If both non-bonding electrons go into different orbitals (unpaired spins) then the carbene is said to be in triplet state. This is a paramagnetic state. The triplet carbene can be linear (sp hybridized) or bent (sp^2 hybridized).



Concept Check

- Explain the stability of alkyl free radicals on the basis of ease of formation.
- Account for the following order of stability of alkyl free radicals on the basis of hyperconjugation.
tert-Butyl > Isopropyl > Ethyl
- Allylic and benzylic free radicals are more stable than alkyl free radicals. Explain.
- The order of stability of alkyl carbocation is Tertiary > Secondary > Primary > Methyl
- Explain on the basis of inductive effect.
- The stability of carbocation with a heteroatom containing a lone pair of electrons increases. Why?
- Explain the following order of stability in carbanions.
Benzyl > Vinyl > Phenyl > Ethyl > Isobutyl > Neopentyl
- How are carbenes formed and what are the two forms of their existence?

4.11 Attacking Reagents in an Organic Reaction

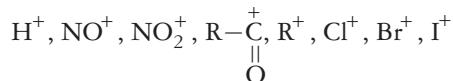
Electrophiles

Electrophiles (meaning electron loving) are electron-deficient species seeking a site of high electron density. Electrophiles have an incomplete outer electron shell and are very reactive. They could be (a) neutral species in which the central atom has six electrons or (b) positively charged species, both of which are deficient in electrons.

- 1. Examples of neutral electrophiles are



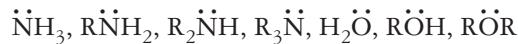
- 2. Examples of positively charged electrophiles are



Nucleophiles

Nucleophiles (meaning nucleus loving) are electron-rich species with a tendency to donate a pair of electrons. They attack electron deficient sites and could be neutral or negatively charged.

- Examples of neutral nucleophiles are



- Examples of negatively charged nucleophiles are



Nucleophiles that have more than one site for attacking the substrate are known as ambident nucleophiles. For example

$\text{C}\equiv\text{N}^-$	$\text{S}-\text{C}\equiv\text{N}$	O \parallel $\text{N}-\text{O}^-$
Cyanide	Isothiocyanate	Nitrite
$\text{C}=\text{N}^-$	$\text{S}=\text{C}=\text{N}^-$	NO_2^-
Isocyanide	Thiocyanate	Nitro

Concept Check

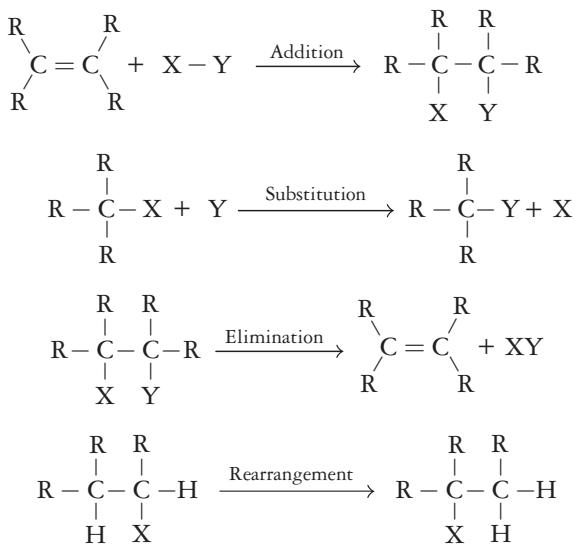
- Classify the following into electrophiles and nucleophiles:
 - What is an ambident nucleophile? Give two examples.
- $\text{BF}_3, \text{RCOO}^-, \text{ROH}, \text{NO}_2^+, \text{CN}^-, \text{RNH}_2, \text{OR}^-$

4.12 Types of Organic Reactions

Organic reactions may be broadly classified into

1. Substitution
2. Addition
3. Elimination
4. Rearrangement

These may be represented as follows:



Concept Check

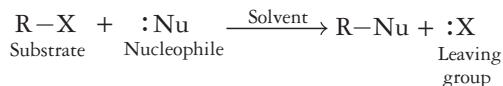
- What are the different kinds of organic reactions?
- Distinguish between substitution and rearrangement reactions.

4.13 Substitution Reactions

In these types of reactions, an atom or group replaces another atom or group present in a compound, without causing a change in the structure of that compound. Free radicals, electrophiles or nucleophiles may be involved in these reactions as reactive intermediates to bring about free radical, electrophilic and nucleophilic substitutions, respectively.

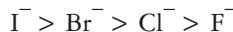
Nucleophilic Substitution (S_N)

These reactions occur in the presence of nucleophiles. Apart from nucleophiles, nucleophilic substitution reaction requires a substrate (which contains an alkyl group and a leaving group) and solvent.



Both nucleophiles and leaving groups are bases, but out of the two, the leaving group is a weaker base. Some terms related to nucleophilic substitution reactions are as follows:

- Nucleophilicity:** The interaction of the nucleophile with carbon is determined by its nucleophilicity. A good nucleophile should have a large attacking atom, high polarizability and should be weakly solvated.
- Nucleophilicity order:** Iodide ion being large, highly polarizable and weakly solvated is a strong nucleophile as compared to the small, less polarizable and strongly solvated fluoride ion. Therefore, the order is



- Leaving group:** A leaving group leaves with the electrons of the σ bond. Better the leaving group, faster is the reaction. The leaving ability of the leaving group (X) depends on three factors:

- strength of the R–X bond;
- polarizability of R–X bond;
- stability of X^- .

A good leaving group should be a weak base.

Nucleophilic substitutions take place mainly by two mechanisms: unimolecular and bimolecular. This can be determined by kinetic studies.

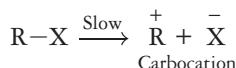
Unimolecular Mechanism (S_N1)

In S_N1 reactions, the rate of the reaction depends only on the concentration of the substrate and is independent of concentration of nucleophile.



Mechanism

It follows first order kinetics and is a two-step mechanism. The first step is the slow step and is the rate determining step.

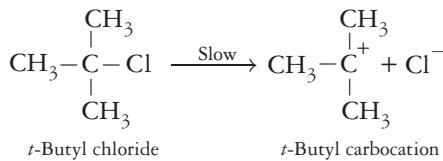


The second step, which is the fast step, involves the attack of the nucleophile on the carbocation. For example

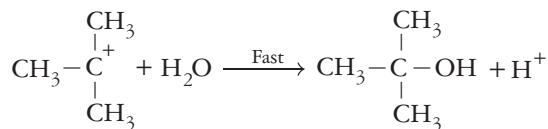


For example, consider nucleophilic substitution on *t*-butyl chloride

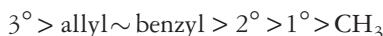
Step 1:



Step 2:

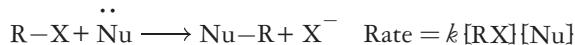


Since the nucleophile can attack the carbocation from either side, the reaction proceeds with racemization. Also, as the rate determining step in S_N1 mechanism is the formation of the carbocation, therefore, the order of reactivity of substitutes will depend on the stability of the carbocation formed after ionization of substrate. Thus, the order of reactivity of alkyl halides is similar to the order of stability of carbocations:



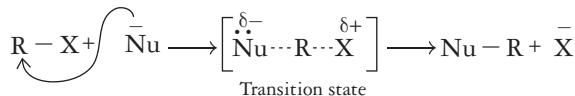
Bimolecular Mechanism (S_N2)

In an S_N2 reaction, the rate of the reaction is dependent both on the concentration of the substrate as well as the nucleophile.



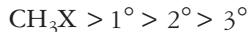
Mechanism

The S_N2 reaction proceeds in a single step via a transition state.



In an S_N2 reaction, there is a simultaneous attack by the nucleophile on the opposite side of the substrate followed by the departure of leaving group. Therefore, in the transition state the nucleophile–carbon bond is partially formed and the C–X bond is partially broken. The nucleophile cannot attack from the side of the molecule bearing the leaving group due to electrostatic repulsion and also due to steric factors. Thus, the attack will be from side opposite to the leaving group and the substitution reaction will proceed with inversion of configuration. This inversion is called Walden inversion.

Steric hindrance around the central carbon atom plays a significant role in the rate of S_N2 reaction. The reactivity towards S_N2 mechanism decreases with increase in number of substituents on the carbon bearing the leaving group. The reactivity in S_N2 mechanism follows the order:

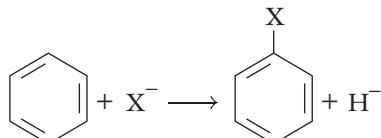


In the reactant and product, the central carbon atom is tetrahedral and in the transition state it is bonded to five atoms or groups. Therefore, we see that there is an increase in crowding moving from the reactant to the transition state. As the hydrogen atoms are replaced by the larger methyl groups, there is increased crowding about the central carbon atom and hence, it is difficult for the nucleophile to attack.

Nucleophilic Aromatic Substitution

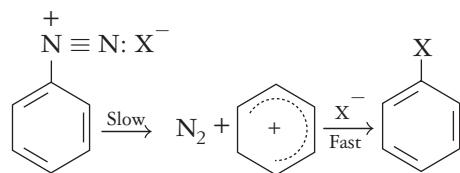
When either hydrogen or any other substituent is replaced by a nucleophilic agent in an aromatic ring, the reaction is known as *nucleophilic aromatic substitution*. Significantly, the substitution does not take place with benzene but with substituted benzene derivatives and naphthalene. Benzene does not undergo nucleophilic substitution due to

- the concentration of a negative charge above and below the plane of the carbon atoms of the ring and
- the formation of the less stable hydride ion.



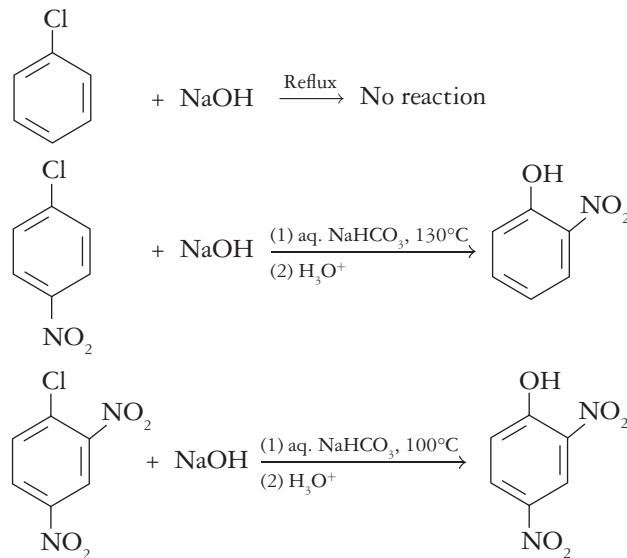
The three main mechanisms through which nucleophilic aromatic substitutions can take place are as under:

- Unimolecular mechanism:** Nucleophilic aromatic substitution does not usually occur by unimolecular mechanism because phenyl cations are unstable. There is only one example of such a reaction, which is the uncatalyzed decomposition of the aryl diazonium cation.

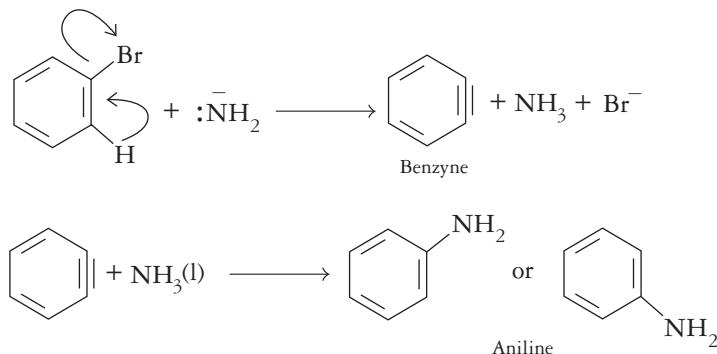


where $X^- = OH^-$, OR^- , Cl^- , CN^- and NO_2^- .

- Bimolecular mechanism:** The aryl halides do not readily undergo substitution by bimolecular mechanism because the benzene ring prevents the back-side attack. Also, the carbon–halogen bond is strong and develops double bond character stabilized by resonance structures. However, they become reactive towards nucleophiles and readily undergo substitution in presence of strongly electron withdrawing groups present *ortho* or *para* to the halogen atom. For example, chlorobenzene boiled with sodium hydroxide does not produce phenol except under high temperature and pressure conditions. However, *mono*-, *di*-, and *tri*-substituted chlorobenzenes react with sodium hydroxide at increasingly milder conditions to yield phenol.



3. **Benzyne mechanism:** Although unreactive, aryl halides react with nucleophiles under extreme conditions of temperature and pressure. The reaction proceeds through an elimination-addition mechanism involving a reactive intermediate benzene. In the first step of the reaction, hydrogen halide (HX) is eliminated from aryl halide. This leads to the formation of highly unstable benzene intermediate with a triple bond. Finally, the product is formed by addition of the nucleophile to this intermediate. Formation of aniline from bromobenzene is one example:



Concept Check

- The reactivity of alkyl halides towards $\text{S}_{\text{N}}1$ mechanism follows same order as stability of carbocations. Explain.
- Arrange the following in decreasing order of reactivity towards $\text{S}_{\text{N}}2$ substitution:
 $\text{CH}_3-\text{Cl}, \text{CH}_2\text{CH}_2-\text{Cl}, (\text{CH}_3)_2\text{CH}-\text{Cl}, (\text{CH}_3)_3\text{C}-\text{Cl}$
- What are the steps involved in electrophilic substitution on aromatic compounds?
- How does the presence of electron donating and electron withdrawing groups affect the reactivity and orientation of further electrophilic substitution in aromatic compounds?
- Why is an aromatic ring unreactive towards nucleophilic substitution? Give an example of nucleophilic aromatic substitution reaction.

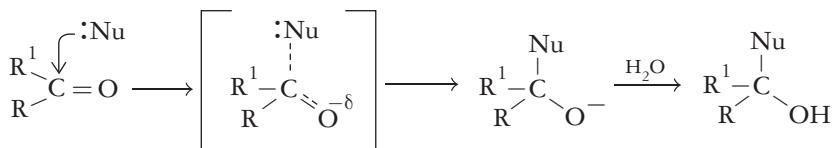
4.14 Addition Reactions

Addition reactions occur in compounds containing multiple bonds, for example, $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{C}=\text{O}$, $\text{C}\equiv\text{N}$, etc. The addition reactions can proceed through:

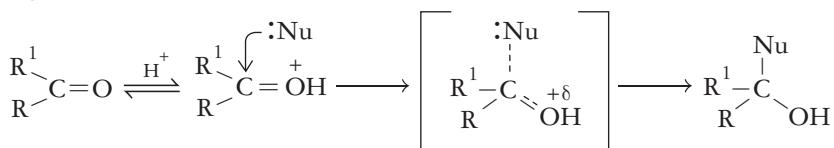
1. nucleophilic addition;
2. electrophilic addition;
3. free radical addition.

Nucleophilic Addition

Nucleophilic addition generally occurs in compounds containing polar functional groups; for example, $\text{C}=\text{O}$, $\text{C}\equiv\text{N}$, $\text{C}=\text{S}$, etc., most important of them being $\text{C}=\text{O}$.

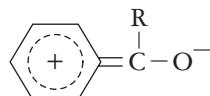


Nucleophilic addition to carbonyl compounds is catalyzed by an acid. The protonated carbonyl group undergoes nucleophilic attack more readily because oxygen can take electrons without acquiring a negative charge.



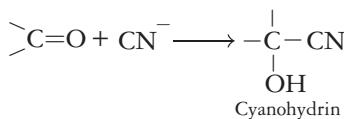
Aldehydes undergo nucleophilic addition more readily than ketones. This is because a ketone contains a second alkyl or aryl group and hence causes crowding. An alkyl group also releases electrons and thus destabilizes the transition state by intensifying the negative charge developing on oxygen.

An aryl group has an electron withdrawing inductive effect, and thus it is expected that it will stabilize the transition state and increase the rate of the reaction. However, it seems to stabilize the reactant even more by resonance and thus causes net deactivation.

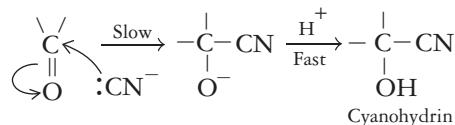


The examples of nucleophilic addition are as follows:

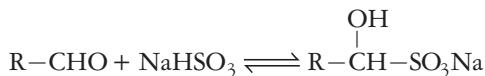
1. Addition of a cyanide to carbonyl group (cyanohydrin formation)



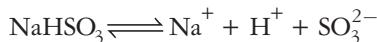
Mechanism

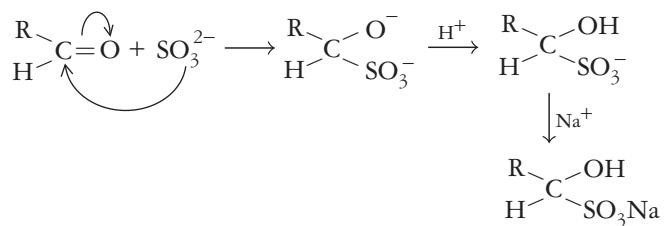


2. Addition of bisulphite to carbonyl group

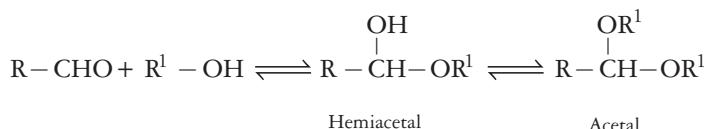


Mechanism

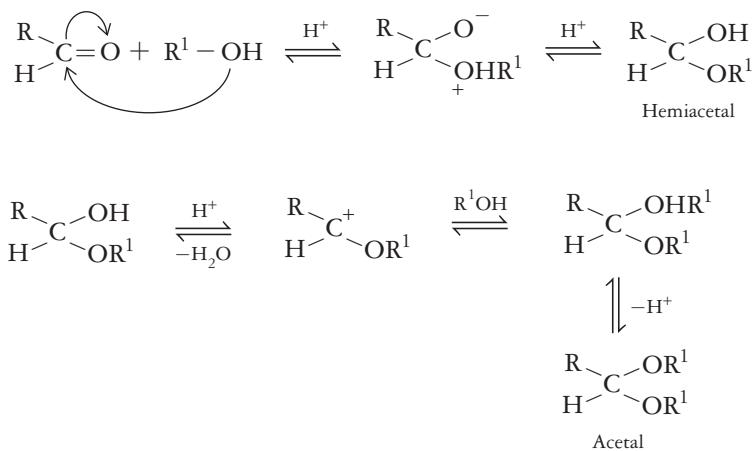




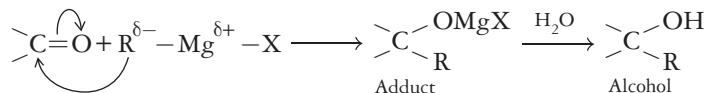
3. Addition of alcohol to carbonyl compounds



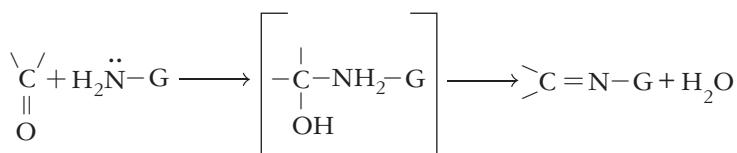
Mechanism



4. Addition of Grignard reagent



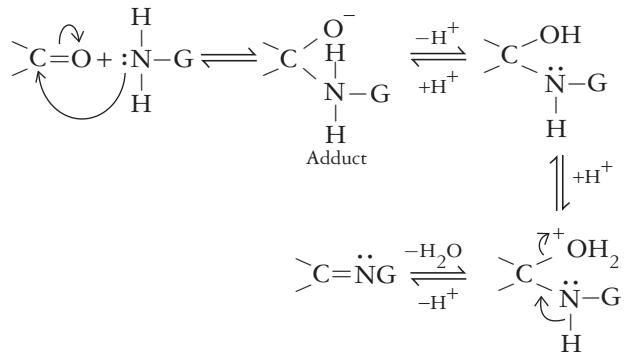
5. Addition of derivatives of ammonia to carbonyl compounds



The derivatives and the products formed from them are shown as follows:

H_2N-G	Name	Product	Name
H_2N-OH	Hydroxilamine	$\begin{array}{c} \diagup \\ C=N-OH \end{array}$	Oxime
H_2N-NH_2	Hydrazine	$\begin{array}{c} \diagup \\ C=N-NH_2 \end{array}$	Hydrazone
$H_2N-NHC_6H_5$	Phenylhydrazine	$\begin{array}{c} \diagup \\ C=N-NHC_6H_5 \end{array}$	Phenylhydrazone
$H_2N-NHCONH_2$	Semicarbazide	$\begin{array}{c} \diagup \\ C=N-NHCONH_2 \end{array}$	Semicarbazone

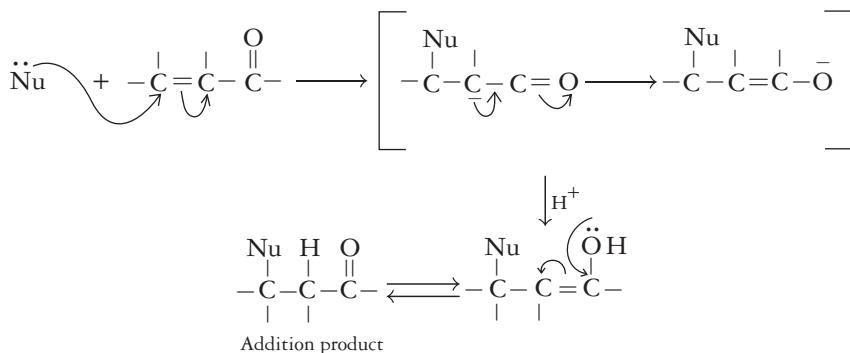
Mechanism



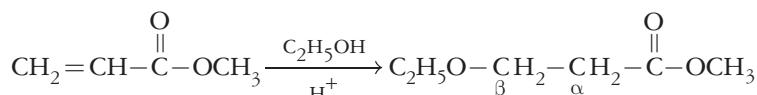
6. Nucleophilic addition to activated carbon–carbon double bond

Carbon–carbon double bonds conjugated with electron withdrawing substituents are called activated carbon–carbon double bonds. Such nucleophilic additions reactions are observed in α, β -unsaturated aldehydes, ketones, esters, nitriles, etc. Because of the presence of electron withdrawing substituents, the π electron density on the carbon–carbon double bond is reduced and this results in the facilitation of nucleophilic attack.

Mechanism

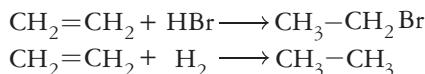


For example,



Electrophilic Addition

These reactions are brought about by electrophiles and occur in compounds containing carbon–carbon double or triple bonds. For example,

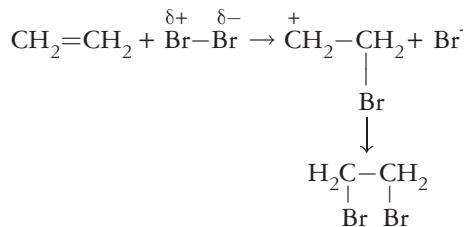


A carbon–carbon double bond is made up of

1. a strong σ bond, with electron distribution along the line joining the two carbon nuclei and
2. a weaker π bond, with electron pair in orbitals perpendicular to the plane of carbon nuclei.

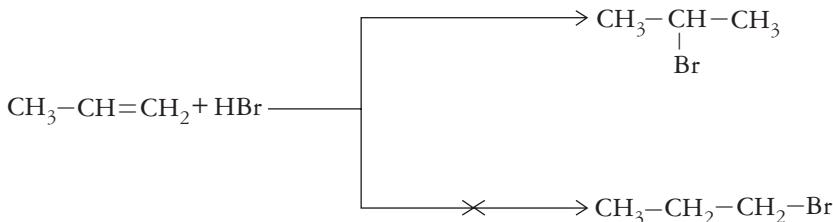
These π electrons are held less firmly by the carbon nuclei and are more readily polarizable than σ bond. Also, these π -electrons attract electrophilic species and undergo electrophilic addition reactions.

1. **Addition to symmetrical alkenes:** In the following reaction when bromine comes in proximity of an alkene, it gets polarized due to the π electrons of the alkene. The positive end of the polarized bromine molecule gets attached to the π electron cloud of the alkene leading to the formation of a π complex, which further reacts with bromine to form dibromoethane.

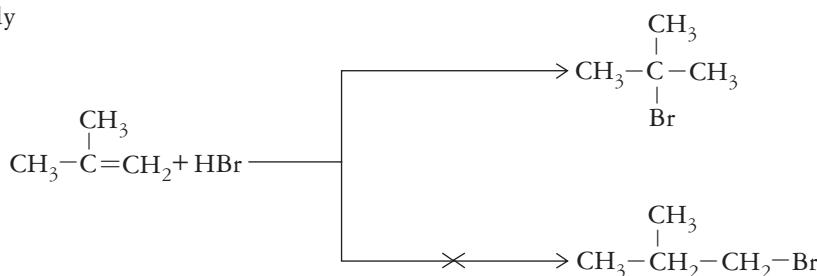


Electrophilic addition reactions are facilitated by the presence of electron donating substituents because they stabilize the transition state carrying a positive charge.

2. **Addition to unsymmetrical alkenes:** It is observed that in nucleophilic addition to unsymmetrical alkenes, one addition product is formed in preference over the other. For example,



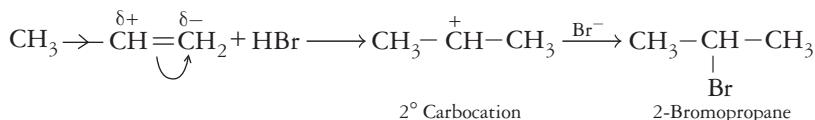
Similarly



Markownikoff, a Russian chemist, formulated an empirical rule called Markownikoff's rule to explain this reaction. According to this rule, the negative end of the reagent goes to the carbon atom containing lesser number of hydrogen atoms. In other words, negative part of the addendum goes to the highest substituted carbon.

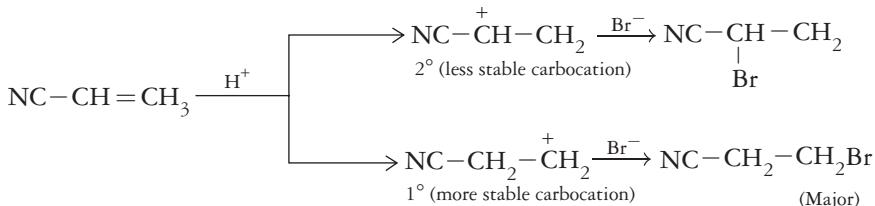
Mechanism

Mechanistically, Markownikoff's rule can be explained as follows:

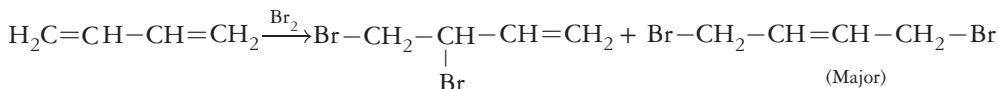


In this case, $+I$ effect of the methyl group displaces the π electrons towards the terminal carbon atom, because of which it gets a partial negative charge. So H^+ adds to the terminal C atom, followed by addition of bromide ion.

Markownikoff's rule is, however, not applicable to alkenes which contain electron withdrawing groups. For example,

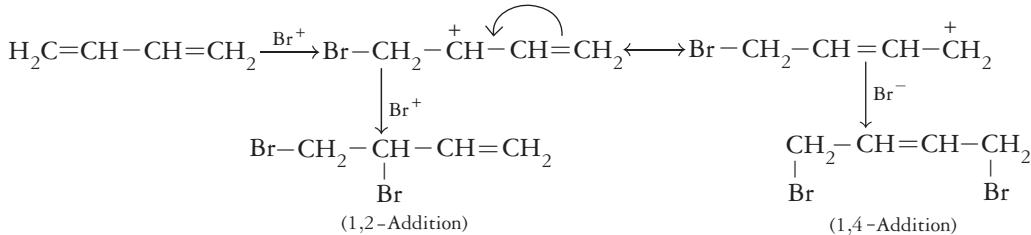


3. **Addition to conjugated dienes:** When a conjugated diene like 1,3-butadiene reacts with bromine, the major product obtained is 1,4-dibromo-2-butene.



Mechanism

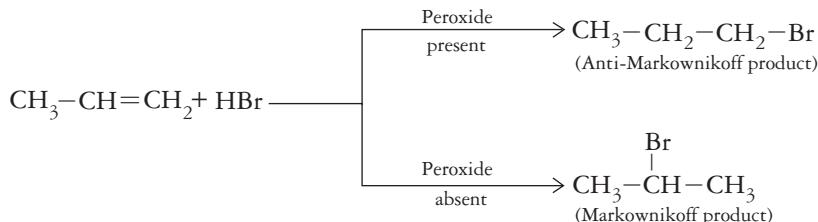
Mechanistically, this can be explained as follows:



In this reaction, the 1,2-addition product predominates at lower temperatures and 1,4-addition product predominates at higher temperatures.

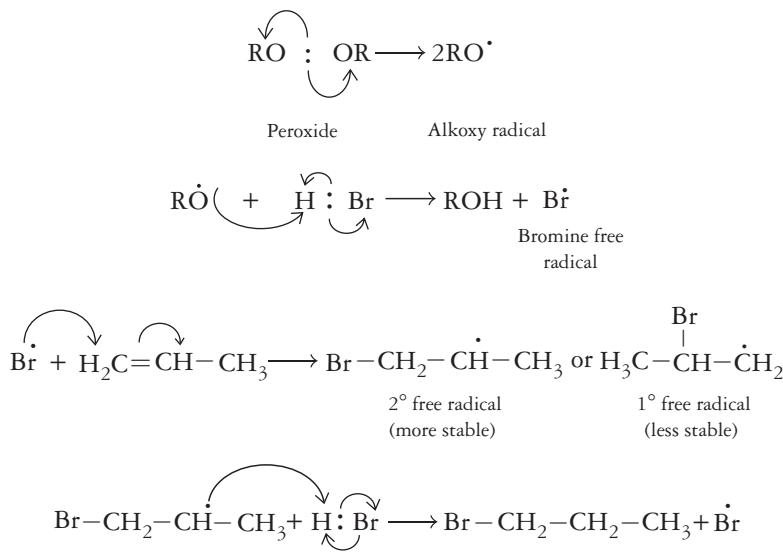
Free Radical Addition

In the presence of peroxide, addition of HBr to unsymmetrical alkenes leads to the formation of a product which is different from the Markownikoff's product. This effect was observed by Kharasch and Mayo and is also known as Peroxide effect.



Mechanism

Mechanistically it can be explained as follows:



Concept Check

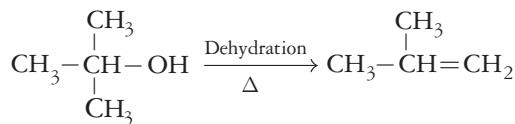
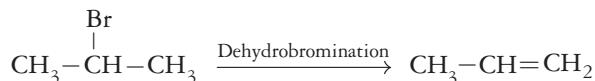
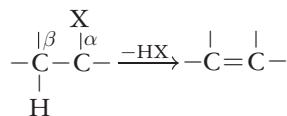
- Nucleophilic addition to carbonyl compounds is catalyzed in the presence of acid. Explain.
- Why are aldehydes more reactive towards nucleophilic addition than ketones?
- How will you obtain an acetal from a carbonyl compound?
- Electrophilic addition reactions are facilitated by the presence of electron donating substituents. Why?
- Which of the two alkenes will give Markownikoff's addition products?

$$\begin{array}{l}
 \text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow \\
 \text{NO}_2-\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow
 \end{array}$$
- In presence of peroxide, anti-Markownikoff's product is obtained. Why?

$$\begin{array}{l}
 \text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow \\
 \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Br}
 \end{array}$$

4.15 Elimination Reactions

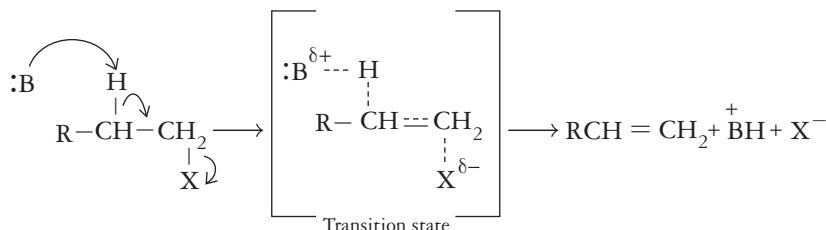
As the term suggests, elimination involves the removal of two atoms or groups. In these reactions, an atom or a group from α -carbon atom and a proton from the β -carbon are eliminated.



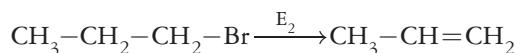
Elimination reactions proceed through two mechanisms: bimolecular and unimolecular.

Bimolecular Elimination Reactions (E_2)

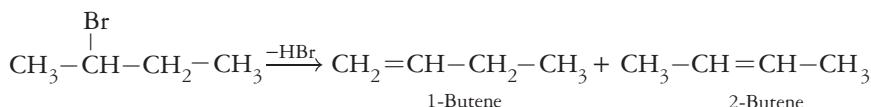
The rate of elimination depends on the concentration of the substrate and the nucleophile in these reactions. The reaction is of second order and is a one-step process just like the S_N2 reaction.



It is also called 1,2-elimination or β -elimination. For example,

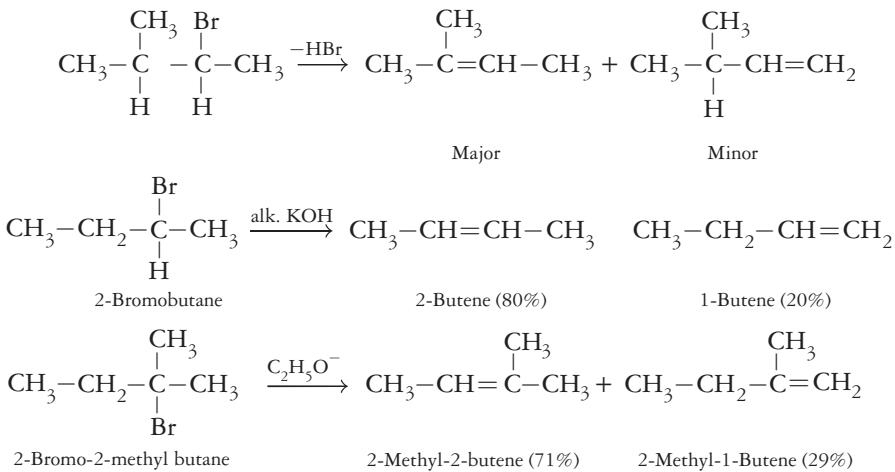


Unsymmetrical substrate, which has hydrogen attached to two different β -carbons, can afford two alkenes. For example, 2-bromobutane on dehydrohalogenation may give 1-butene or 2-butene.



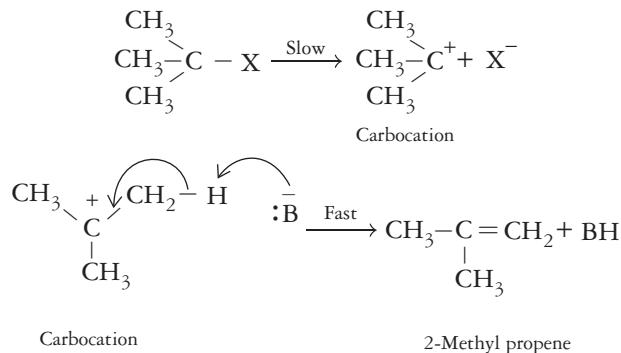
The alkene, which will be obtained in major amount, in the above dehydrohalogenation is decided by Saytzeff rule.

Saytzeff rule: According to this rule, hydrogen is eliminated preferentially from the carbon atom which has less number of hydrogen atoms and so the highly substituted alkene is the major product.



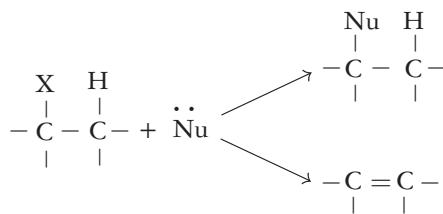
Unimolecular Elimination Reactions (E_1)

The rate of elimination depends only on the concentration of the substrate. The reaction is of first order (E_1).



Elimination versus Substitution

In alkyl halides, elimination and nucleophilic substitution are two competing reactions that may take place.

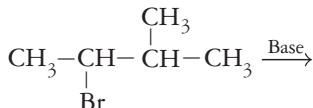


The course of reaction is greatly influenced by the amount of alkyl substitution on the carbon bonded to halide. Some observations are as follows:

1. Methyl halides will undergo only substitution reaction.
2. Primary halides will undergo mainly substitution. Elimination may predominate in presence of a strong base.
3. Secondary halides will give substitution products with weak bases and elimination product will predominate in the presence of a strong base.
4. Tertiary halides will undergo S_N1 reactions at low temperatures and in the presence of weak base. Elimination reactions by E_1 and E_2 mechanisms take place at high temperatures with weak and strong bases, respectively.

Concept Check

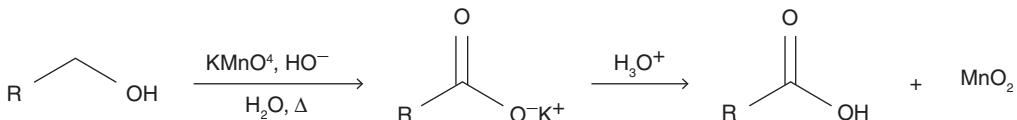
- What is Saytzeff's rule? Predict the major and minor products in the following reaction on the basis of this rule:
- Secondary halides will give substitution products with weak bases and elimination products in the presence of strong base. Why?



4.16 Oxidation Reactions

Oxidation of Alcohols using KMnO_4

Primary alcohols can be oxidized by potassium permanganate (KMnO_4) to the corresponding carboxylic acids. The reaction is usually carried out in basic aqueous solution, from which MnO_2 precipitates as the oxidation takes place. After the oxidation is complete, filtration allows removal of the MnO_2 and acidification of the filtrate gives the carboxylic acid.



Primary alcohol such as octan-1-ol can be oxidized efficiently by KMnO_4 in the presence of basic copper salts, however, the product formed is predominantly octanoic acid (due to overoxidation) with very small amounts of aldehyde.

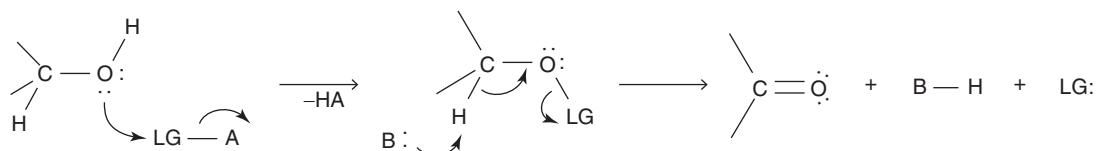


Secondary alcohols can be oxidized to ketones. Although overoxidation is less of a problem, KMnO_4 is still not considered as a well-suited reagent for conversion of alcohols to aldehydes and ketones.

Aldehydes (or ketone) formed are readily oxidized to carboxylic acids. The oxidation reactions with KMnO_4 occur under basic conditions and the most effective conditions of aldehyde oxidation are use of *tert*-butanol as solvent along with NaH_2PO_4 as buffer.

Oxidation of Alcohols using Chromic Acid

In the general pathway for oxidation reactions, the oxidizing reagents temporarily install a leaving group (LG) on the hydroxyl oxygen during the reaction. Loss of a hydrogen from the hydroxyl carbon and departure of the leaving group from the oxygen result in an elimination that forms the $\text{C}=\text{O}$ π -bond.



Oxidations involving chromium (VI) reagents such as H_2CrO_4 are simple to carry out and have been widely used. These reactions involve formation of chromate esters, and include an elimination step as shown in the mechanism below.

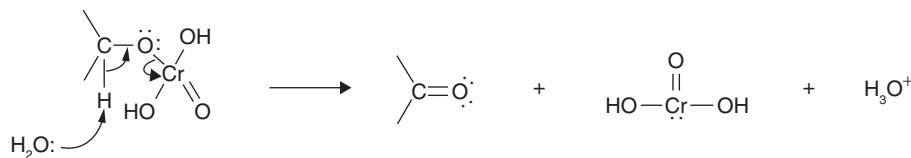
Step 1: Formation of chromate ester

The primary or secondary alcohol reacts with chromic acid to form chromate ester with loss of water, installing a leaving group on alcohol oxygen.



Step 2: Oxidation by elimination of H_2CrO_3

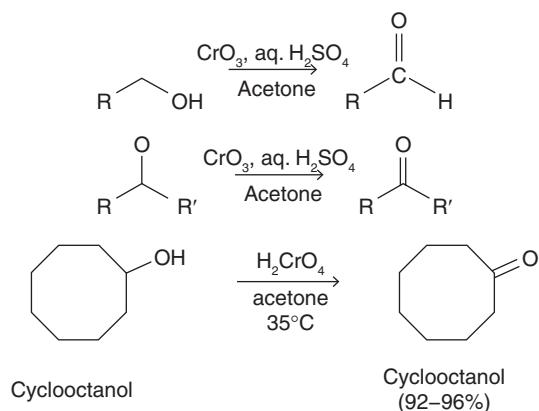
A water molecule abstracts a proton from the alcohol carbon, forming the $\text{C}=\text{O}$ π -bond. The chromium atom is reduced as H_2CrO_3 is eliminated, resulting in the formation of oxidized product.



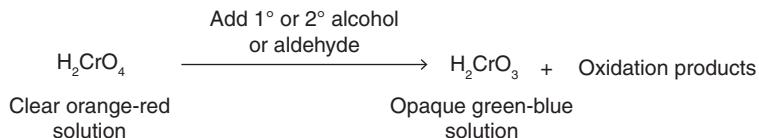
Chromium (VI) is a carcinogen and an environmental hazard, however and for this reason, methods like the Swern oxidation and others are increasingly important.

Jones reagent is one well-known source of H_2CrO_4 which contains chromium in oxidation state (VI). It can be prepared by adding CrO_3 or Na_2CrO_4 to aqueous sulphuric acid. Jones reagent is typically used by addition to solutions of an alcohol or aldehyde in acetone or acetic acid (solvents that cannot be

oxidized). Primary alcohols are oxidized to carboxylic acids, via the aldehyde hydrate mentioned above, secondary alcohols are oxidized to ketones. The following are examples of an oxidation using Jones reagent.

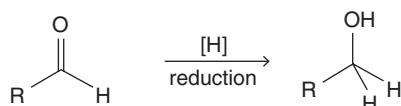


Chromic acid solutions are orange-red in color, and the product mixture, containing Cr(III), is a greenish blue. Thus, reagents like Jones reagent can serve as a color-based functional group test. Primary or secondary alcohols and aldehydes are rapidly oxidized by Jones reagent, turning the solution an opaque greenish blue within a few seconds. If none of these groups are present, the solution remains orange-red until side reactions eventually change the color.

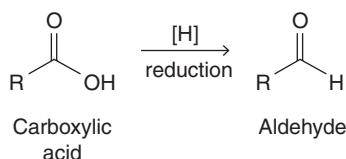


4.17 Reduction Reactions of Carbonyl Compounds

Reduction of an organic molecule usually corresponds to increasing its hydrogen content or decreasing its oxygen content. For example, conversion of an aldehyde to an alcohol is a reduction as hydrogen content increases.



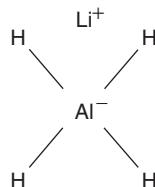
Conversion of a carboxylic acid to an aldehyde is a reduction because oxygen content decreases.



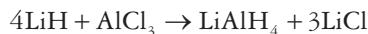
Two important pathways for reduction of carbonyl compounds is through the addition of hydride ions from complex metal hydrides such as LiAlH_4 or NaBH_4 .

Reduction using Lithium Hydride

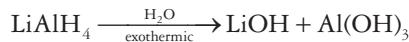
Lithium aluminium hydride (LiAlH_4 or LAH) is a white crystalline solid.



It is prepared by the following reaction and is a source for hydride ion. 1 equivalent of LAH can be related to 4 equivalents of hydride ions.

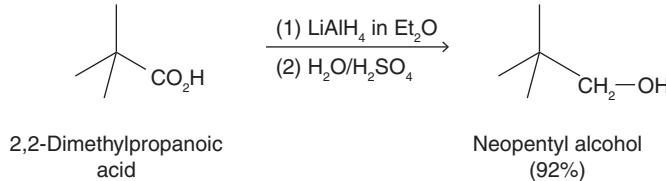


LAH reacts violently with water or moisture to release hydrogen gas. Hence, reduction reactions using LAH are carried out under anhydrous conditions. The solvents used are dry or anhydrous ethers (diethyl ether or THF).

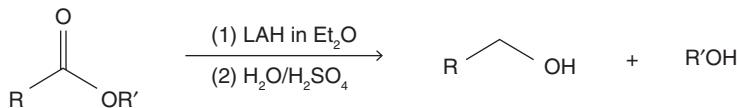


LAH is a powerful, versatile and non-selective reducing agent. It reduces almost all types of organic functional groups.

LAH reduces carboxylic acids and esters to primary alcohols. An example of this reduction is the conversion of 2,2-dimethylpropanoic acid to 2,2-dimethylpropanol (neopentyl alcohol).



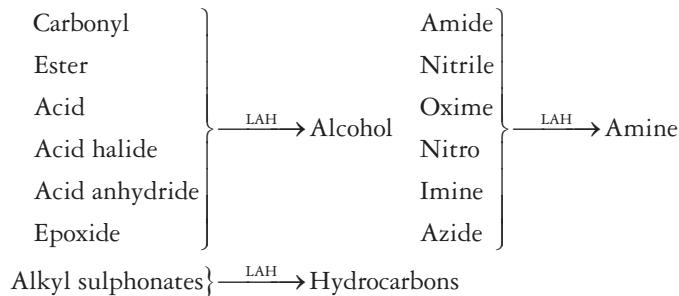
LAH reduction of an ester yields two alcohols, one derived from the carbonyl part of the ester group, and the other from the alkoxy part of the ester.



Carboxylic acids and esters are more difficult to reduce than aldehydes and ketones.

LAH, however, is a strong reducing agent to accomplish this transformation. Sodium borohydride (NaBH_4) (discussed next) is commonly used to reduce aldehydes and ketones, but it is not strong enough to reduce carboxylic acids and esters.

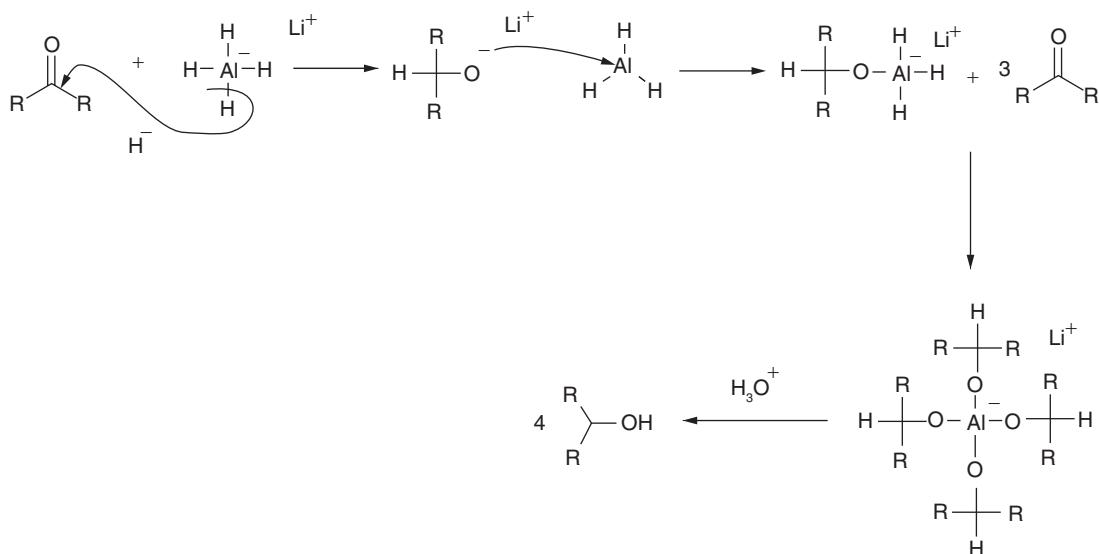
Other functional groups that can be reduced using LAH are listed as follows:



Groups that cannot be reduced with LAH include isolated olefin functions and simple aromatic hydrocarbons (benzene, naphthalene, etc.).

Mechanism of LAH Reduction

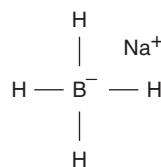
Lithium aluminium hydride is a powerful reducing agent and hydride ion attacks the carbonyl group. Aluminium (III) hydride which is released *in situ* in the reaction acts as a Lewis acid and reacts with three more moles of the carbonyl compound and finally produces four moles of alcohol as product. (Aldehydes produce primary alcohols whereas ketones produce secondary alcohols as products.)



After all the LAH has been consumed by the reduction step of the reactions, water and acid are added to neutralize the resulting salts and aid isolation of alcohol products. With increase in alkoxy groups at Al, the reactivity of LAH decreases due to $-I$ effect from alkoxy groups.

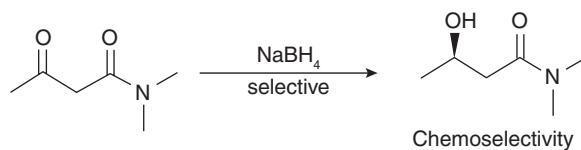
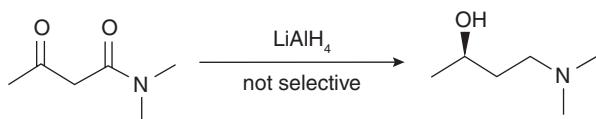
Reduction using Sodium Boron Hydride

Sodium borohydride (NaBH_4) is a white crystalline solid that is stable even in aqueous medium. So aqueous solvents such as alcohols (MeOH , EtOH , *et al.* -BuOH , etc.) can be used in the reduction reactions.

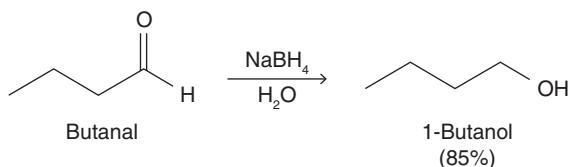


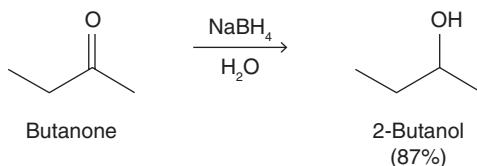
Complexes of NaBH_4 can be decomposed by aq. NH_4Cl or NaOH solution and aqueous mineral acids.

Compared to $\text{Al}-\text{H}$ bond, $\text{B}-\text{H}$ bond is stronger (as the electronegativity difference is less). Therefore, NaBH_4 is slower in release of hydride ion as compared to LiAlH_4 . So, NaBH_4 is less reactive but more selective than LiAlH_4 .

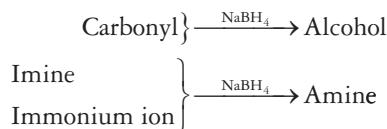


Aldehydes and ketones are easily reduced by sodium borohydride. Sodium borohydride is usually preferred over LAH for the reduction of aldehydes and ketones. Sodium borohydride can be used safely and effectively in water as well as alcohol solvents, whereas special precautions are required when using LAH.

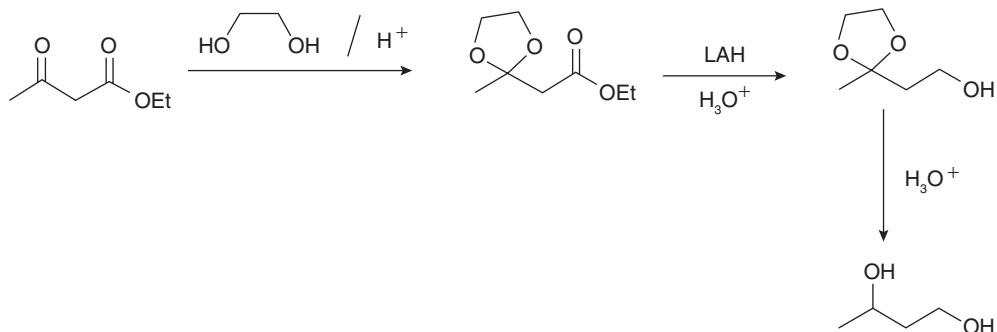
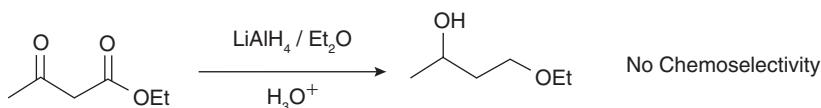
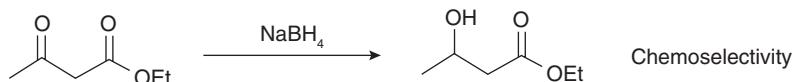




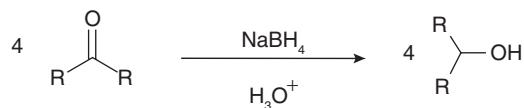
Other functional groups that can be reduced using NaBH_4 are as follows:



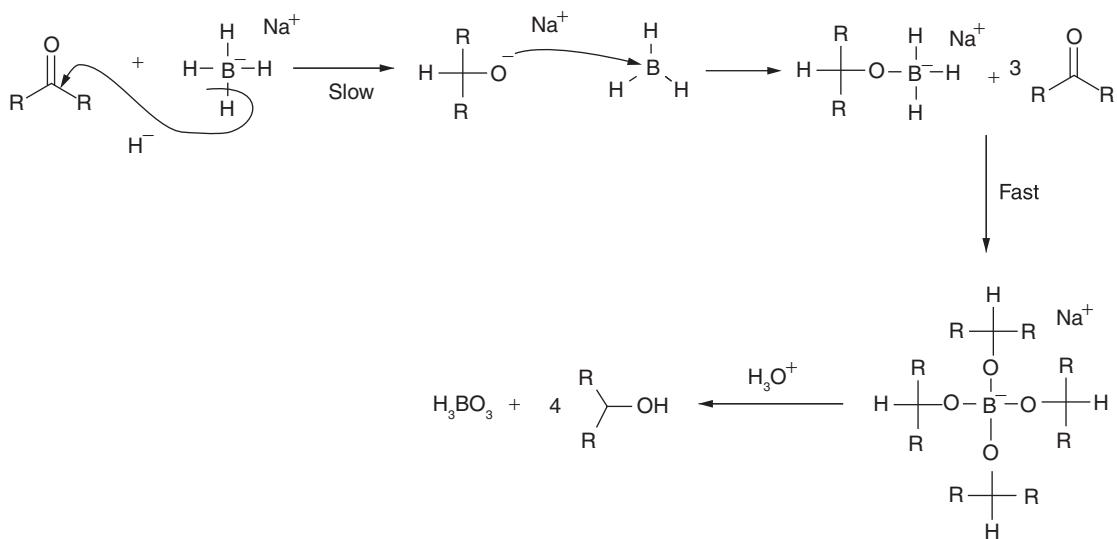
Esters under specific conditions can be reduced to alcohols. For example,



The detailed mechanism is depicted as follows:

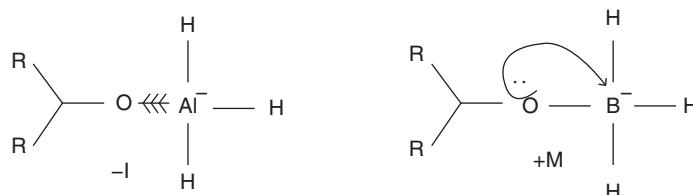


Mechanism:



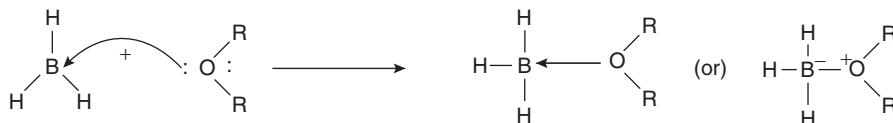
The reactivity order in releasing the hydride ions for NaBH_4 is opposite to that of LAH. Unlike in LAH, increasing the number of alkoxy groups on B increases the reactivity of borohydrides.

Reactivity: $\text{NaBH}_4 < \text{Alkoxy boranes}$

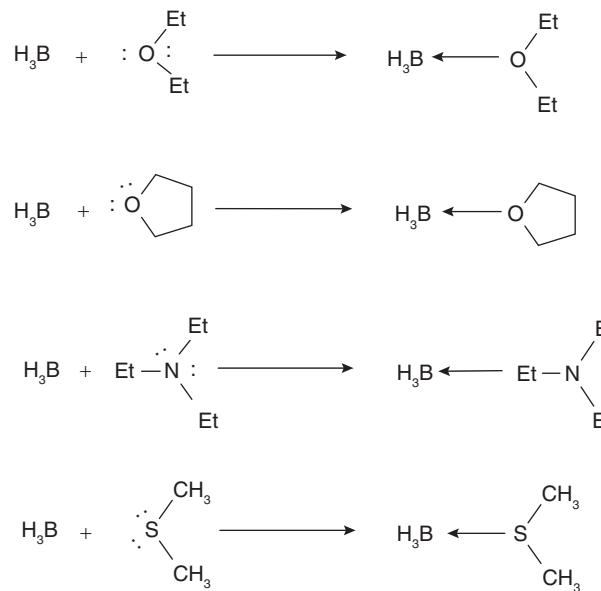


4.18 Hydroboration of Olefins

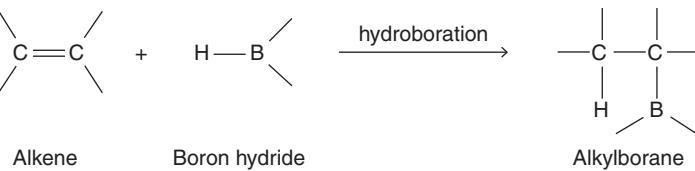
Borane (BH_3) is unstable and exists in the form of diborane (B_2H_6), a colorless gas. To stabilize boron hydride in the form of BH_3 , Lewis bases such as amines and ethers are used.



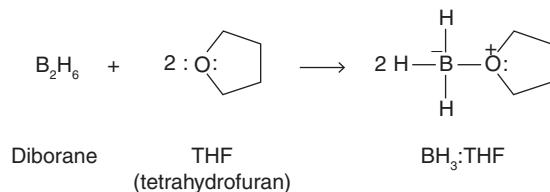
For example,



Addition of BH_3 group to an alkene or alkyne using boranes is called hydroboration reaction and the resulting products are called alkyl boranes. Hydroboration can be represented in its simplest terms as follows:

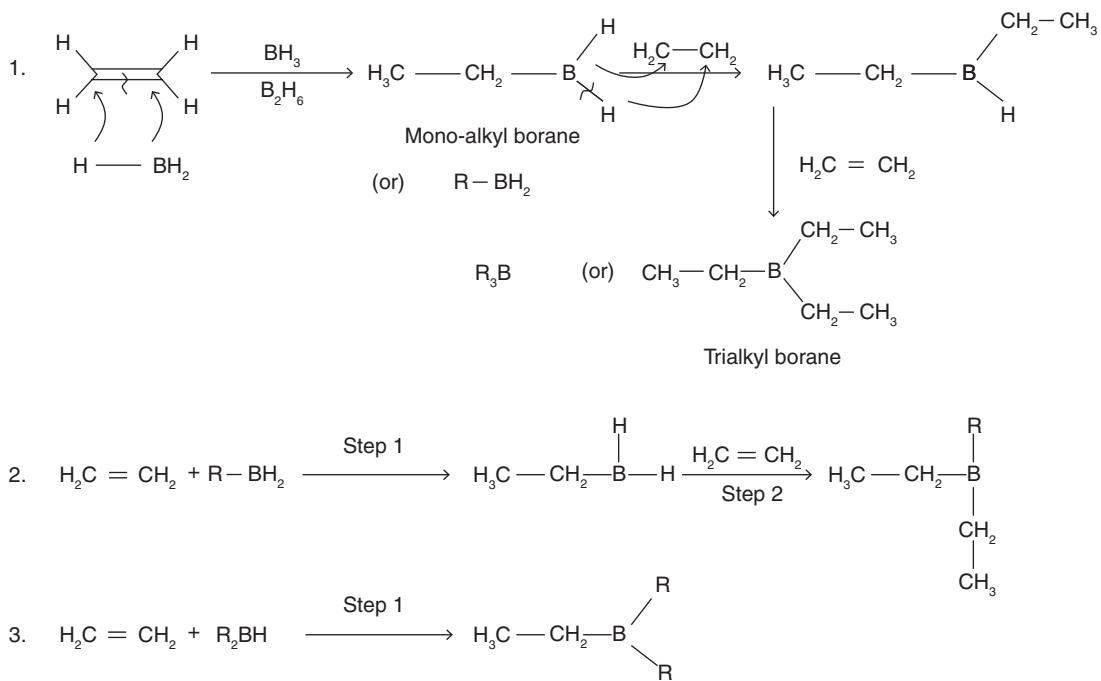


Hydroboration can be accomplished with diborane (B_2H_6), or more conveniently with a reagent prepared by dissolving diborane in THF. When diborane is introduced to THF, it reacts to form a Lewis acid–base complex of borane (the Lewis acid) and THF. The complex is represented as $\text{BH}_3\text{:THF}$.



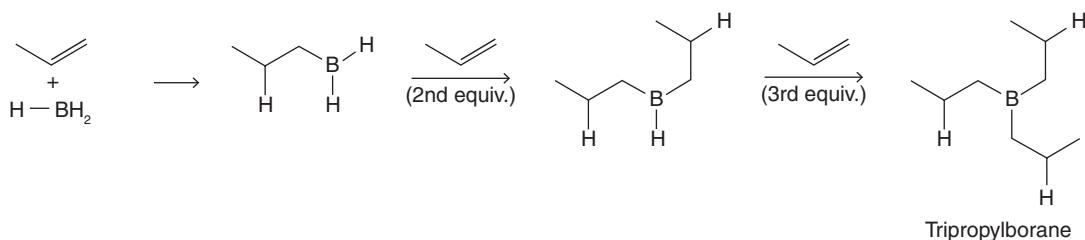
Hydroboration reactions are usually carried out in ethers: diethyl ether, $(\text{CH}_3\text{CH}_2)_2\text{O}$, or higher molecular weight ether such as diglyme $\{(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{O}\}$. Diborane and alkylboranes must be handled with care because they ignite spontaneously in air. The solution of $\text{BH}_3:\text{THF}$ must be used in an inert atmosphere (e.g., argon or nitrogen) and with care.

The extent of hydroboration depends on the number of hydrogen atoms on boron in boron hydride and the nature of olefin. If BH_3 is used, hydroboration will proceed through three steps resulting in trialkyl borane intermediate. If $\text{R}-\text{BH}_2$ is used, the reaction proceeds in two steps and dialkyl boranes are formed as products; with R_2-BH , one step reaction is observed and with R_3B no reaction is observed. Sterically less crowded olefins undergo hydroboration in borane. With increasing steric crowding, the extent of hydroboration decreases. If olefin is highly sterically crowded, even single step hydroboration may not take place. Some examples are as follows:

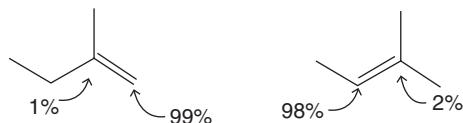


Mechanism of Hydroboration

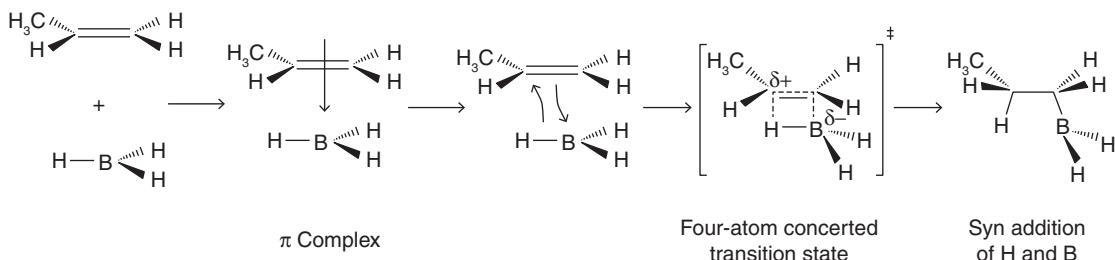
When a terminal alkene such as propene is treated with a solution containing $\text{BH}_3:\text{THF}$, the boron hydride adds successively to the double bonds of three molecules of the alkene to form a trialkylborane. In each addition step *the boron atom becomes attached to the less substituted carbon atom of the double bond*, and a hydrogen atom is transferred from the boron atom to the other carbon atom of the double bond.



Hydroboration is *regioselective* and it is *anti-Markovnikov* (the hydrogen atom becomes attached to the carbon atom with fewer hydrogen atoms). This observed attachment of boron to the less substituted carbon atom of the double bond is partly due to steric factors, that is, the bulky boron-containing group can approach the less substituted carbon atom more easily. For example, the observed percentage where boron atom becomes attached are illustrated as follows.

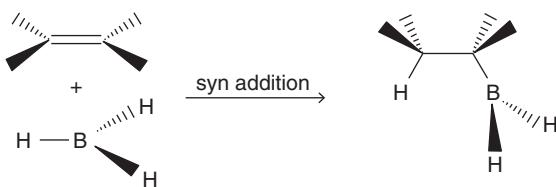


In the mechanism proposed for hydroboration, addition of BH_3 to the double bond begins with a donation of π electrons from the double bond to the vacant p orbital of BH_3 (see the following mechanism). In the next step an addition product is formed by passing through a four-atom transition state in which the boron atom is partially bonded to the less substituted carbon atom of the double bond and one hydrogen atom is partially bonded to the other carbon atom. The electrons shift in the direction of the boron atom and away from the more substituted carbon atom of the double bond. As a result, the more substituted carbon atom develops a partial positive charge, *and this is stabilized by the electron-releasing alkyl group on the carbon atom of the double bond*. Hence, both electronic and steric factors favor addition of boron at the least substituted carbon and account for the anti-Markovnikov orientation of the addition.

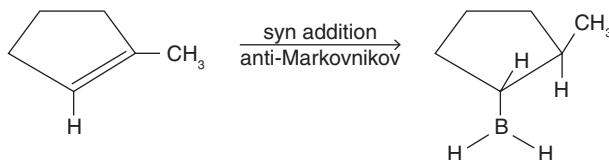


Stereochemistry of Hydroboration

The transition state for hydroboration requires that the boron atom and the hydrogen atom to add to the same face of the double bond:



We can see the results of a syn addition in our example involving the hydroboration of 1-methylcyclopentene. Formation of the enantiomer, which is equally likely, results when the boron hydride adds to the top face of the 1-methylcyclopentene ring:

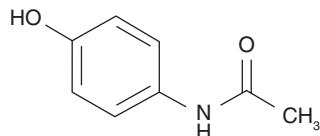


STRUCTURE, SYNTHESIS AND APPLICATIONS OF DRUG MOLECULES

A vast majority of drugs and medicines available for use are small organic molecules. A chemist designing new drugs synthesizes new molecules with expected pharmacological activity and then sends them off for biological testing. The structure of the new molecule continues to be worked upon until the compound with optimum biological properties is obtained. A chemist therefore, needs to prepare molecules and analyze them to ensure that the correct compound has been made before sending them for testing.

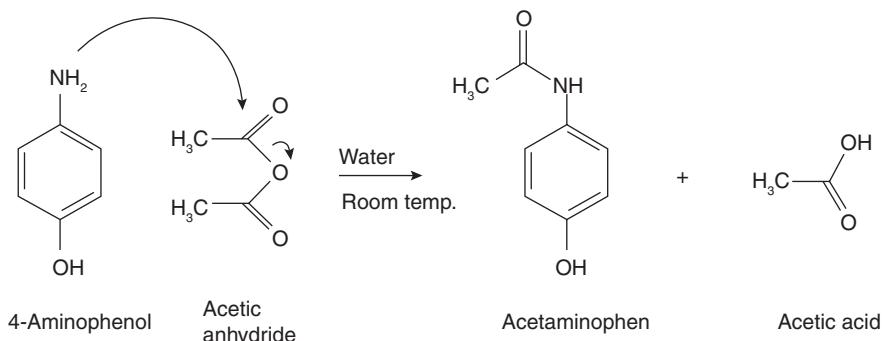
4.19 Paracetamol

Paracetamol is a non-narcotic (non-addictive) analgesic. Also known as acetaminophen or APAP, it is a medicine used to treat pain and fever. It is typically used for mild to moderate pain relief and when taken does not result in the loss of consciousness. The chemical structure of paracetamol is depicted as follows.



Synthesis

Paracetamol is synthesized by the reaction of 4-aminophenol with ethanoic (acetic) anhydride. The reaction leads to the formation of an amide bond and ethanoic(acetic) acid is the byproduct. At the completion of reaction, paracetamol is isolated and purified.



The steps involved in the synthesis of paracetamol can be listed as follows:

1. In a conical flask take calculated amount of 4-aminophenol, add appropriate amount of water and stir the suspension vigorously (magnetic stirrer) for a few minutes.
2. Add calculated amount of ethanoic anhydride and continue stirring until the suspension dissolves and a precipitate (of paracetamol) forms.
3. After 10 minutes filter the precipitate and wash with small amounts of cold, distilled water.
4. After drying, the crude product is placed in a clean conical flask containing small amount of water. It is recrystallized by first heating the flask to dissolve crude product in water and then cooling the flask in ice until crystals of pure paracetamol are obtained.
5. Filter the crystals under vacuum and dry in a warm oven. Repeat recrystallisation process to achieve a purer product

Pharmaceutical Applications

Paracetamol is available in the market under different trade names in simple (sold over the counter) or more complex preparations combined with an additional active substance (e.g., with tramadol) obtainable only by prescription or without it (in combination with codeine phosphate, ascorbic acid or diphenhydramine hydrochloride) as well as NSAIDs such as ibuprofen or propyphenazone. Paracetamol occurs in form of tablets, effervescent tablets, suspension, powder to prepare oral liquid medicine and rectal suppositories. The paracetamol content in oral medicaments is frequently equal to 500 mg, however, there are preparations which contain 325 mg, 750 mg or even 1000 mg.

When administered orally, clinical effect of paracetamol appears after 30 min. The fastest action of paracetamol occurs after 15 min, in the case of fast-release tablets enriched with sodium bicarbonate (e.g., Panadol rapid, etc.) which enhances the emptying of stomach. As a result, paracetamol passes quickly to the small intestines and undergoes absorption readily. The bioavailability of paracetamol on rectal administration is about two-thirds as compared to oral administration. The analgesic action in case of rectal administration is after 2–3 hours of drug intake. Bioavailability and speed of adsorption of paracetamol in form of suppositories depends on the following factors:

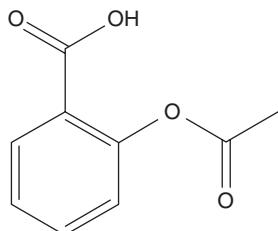
1. The drug dose (650 mg for adults and 80–325 mg for children)
2. Size of the suppository (better bioavailability with smaller or lower doses)
3. The type of vehicle (greater bioavailability with vehicles of higher lipophilicity; faster but shorter time of effect)
4. Degree of rectal vascularization

Side Effects

When paracetamol is administered in appropriate doses (i.e., maximum of 4 g/24 h or as mentioned on the leaflet), no serious side effects have been observed, apart from allergic skin reactions. Higher or prolonged doses may lead to some side effects, especially in the liver.

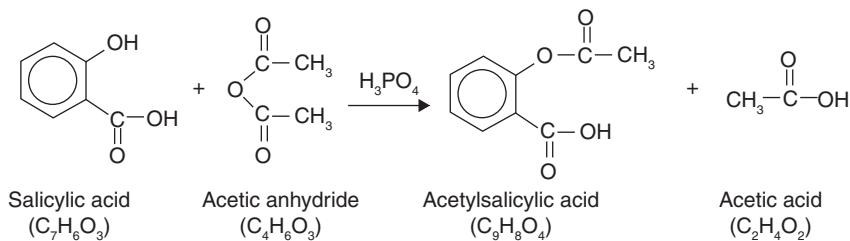
4.20 Aspirin

Aspirin is a non-narcotic (non-addictive) analgesic prepared from salicylic acid. It is widely used as fever and pain reliever. Salicylic acid is a compound found in the bark of the willow tree that has been used for medicinal properties for thousands of years. In modern time, salicylic acid is administered in form of aspirin which is less irritating to the stomach. The chemical structure of aspirin is depicted as follows.



Synthesis

To prepare aspirin, salicylic acid is reacted with an excess of acetic anhydride. A small amount of a strong acid is used as a catalyst (phosphoric acid) which speeds up the reaction. The excess acetic acid is quenched with the addition of water. Aspirin obtained is not very soluble in water, so can be precipitated out. Acetic acid being soluble in water, is easily separated from the aspirin formed as product. The aspirin isolated is a crude product which can be purified through recrystallization from ethanol. The overall reaction is given as:



The steps in the synthesis of aspirin are listed as follows:

1. Take measured amount of salicylic acid in a conical flask and add acetic anhydride to it, along with 3 drops of phosphoric acid and shake well.
2. The flask is heated on water bath at a temperature of 60–70°C for 15 min.
3. The solution is allowed to cool to room temperature and 100 ml of cold water is poured in it.

4. The solution is stirred till white solid appears, which is separated using a funnel and dried in folds of filter paper.
5. Recrystallization of solid is done by dissolving solid in 20 ml of glacial acetic acid followed by heating and subsequently cooling to obtain pure crystals.

Pharmaceutical Applications

Aspirin is an effective analgesic (pain reliever), antipyretic (fever reducer) and anti-inflammatory drug. It prevents aggregation of platelets and evidenced suggests that it can prevent stroke. It is also used in the treatment of rheumatoid arthritis and osteoarthritis.

Different individuals show differences with regard to absorption, tolerance and therapeutic usefulness of aspirin. The clinical symptoms of aspirin sensitivity are similar to those observed for allergy and may lead to a rare and acute condition of swelling in the brain and liver in children suffering from viral fever.

Key Terms

Isomerism	Racemic mixtures	Hyperconjugative (Baker-Nathan) effect
Stereoisomers	Absolute configuration	Electrophiles
Configurational isomerism	Relative configuration	Nucleophiles
Conformational isomerism	Geometrical isomerism	Rearrangement reaction
Optical isomerism	<i>Cis</i> and <i>trans</i> nomenclature	Nucleophilic addition
Optical activity	<i>E</i> and <i>Z</i> nomenclature	Electrophilic addition
Specific rotation	Conformers	Free radical addition
Plane polarized light	Newman projections	Markownikoff's rule
Polarimeter	Staggered	Unimolecular nucleophilic substitution
Dextrorotatory	Eclipsed	Bimolecular nucleophilic substitution
Laevorotatory	Homolytic fission	Free radical substitution
Chirality	Heterolytic fission	Nucleophilic aromatic substitution
Asymmetry	Free radicals	Saytzeff's rule
Mirror images	Carbocation	Unimolecular elimination
Elements of symmetry	Carbanion	Bimolecular elimination
Plane of symmetry	Carbene	Oxidation reactions
Center of symmetry	Inductive effect	Reduction reactions
Axis of symmetry	Electron withdrawing group	Hydroboration of alkenes
Fischer projections	Electron donating group	Paracetamol and aspirin-structure, synthesis and applications
Enantiomers	Inductometric effect	
Diastereomers	Electrometric effect	
<i>Meso</i> compounds	Mesomeric (resonance) effect	

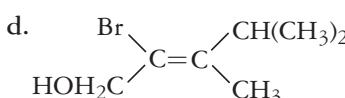
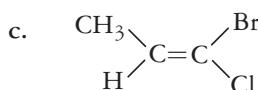
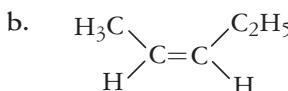
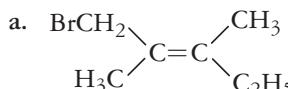
Objective-Type Questions

Multiple-Choice Questions

1. An alkane forms isomers if the least number of carbon atoms is
 - a. 1.
 - b. 2.
 - c. 3.
 - d. 4.
2. Rotation of polarized light can be measured by
 - a. monometer.
 - b. galvanometer.
 - c. polarimeter.
 - d. viscometer.
3. Which of the following is optically active?
 - a. *n*-Propanol
 - b. *n*-Butanol
 - c. 2-Chlorobutane
 - d. 3-Methylpentane
4. Which of the following compounds would show optical isomerism?
 - a. $\text{H}_2\text{NCH}_2\text{COOH}$
 - b. $(\text{CH}_3)_2\text{CHCHO}$
 - c. $\text{H}_2\text{NCH}(\text{CH}_3)_2$
 - d. $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$
5. A compound has three chiral carbon atoms. The number of possible optical isomers it can have is
 - a. 3.
 - b. 2.
 - c. 8.
 - d. 4.
6. The number of stereoisomers for the compound $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}=\text{CH}-\text{CH}_3$ is
 - a. 2.
 - b. 3.
 - c. 4.
 - d. 0.
7. How many optical stereoisomers are possible for 2-bromo-4-hydroxycyclohexane carboxylic acid?
8. How many chiral carbons are present in glucose molecule $\text{CHO}(\text{CHOH})_4\text{CH}_2\text{OH}$?
 - a. 4
 - b. 3
 - c. 2
 - d. 1
9. The number of optical isomers of the compound $\text{CH}_3\text{CH}(\text{Br})\text{CH}(\text{Br})\text{COOH}$ is
 - a. 0.
 - b. 1.
 - c. 3.
 - d. 4.
10. How many carbon atoms in the molecule $\text{HOOC}-(\text{CHOH})_2-\text{COOH}$ are asymmetric?
 - a. 1
 - b. 2
 - c. 3
 - d. None of the above
11. Which of the following is an optically active compound without a chiral carbon atom?
 - a. 2,3-Butanediol
 - b. Glyceraldehyde
 - c. *meso*-Tartaric acid
 - d. 1,3-Diphenylpropadiene
12. Optically active stereoisomers that are not mirror images are called
 - a. enantiomers.
 - b. mesomers.
 - c. tautomers.
 - d. diastereomers.
13. The *d*- and *l*-tartaric acids are
 - a. diastereomers.
 - b. enantiomers.
 - c. achiral molecules.
 - d. tautomers.

14. A *meso* compound is optically inactive due to the presence of
 a. center of symmetry.
 b. plane of symmetry.
 c. alternating axis of symmetry.
 d. none of the above.
15. Which of the following is not a *meso* compound?
- a.
$$\begin{array}{c} \text{COOH} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{COOH} \end{array}$$
- b.
$$\begin{array}{ccccc} \text{H} & & \text{H} & & \\ \diagdown & & \diagup & & \\ \text{HOOC} & - & \text{C} & - & \text{COOH} \\ & & \diagup & & \diagdown \\ & & \text{H} & & \text{H} \end{array}$$
- c.
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}=\text{CH}-\text{CH}_3 \end{array}$$
- d.
$$\begin{array}{c} \text{COOH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{COOH} \end{array}$$
16. Which has the highest priority among the following according to Cahn–Ingold–Prelog sequence rule?
 a. CH_3
 b. C_2H_5
 c. ClCH_2
 d. BrCH_2
17. Which of the following has *R*-configuration?
- a.
$$\begin{array}{c} \text{CHO} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$
- b.
$$\begin{array}{c} \text{Cl} \\ | \\ \text{Br}-\text{C}-\text{COOH} \\ | \\ \text{H} \end{array}$$
- c.
$$\begin{array}{c} \text{F} \\ | \\ \text{H}-\text{C}-\text{Cl} \\ | \\ \text{Br} \end{array}$$
- d.
$$\begin{array}{c} \text{H} \\ | \\ \text{H}_5\text{C}_6-\text{C}-\text{CH}(\text{CH}_3)_2 \\ | \\ \text{NH}_2 \end{array}$$
18. The lowest alkene that can show geometrical isomerism is
 a. ethene.
 b. propene.
 c. 1-butene.
 d. 2-butene.
19. Which of the following compounds can exist as geometrical isomers?
 a. $\text{CH}_2\text{Cl}-\text{CH}_2\text{Br}$
 b. $\text{CHCl}=\text{CHBr}$
 c. CH_2Cl_2
 d. $\text{CH}_2\text{Cl}-\text{CHCl}-\text{CH}_2\text{Cl}$
20. Which of the following show geometrical isomerism?
 a. 1,2-Dichloroethene
 b. Ethylene
 c. Propylene
 d. Isobutylene

21. Which of the following has *E* configuration?



b. chair.

c. twist boat.

d. half chair.

26. The homolytic fission of a hydrocarbon results in the formation of

a. carbocation.

b. free radicals.

c. carbanions.

d. carbenes.

27. Which of the following will undergo homolytic fission?

a. Br_2

b. HBr

c. H_2O

d. HCl

28. Which of the following is a temporary electron displacement effect?

a. Inductive

b. Inductometric

c. Mesomeric

d. All of the above

29. Which among the following is most basic?

a. NH_3

b. CH_3NH_2

c. $(\text{CH}_3)_2\text{NH}$

d. $(\text{CH}_3)_3\text{N}$

30. Electromeric effect is due to

a. electronegative elements.

b. double bonds.

c. triple bonds.

d. all of the above.

31. The dipole moment of $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_2=\text{CH}-\text{Cl}$ because of

a. inductive effect.

b. mesomeric effect.

c. electromeric effect.

d. inductometric effect.

32. Which among the following is least acidic?

a. CH_3OH

b. $\text{CH}_3\text{CH}_2\text{OH}$

c. $(\text{CH}_3)_2\text{CHOH}$

d. $(\text{CH}_3)_3\text{COH}$

22. Which of the following is not true for geometrical isomers?

- a. Geometrical isomers differ in their physical and chemical properties.
- b. Melting point and stability of *cis* isomers are higher than those of the *trans* isomers.
- c. Cyclic compounds can exhibit geometrical isomerism.
- d. Dipole moment, solubility and density are higher in *cis* isomers than *trans* isomers.

23. Isomers that can be inter-converted through rotation around a single bond are

- a. conformers.
- b. diastereomers.
- c. enantiomers.
- d. positional isomers.

24. The most stable conformation of *n*-butane is

- a. partially eclipsed.
- b. eclipsed.
- c. *gauche*.
- d. staggered *anti*.

25. The most stable conformation of cyclohexane is

- a. boat.

33. In which of the following species is the central carbon atom negatively charged?
- carbocation.
 - carbanion.
 - free radical.
 - carbene.
34. The shape of a carbanion is
- linear.
 - planar.
 - pyramidal.
 - none of the above.
35. Which carbocation is most stable among the following?
- $(CH_3)_3C^+$
 - $(CH_3)_2HC^+$
 - $(C_6H_5)_3C^+$
 - $(C_6H_5)_2HC^+$
36. Which of the carbanion among the following is least stable?
- $C_6H_5^-$
 - $C_6H_5CH_2^-$
 - $(C_6H_5)_2CH^-$
 - $(C_6H_5)_3C^-$
37. Which among the following is an electrophile?
- NH_3
 - SO_3
 - H_2O
 - ROH
38. Which of the following species is a nucleophile?
- NO_2^+
 - $:CX_2^-$
 - $:NH_2^-$
 - $:CH_3$
39. Which among the following will show highest reactivity in nucleophilic substitution reactions?
- CH_3F
 - CH_3Cl
 - CH_3Br
 - CH_3I
40. The formation of cyanohydrins from a ketone is an example of
- electrophilic addition.
 - electrophilic substitution.
 - nucleophilic addition.
 - nucleophilic substitution.
41. Markownikoff's rule can be used to predict the addition of HBr on
- $CH_2=CH_2$
 - $CH_3CH=CH_2$
 - $CH_3CH=CHCH_3$
 - $CH_3-CH=CHBr$
42. Which among the following will undergo nucleophilic substitution reaction by S_N2 mechanism?
- CH_3Br
 - $(CH_3)_2CHBr$
 - $(CH_3)_3CBr$
 - $C_6H_5CH_2Br$
43. Which among the following alkyl halides will react most readily with NaCN with S_N2 mechanism?
- $CH_3CH(CH_3)CH_2CH_2I$
 - $CH_3CH(CH_3)CHI CH_3$
 - $CH_3Cl(CH_3)CH_2CH_3$
 - $CH_3CHICH(CH_3)_2$
44. Which among the following alcohols undergoes the fastest reaction with HBr by S_N1 mechanism?
- Propan-1-ol
 - Propan-2-ol
 - 2-Methylpropan-1-ol
 - 2-Methylpropan-2-ol
45. Which among the following compounds will undergo sulphonation readily?
- Benzene
 - Nitrobenzene
 - Toluene
 - Chlorobenzene

Fill in the Blanks

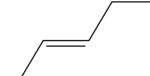
1. A compound with n different chiral atoms can have _____ stereoisomers.
2. A molecule that cannot be superimposed on its mirror image is called _____.
3. A _____ is one which divides the molecule into two equal halves, so that each half is the mirror image of the other half.
4. _____ are two-dimensional representations of three-dimensional molecules.
5. The relative instability of the eclipsed conformation is due to _____.
6. The _____ conformation of cyclohexane is its most stable conformation.
7. The _____ conformation of *n*-butane is its most stable conformation.
8. A compound is said to be _____ when it rotates the plane of polarized light.
9. If the compound rotates the plane of light in counterclockwise direction, it is called _____.
10. A _____ compound has an internal plane of symmetry.
11. A type of stereoisomerism in which the isomers differ in the spatial arrangement of groups attached to the two carbon atoms of the double bond is called _____.
12. The number of stereoisomers that are possible for 2,3-butanediol are _____.
13. Both *anti* and *gauche* conformations in *n*-butane are free of _____ strain but *gauche* conformation show _____ strain.
14. For an organic compound to show optical activity, it should have _____ carbon atom and should not have a _____.
15. *E* and *Z* nomenclature is based on _____ priority rules.
16. Maleic acid and fumaric acids are _____ isomers.
17. The electronegativity of an atom _____ with its positive oxidation state.
18. The process of electron shift along the chain of atoms due to presence of polar bonds is called _____.
19. _____ is a temporary effect operating only under the influence of the attacking of reagent.
20. A _____ species is paramagnetic in nature.
21. A carbocation has _____ structure whereas a carbanion has a _____ structure.
22. A nucleophile which has more than one electron rich atom and can attack substrate through either of the atom is called _____.
23. _____ states that in dehydrohalogenation, the more stable the alkene, faster it is formed.
24. In nucleophilic substitution reactions, _____ is observed in S_N1 reaction and _____ is observed in S_N2 reaction.
25. Vinyl halides do not undergo nucleophilic substitution reactions due to stabilization of R-X bond by _____.

Review Questions

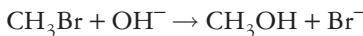
Short-Answer Questions

1. What are stereoisomers? How are they classified?
2. Differentiate between configurational and conformational isomers.

3. What is optical activity?
4. Define specific rotation and write its mathematical expression.
5. Explain the term *chirality*.
6. What are the conditions necessary for chirality?
7. Which of the following compounds are optically active: *n*-propanol, 2-chlorobutane and 2,3-pentadiene? Given reasons.
8. Identify the chiral center in each of the following compounds: (a) 2-chlorobutane (b) 1,2-dichloropropane (c) 3-bromopentene.
9. What is the role of elements of symmetry in optical activity? Name the elements of symmetry.
10. Define alternating axis of symmetry. How is it related to the other elements of symmetry?
11. An optically pure compound A has molecular formula C_6H_{12} . The compound on hydrogenation gives an inactive compound B with molecular formula C_6H_{14} . What are structures of A and B?
12. Write two examples of optically active compounds without chiral center.
13. Define enantiomers and diastereomers.
14. Write the structures of all enantiomers and diastereomers of 2-bromo,3-chlorobutane.
15. Explain the difference between a *meso* compound and a racemic mixture.
16. What do you understand by racemic mixture (racemates)? Comment on their optical activity.
17. Identify chiral centers, calculate the number of possible stereoisomers and draw all possible optical isomer for tartaric acid.
18. Arrange the following ligands in decreasing order of priority:
- a. $-\text{CH}(\text{OH})-\text{CH}_3$, $-\text{OH}$, $-\text{COOH}$ and CH_2OH
- b. $-\text{CH}_2\text{NH}_2$, $-\text{NO}_2$, $-\text{C}\equiv\text{N}$, $-\text{NH}_2$
19. Assign *R* and *S* configuration to the following compounds:
- a.
- $$\begin{array}{c} \text{H} & & \text{O} \\ & \diagdown & / \\ & \text{C} & \\ & | & \\ \text{H} & - & \text{C} - \text{OH} \\ & | & \\ & & \text{CH}_2\text{OH} \end{array}$$
- b.
- $$\begin{array}{c} \text{F} \\ | \\ \text{H} & - & \text{C} \\ | & & | \\ \text{H} & - & \text{Cl} \\ | & & \\ \text{Br} & & \end{array}$$
- c.
- $$\begin{array}{c} \text{H} \\ | \\ \text{HO} & - & \text{CH}_3 \\ | & & \\ \text{HO} & - & \text{CH}_3 \\ & & \text{CH}_3 \end{array}$$
20. Write the three-dimensional structure for the following:
- a. $\text{CH}(\text{Cl})(\text{Br})(\text{I})$ (*R* and *S* configuration)
- b. 3*R*,4*S*-dimethylhexane
21. What is the relation between the following pair.
-
22. What is geometrical isomerism? What are the necessary conditions for a molecule to show a geometrical isomerism?
23. Which of the following exhibit geometrical isomerism? Give the structure of the *cis* and *trans* isomers.

- a. 2-Butane
 b. 2-Methyl-2-butane
 c. 2-Pentene
 d. 1,2-Dichloropropane
24. What is the limitation of *cis* and *trans* nomenclature?
25. Write the *E* and *Z* configuration of the following molecules:
- a. Two geometric isomers of 3-methyl-2-hexane
- b.
- 
- c.
- $$\begin{array}{c} \text{H}_2\text{N} \\ | \\ \text{O}_2\text{N} \diagdown \text{C}=\text{C} \diagup \text{H} \\ | \\ \text{Br} \end{array}$$
26. Write the structural formulae for the following compounds:
- a. *Trans*-2-phenyl-but-2-ene
 b. *Cis*-1,2-dimethylcyclopropane
 c. (*Z*)-1-bromo-1-chloropropane
27. Write all possible structural and geometrical isomers of C_4H_8 .
28. In the following compounds, identify the structural isomers and geometric isomers.
- a.
- $$\begin{array}{c} \text{Cl} \\ | \\ \text{H} \diagdown \text{C}=\text{C} \diagup \text{Br} \\ | \\ \text{CH}_3 \end{array}$$
- b.
- $$\begin{array}{c} \text{Cl} \\ | \\ \text{H}_3\text{C} \diagdown \text{C}=\text{C} \diagup \text{Br} \\ | \\ \text{H} \end{array}$$
- c.
- $$\begin{array}{c} \text{Cl} \\ | \\ \text{H} \diagdown \text{C}=\text{C} \diagup \text{CH}_3 \\ | \\ \text{Br} \end{array}$$
- d.
- $$\begin{array}{c} \text{Cl} \\ | \\ \text{Br} \diagdown \text{C}=\text{C} \diagup \text{CH}_3 \\ | \\ \text{H} \end{array}$$
- e.
- $$\begin{array}{c} \text{Cl} \\ | \\ \text{H}_3\text{C} \diagdown \text{C}=\text{C} \diagup \text{Br} \\ | \\ \text{H} \end{array}$$
- f.
- $$\begin{array}{c} \text{Cl} \\ | \\ \text{Br} \diagdown \text{C}=\text{C} \diagup \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
29. Draw the Newman projection for the most stable conformation of *n*-butane.
30. Discuss the relative stability of staggered and eclipsed conformations of ethane.
31. What is electromeric effect? How does it differ from inductive effect?
32. What are different types of reactive intermediates involved in organic reactions?
33. What are carbocations? Arrange the following according to increasing stability:
- a.
- $$\text{CH}_3\text{CH}_2\text{CH}_2\overset{+}{\text{C}}$$
- b.
- $$(\text{CH}_3)_3\overset{+}{\text{C}}$$
- c.
- $$\text{CH}_3-\text{CH}_2-\overset{+}{\text{C}}\text{HCH}_3$$
34. What are carbenes? What are the two different forms of carbenes?
35. What are the factors that influence the relative stability of carbocations, carbanions and free radicals?
36. Explain why benzyl carbocation is more stable than ethyl carbocation.
37. Why are alcohols weaker acids than water?
38. Justify the following order of acidic character of monohydric alcohols:
- Primary > Secondary > Tertiary
39. Chloroacetic acid is a stronger acid than acetic acid. Explain.
40. What is order of acidic strength of following acids: former acid, acetic acid and benzoic acid?
41. Define the following, giving two examples of each:
- a. electrophiles;
 b. nucleophiles.
42. Why do aldehydes and ketones undergo nucleophilic addition reactions? Why are ketones less reactive than aldehydes?
43. Why does the halogen atom of an alkyl halide readily undergo nucleophilic substitution?
44. Why are nucleophilic addition reactions facilitated in α , β -unsaturated carbonyl compounds?

45. Which of the following do not show electro-
meric effect?
Alkenes, ethers, aldehydes, ketones, esters,
alkanes
46. Why is the rate of S_N1 reaction much faster
in a polar solvent than in a non-polar solvent?
47. S_N1 reaction occurs with retention of configura-
tion. Why?
48. Why does S_N2 reactions give rise to inverted
product?
49. How can it be decided whether the following
reaction proceeds by S_N1 or S_N2 mechanism.



50. Haloalkanes undergo nucleophilic substi-
tution whereas haloarenes undergo electro-
philic substitution. Explain.
51. What is Markownikoff's rule? Explain
giving example.
52. Arrange the following ions in decreasing
order as leaving groups in nucleophilic
substitution:

- a. H_2O , $\text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_3^-$
- b. H^- , Cl^- , Br^- , CH_3COO^- , HO^-

53. The reaction of alkyl chloride with aqueous
KOH leads to the formation of alcohols;
whereas alkenes are formed as major prod-
ucts in the presence of alc. KOH. Explain.
54. Arrange the following in order of decreasing
 S_N2 reactivity:



Long-Answer Questions

1. What is optical activity and how is it mea-
sured using a polarimeter? Describe its

- construction and working with the help of a
diagram.
2. Explain the term chirality. Discuss the opti-
cal isomerism of chiral organic compounds
using the example of tartaric acid.
3. Describe the various elements of symmetry
and their role in optical activity.
4. Write all possible isomeric forms of
1,3-dichloro-2-methylbutane and specify
which of the isomers will be optically active.
5. a. What are relative and absolute configura-
tions?
b. How are *R* and *S* configurations speci-
fied?
6. a. Draw all possible stereoisomers of
2,3-butanediol and comment on their
optical activity
b. Assign *R* and *S* configurations to the ste-
reoisomers
c. Identify enantiomers and diastereomers
in the structures.
7. Draw and specify *R* and *S* configuration for
the following compounds:
 a. $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$
 b. 3-chloro-1-pentene
 c. 3-bromohexane
 d. $\text{CH}_3\text{CH}(\text{Br})\text{CH}(\text{OH})\text{CH}_3$
8. Assign *R* or *S* configuration to the following
compounds.
 a. $\begin{array}{c} \text{CHO} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$ b. $\begin{array}{c} \text{COOH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{CH}_3 \end{array}$
 c. $\begin{array}{c} \text{Br} \\ | \\ \text{H}-\text{C}-\text{I} \\ | \\ \text{Cl} \end{array}$ d. $\begin{array}{c} \text{Br} \\ | \\ \text{H}-\text{C}-\text{C}_2\text{H}_5 \\ | \\ \text{I} \end{array}$

- e.
- f.
9. Discuss the *E-Z* system of nomenclature. How is it better than *cis, trans* nomenclature?
10. Assign *E* and *Z* configuration to the following compounds:
- a.
- b.
- c.
- d.
- e.
- f.
- g.
- h.
11. a. What do you understand by conformations and conformational analysis?
b. Draw and describe the conformational isomers of ethane and discuss their relative stability.
12. a. Discuss the conformational isomers of *n*-butane.
b. Draw the potential energy diagram for various conformations of *n*-butane and explain their order of stability.
13. Draw and describe the conformations of cyclohexane. Discuss the relative stability of the conformers.
14. Draw structures for the equilibrating chair conformers of *trans*- and *cis*-1,2-dimethylcyclohexanes. Show all methyl/hydrogen 1,3-diaxial interactions. Select the most stable conformation for each diastereomer.
15. Write the structure of the following using Newman projections:
a. The three conformations of 2-methylbutane.
b. Two conformations of *cis*- and two conformations of *trans*-1,3-dimethylcyclohexane.
c. Two conformations of *cis*- and two conformations of *trans*-4-isopropyl-1-methylcyclohexane.
16. Discuss the following, giving their characteristic features and differences:
a. mesomeric (resonance) effect;
b. hyperconjugation.
17. Discuss the stability and structures of:
a. carbanions;
b. carbocations;
c. free radicals.
18. Explain why:
a. Phenol is more acidic than ethanol.
b. Methylamine is a stronger base than ammonia.
c. Ammonia is a stronger base than aniline.
19. What are carbocations? Show hybridization in carbocations and discuss stability of primary, secondary and tertiary carbocations.

20. What are addition reactions? Explain the possible mechanisms for addition reactions with an example each.
21. Explain S_N1 and S_N2 mechanism for nucleophilic substitution reactions. Discuss their stereochemical implications.
22. Discuss elimination and substitution reactions with examples.
23. Comment on the following:
 - a. Effect of bulky group on S_N1 reactions.
 - b. Elimination vs. substitution.
24. Explain how competing E_2 and S_N2 reactions are affected by the following factors:
 - a. structures of R and X;
 - b. reagent;
 - c. solvent.

Numerical Problems

1. A mixture of (*S*)- and (*R*)-2-bromobutane has specific rotation of -10.5° . (*S*)- and (*R*)-bromobutane have a specific rotation of $+23.1^\circ$ and -23.1° , respectively. Calculate
 - a. optical purity of the mixture.
 - b. percentage composition of the mixture.
2. Calculate the specific rotation of cholesterol, given that 5.25 g cholesterol dissolved in 100 ml chloroform has optical rotation of $+1.2^\circ$ when measured in a 10 cm polarimeter tube.
3. 2-Butanol is dissolved in chloroform in a concentration of 6.30 g per 100 ml.
 - a. Calculate the specific rotation if the solution placed in a 5 cm polarimeter tube shows a rotation of $+2.3^\circ$.
 - b. What would be the observed rotation if 10 ml of the solution was diluted to 25 ml and placed in 10 cm tube?

Answers

Multiple-Choice Questions

1. (b)
2. (c)
3. (c)
4. (d)
5. (c)
6. (c)
7. (c)
8. (a)
9. (d)
10. (b)
11. (d)
12. (d)
13. (b)
14. (b)
15. (c)
16. (d)
17. (b), (d)
18. (d)
19. (b)
20. (a)
21. (a)
22. (b)
23. (a)
24. (d)

- | | |
|--------------|---------|
| 25. (b) | 36. (a) |
| 26. (b) | 37. (b) |
| 27. (a) | 38. (c) |
| 28. (b) | 39. (d) |
| 29. (c) | 40. (c) |
| 30. (b), (c) | 41. (b) |
| 31. (b) | 42. (a) |
| 32. (d) | 43. (a) |
| 33. (b) | 44. (d) |
| 34. (c) | 45. (c) |
| 35. (c) | |

Fill in the Blanks

- | | |
|---------------------------|--|
| 1. 2^n | 14. chiral, plane of symmetry |
| 2. chiral | 15. Cahn-Ingold-Prelog |
| 3. plane of symmetry | 16. geometric |
| 4. Fischer projections | 17. increases |
| 5. torsional strain | 18. inductive effect |
| 6. chair | 19. Electromeric |
| 7. <i>anti</i> | 20. free radical |
| 8. optically active | 21. trigonal planar, pyramidal |
| 9. laevorotatory | 22. ambident nucleophile |
| 10. <i>meso</i> | 23. Saytzeff's rule |
| 11. geometrical isomerism | 24. racemization, stereochemical inversion |
| 12. four | 25. resonance |
| 13. torsional, stearic | |

Numerical Problems

1. a. The pure (*R*)-2-bromobutane is in 45.45% enantiomeric excess.
b. The composition of mixture is 72.72% of (*R*)-isomer and 27.27% of (*S*)-isomer.
2. Specific rotation $[\alpha] = 22.86^\circ$.
3. a. Specific rotation $[\alpha] = 73^\circ$.
b. Observed rotation $\alpha_{\text{obs}} = 1.84^\circ$.

5

Spectroscopic Techniques and Applications

LEARNING OBJECTIVES

After completing this chapter, you will be able to understand the following:

- Characteristics of electromagnetic radiations and electromagnetic spectrum.
- Molecular spectroscopy arising from interaction of molecules with various regions of electromagnetic radiation.
- Laws of absorbance – Lambert–Beer's law.
- Emission and absorption spectrophotometers.
- Significance of signal-to-noise ratio, width and intensity of spectral lines.
- Infrared, NMR and UV–visible spectroscopy as a spectroanalytical techniques of analysis – their theory and applications.

Spectroscopic techniques, particularly those based on visible region of electromagnetic radiation, are most commonly used for analysis of chemical compounds. The absorption of radiation by the molecules and its relation to the molecular structure forms the basis of spectroscopic techniques. This chapter describes the characteristics of electromagnetic radiation and molecular spectroscopy arising from interaction of molecules with the various regions of electromagnetic spectrum. The relation of amount of radiation absorbed with concentration of absorbent and the distance travelled through the sample as well as the instrumentation required for making spectrophotometric measurements are also described. The spectroanalytical techniques of IR, NMR and UV-visible spectroscopy are discussed along with their applications in identification and characterization of organic compounds and quantitative analysis.

5.1 Electromagnetic Radiation

Electromagnetic radiation is a simple harmonic wave with the properties of a sine wave. It travels in a straight line unless it is refracted or reflected. It has both electrical and magnetic components at right angles to each other as shown in Figure 1.

Characteristics of Electromagnetic Radiation

Some important characteristics of electromagnetic radiation are as follows:

1. **Wavelength:** The wavelength of the radiation λ can be defined as the distance between two maxima of either electrical or magnetic components of the wave (crest to crest is also same). It is expressed in meters.
2. **Frequency:** The frequency of radiation, ν , is the number of waves that pass a fixed point in unit time. It is expressed in reciprocal seconds, s^{-1} or Hz.
3. **Wave number:** The wave number $\bar{\nu} = 1/\lambda$ is the reciprocal of wavelength. It is expressed in reciprocal centimeters (cm^{-1}) and energy in joules.

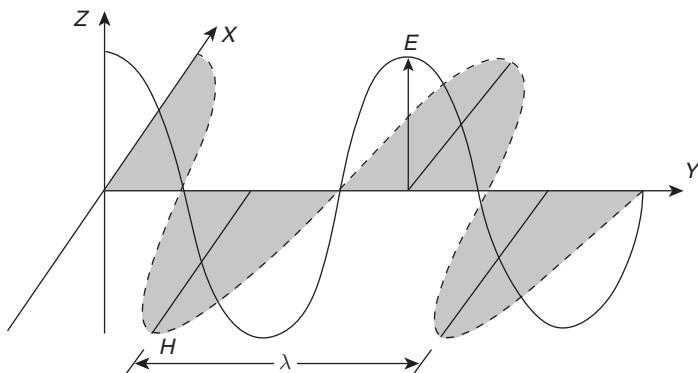


Figure 1 Electromagnetic radiation and its components.

4. **Energy:** The energy associated with regions of the electromagnetic spectrum is related to wavelengths and frequency by the equation

$$E = h\nu = \frac{hc}{\lambda} \quad (5.1)$$

where E = energy of the radiation in joules; h = Planck's constant, 6.626×10^{-34} Js; ν = frequency of radiation in Hz and c = velocity of light, 2.998×10^8 m/s.

When the frequency is high, energy is higher and wavelength is smaller. When the wavelength is large, energy is lower.

Electromagnetic Spectrum

The electromagnetic spectrum is an ordered arrangement of radiation according to wavelength. The range of wavelengths corresponding to these regions and the energy associated with them are given in Table 1.

Table 1 Electromagnetic spectrum

Name of the Region	Range of Wavelengths (nm)	Range of Frequencies (Hz)	Range of Energy per Mole (J/mol)
γ-ray region	10^{-3} to 10^{-1}	3×10^{18} – 3×10^{20}	10^9 – 10^{11}
X-ray region	10^{-1} to 10^{-2}	3×10^{16} – 3×10^{18}	10^7 – 10^9
UV–Visible region	10^4 to 10^3	3×10^{14} – 3×10^{16}	10^5 – 10^7
Infrared region	10^5 to 10^3	3×10^{12} – 3×10^{14}	10^3 – 10^5
Microwave region	10^9 to 10^7	3×10^{10} – 3×10^{12}	10^1 – 10^3
Radiofrequency region	10^7 to 10^5	3×10^6 – 3×10^{10}	10^{-3} – 10^1

Concept Check

- Define (a) wave number and (b) frequency.
- What are the physical properties of a substance that can be recorded?
- What is the wavelength range of UV-visible region?

5.2 Molecular Spectroscopy**Types of Energy Changes in a Molecule**

We know that electromagnetic radiation is associated with electric and magnetic fields. When it falls on molecules, the electric and magnetic fields of light interact with the electric and magnetic effect produced by molecular changes which includes rotation and vibration. The electronic changes in the molecules and nuclear changes are given in Figure 2. This gives rise to transitions between rotational and vibrational energy levels in addition to electronic transitions. The absorption/emission of energy due to these molecular, electronic and nuclear changes occur in different regions of electromagnetic spectrum, which are discussed as follows.

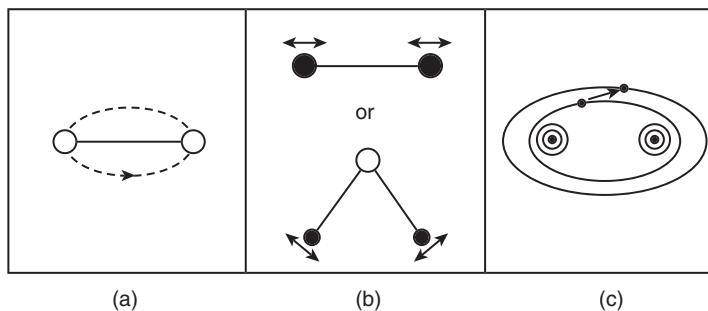


Figure 2 Types of energy changes in a molecule: (a) rotational changes in microwave region; (b) vibrational changes in infrared region and (c) electronic changes in UV-visible region.

- The radio frequency region:** The nucleus and electrons are tiny charged particles. The spins of these charged particles form magnetic dipoles. The change of spin direction causes the change of magnetic dipole. This change of magnetic dipole interacts with magnetic field of electromagnetic radiation in the radio frequency region, which results in an absorption or emission spectrum.
- The microwave region:** A polar molecule like HCl has a permanent dipole moment. On rotating the molecule about its center of gravity, the positive and negative charges change places periodically. As a result of interaction between fluctuating dipole and radiation, energy may be emitted or absorbed. Rotation of polar molecule gives rise to spectrum in the microwave region.
- Infrared region:** In this region, dipole is produced by vibration rather than rotation. For example, in a triatomic molecule of CO_2 , the three atoms are arranged linearly. The carbon atom carries a small positive charge and each oxygen atom carries a small negative charge. During vibration of the molecule, the two C–O bonds are stretched and compressed alternatively. If the two bonds are simultaneously stretched followed by simultaneous compression, the vibrations are termed symmetric stretching vibrations. Dipole moment remains zero through such vibrations [Figure 3(a)].

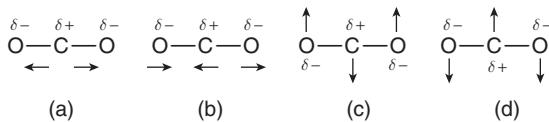


Figure 3 Stretching vibrations of CO_2 : (a) Symmetric stretching; (b) asymmetric stretching (c) and (d) bending of two degenerate modes at right angles.

If, however, one C–O bond is stretched while the other one is compressed or vice versa, the vibration is called asymmetric stretching vibration and periodic alteration occurs [Figure 3(b)], as shown in the figure. During the symmetric and asymmetric stretching vibrations, the center of gravity does not move. The two C–O bonds can also undergo bending in two modes, which are degenerate and at right angles [Figures 3(c) and (d)]. As a molecule vibrates, if there is a change in its dipole moment then this induces an electric field that interacts with the infrared radiation. If there is a match in frequency of the radiation and the natural vibration of the molecule absorption of electromagnetic radiation takes place. These vibrations give rise to spectrum in the infrared region.

4. **The visible and ultraviolet region:** In this region, valence electrons get excited and move from one energy level to another in the molecule. These electronic changes in the molecule cause change in the electric dipole which interacts with the electric field of the electromagnetic radiation. The interaction gives rise to the spectrum in the UV-visible region.

Absorption of Electromagnetic Radiation by Organic Molecules

Organic molecules absorb radiation in discrete packets of energy, given by $\Delta E = h\nu$, which are also called *quanta of energy*. A molecule can only absorb a particular frequency if there exists within the molecule an energy transition of the same magnitude (Figure 4).

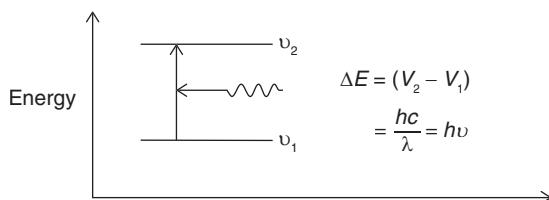


Figure 4 Quanta of energy.

At room temperature, the organic molecules in a sample are in the lowest constant vibrational state. Each bond has its characteristic stretching and bending frequency, capable of absorbing light of that frequency. So, at this temperature, the molecules are vibrating back and forth about an average value of the interatomic distance (bond length). On absorption of light of appropriate energy, the molecules become excited and move to the second vibrational level. This absorption can occur only if the dipole moment of the molecule is different in the two vibrational levels. The variation of the dipole moment of the molecule with change in interatomic distance during the vibration corresponds to an oscillating electric field associated with the electromagnetic radiation. The vibrational levels of a vibrating bond and the variation of energy with interatomic distance are depicted in Figure 5.

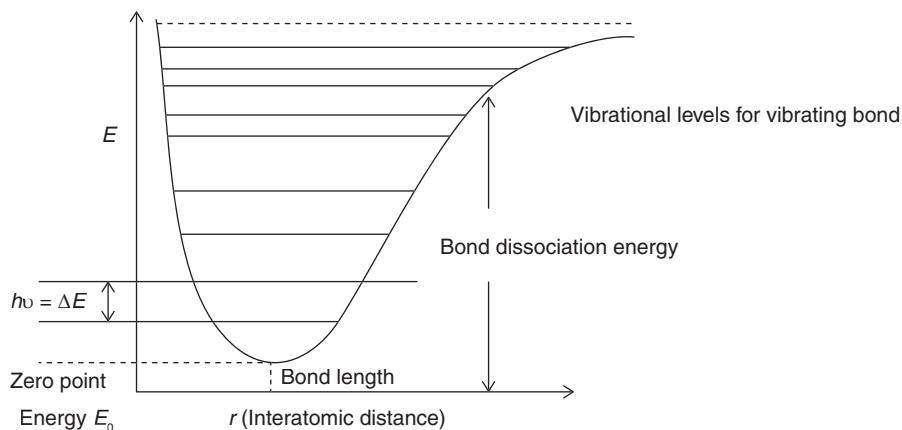


Figure 5 Variation in energy of molecular vibration with interatomic distance.

Molecular vibrations which lead to a change in the dipole moment of the molecule will give rise to absorption bands in the infrared region, otherwise these are known as IR inactive. For example, the symmetrical stretching of --C=C-- bond in ethylene does not produce change in the dipole moment (due to center of symmetry), so this mode of vibration is IR inactive. Atoms of a molecule vibrate in a variety of ways but at specified energy levels which are quantized.

The stretching and bending vibrations of a molecule are important from energy absorption aspect. In stretching, the distance between two atoms increases or decreases, however, the atoms remain on the same bond axis. Vibrations require higher energy and occur at higher frequency. In bending or deformations, the distance between the two atoms remains constant but the position of the atoms may change with respect to the original bond axis. This type of vibration required lower energy and occurs at lower frequency. Bending vibrations are referred to as *deformations*.

When a sample of organic compound is irradiated by an IR radiation, some of the frequencies are absorbed while other frequencies are transmitted through the sample without being absorbed. If we plot absorbance or transmittance against frequency, the result is an IR spectrum. The absorbance of a sample at a particular frequency is defined as

$$A = \log\left(\frac{I_0}{I}\right)$$

where I_0 and I are the intensities of the light before and after interaction with the sample, respectively. Absorbance is, therefore, a logarithmic ratio.

Beer–Lambert’s Law

When a monochromatic light of intensity I_0 is passed through a sample solution in a transparent container, some of the light is absorbed, so the intensity (I) of the transmitted light is less than intensity of incident light (I_0). Some loss in intensity also occurs from scattering by the particles and also from

reflection from interface, but is mainly due to absorptivity of the solution. The relationship between intensity of incident and transmitted light is studied by the laws of absorbance of radiation given separately by Beer and Lambert and later combined as Beer–Lambert law. The law relates the decrease in intensity of the transmitted light or the absorbance to the properties of the material through which the light is travelling. The law describes quantitatively the linear relationship between absorbance with the length of path traversed by the light and the concentration of the absorbing species (Figure 6). Absorbance of a monochromatic incident light is directly proportional to the:

1. Length of the path (x) through which the light travels, that is, the width of the container (*Lambert's law*).
2. Concentration (C) of the solution of the sample used in the experiment (*Beer's law*).

Lambert derived the quantitative relationship between the decrease in intensity of light I with the thickness x of the homogeneous sample through which it passes. The Lambert law states that *the decrease in intensity of light with the thickness of the absorbing material at any point is directly proportional to the intensity of light*.

If a parallel beam of monochromatic light of intensity, I_0 traverses an infinitesimally small distance, dx of an absorber, the decrease in intensity $-dI$ is given by

$$-dI = kIdx$$

The proportionality constant k depends on the wavelength of radiation, the concentration C is assumed constant. On rearranging the equation, $-dI/I = k dx$, which is the mathematical statement of the fact that the intensity of light absorbed is proportional to the thickness of traversed. On integration

$$-\int_{I_0}^I \frac{dI}{I} = k \int_0^x dx$$

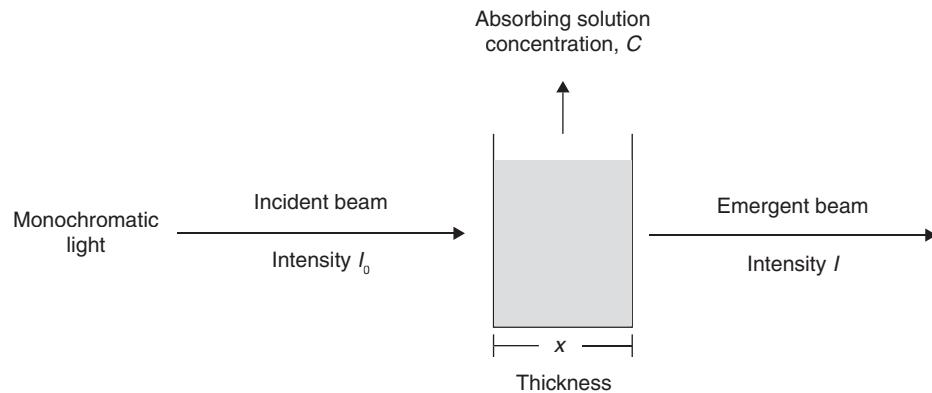


Figure 6 Relation of intensity of incident and transmitted light with concentration and thickness of absorbing solution.

$$\ln I_0 - \ln I = \ln\left(\frac{I_0}{I}\right) = kx \quad (5.2)$$

This is the mathematical representation of Lambert's law.

Lambert law was extended by Beer to show that *when light passes through a solution of given thickness, the fraction of incident light absorbed is dependent not only on the intensity of the light but on concentration C of the solution.* This is known as Beer's law.

The dependence of intensity of light on the concentration of absorbing species is given by

$$-dI = kIdC$$

On integration, we get

$$\begin{aligned} - \int_{I_0}^I \frac{dI}{I} &= k \int_0^C dC \\ \ln I_0 - \ln I &= \ln\left(\frac{I_0}{I}\right) = kC \end{aligned} \quad (5.3)$$

This relation is the mathematical representation of Beer's law.

If both the thickness and concentration are variable, the combined Lambert–Beer's law becomes

$$\ln\left(\frac{I_0}{I}\right) = kCx \quad (5.4)$$

Replacing natural logarithm by base-10 logarithm, the equation becomes

$$\log\left(\frac{I_0}{I}\right) = \alpha_{\text{abs}}cx \quad (5.5)$$

where α_{abs} is the new constant obtained by $k/2.303$.

Absorbance, A is defined as

$$A = \log\left(\frac{I_0}{I}\right) = \alpha_{\text{abs}}cx \quad (5.6)$$

Transmittance, T is defined as the ratio of radiant power transmitted by a sample for the radiant power incident on the sample.

$$T = \left(\frac{I}{I_0}\right) \quad (5.7)$$

The relation between absorbance and transmittance is

$$A = \log\left(\frac{1}{T}\right) = -\log T$$

Absorbance can be defined as the logarithm (to the base 10) of the reciprocal of transmittance.

The proportionality constant, α_{abs} is called *absorptivity* if C is given by grams of absorbing material per liter, and x is in cm. Hence α_{abs} has the units l/g·cm. If the concentration is given in mol/l and x in cm, the

proportionality constant is called *molar absorptivity* and is given by the symbol, ε . Thus, the Lambert–Beer law can be mathematically written as

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon Cx \quad (5.8)$$

where ε is in l/mol-cm. When absorbance is plotted against concentration, it should give a straight line (Figure 7) passing through the origin. However, a deviation in straight line is observed and is called deviation in Lambert–Beer's law. This deviation may originate from instrumental and chemical factors. Instrumental deviation arises when monochromators are not used. Chemical deviations arise due to the refractive index of the solution. At concentration of 10^{-3} M or less, the refractive index is essentially constant; but at high concentration, the refractive index varies considerably and hence absorptivity varies. Chemical deviations are also caused by shifts in position of chemical or physical equilibrium involving the absorbing species. For example, the dichromate ion absorbs in the visible region at 450 nm.



Upon diluting a dichromate solution, the equilibrium shifts to the left. Thus, the necessary conditions for Beer-Lambert law to hold good are:

1. The incident light should be monochromatic.
2. The light beam should not be scattered.
3. The absorbing solution should be dilute.

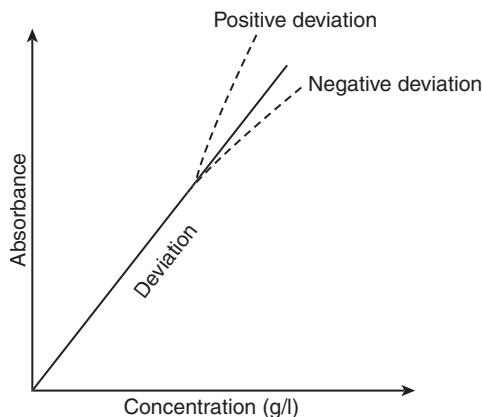


Figure 7 Graphical representation of Lambert–Beer's law (dashed curve indicates deviation).

Concept Check

- What happens when a molecule interacts with IR light?
- Define molar absorptivity and absorptivity.
- What is the mathematical form of Lambert–Beer's law?
- What are the limitations of the Lambert–Beer's law?

5.3 Basic Spectroscopy Instrumentation

Essential Components

All the instruments for absorption and emission spectroscopy consist of five fundamental components. These are as follows:

1. A constant source of radiant energy whose intensity or power can be changed. For example, hydrogen discharge lamps, deuterium lamps, xenon discharge lamps and mercury arc lamps.
2. A dispersing device which can be used for selecting an appropriate wavelength region. A narrow band of the wavelengths is often used in absorption measurements. This is achieved by using monochromators. They include filters, prisms and gratings.
3. An arrangement which would make the emergent light run parallel to enter the transparent material of the cell in which the test solution and solvent are taken.
4. A detector to measure the radiant energy by converting it into any measurable signal. Very often radiant energy is measured as electrical signal.
5. A device for measuring signal. These are called detectors and include barrier layer cell, photosensitive cells and photomultiplier cells.

Block Diagrams for Standard Emission and Absorption Spectrometers

A block diagram showing fundamental components of an instrument used for absorption spectrophotometer is shown in Figure 8.

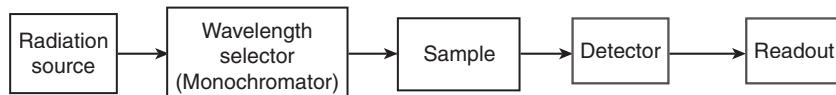


Figure 8 Block diagram of absorption spectrophotometer.

The sample absorbs radiation from the ultraviolet radiant energy source. The energy is absorbed to raise the molecule to excited states. The method is generally applied to a particular group present in the molecule. The region of spectrum in which the absorption occurs is determined by electronic transition by deflection. The block diagram of emission spectrophotometer is given in Figure 9.

The sample is excited to form atoms containing excited electrons. On returning to original state, these electrons emit electromagnetic radiation of a particular wavelength characteristic of the sample. Hence, it is necessary to collect the emitted radiation, analyze and record it as in the case of absorption instrument. The detector does not collect radiation directly from the exciting beam. A modulator is placed between the source of excitation and the sample, together with a tuned detector-amplifier, which ensures that only the emission from the sample which arises directly from excitation is recorded; any other spontaneous emission is ignored.

Resolving Power and Signal-to-Noise Ratio

Almost all modern spectrometers use some form of electronic amplification to magnify the signal produced by the detector. Every recorded spectrum has a background of random fluctuations caused by

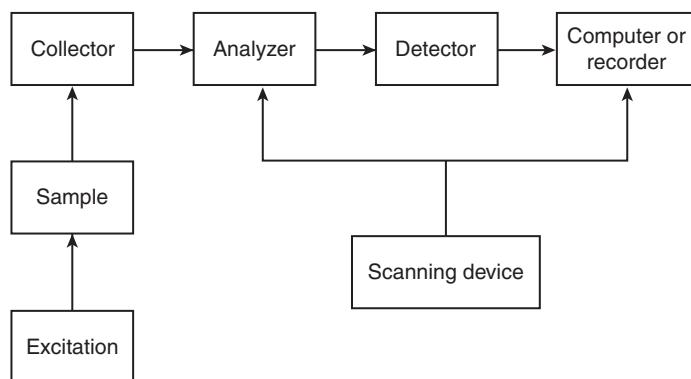


Figure 9 Block diagram of an emission spectrophotometer.

spurious electronic signals produced by the source or detector, or generated in amplifying equipment. These fluctuations are usually referred to as noise. In order to detect a real spectral peak distinguished from the noise, it must have intensity which is three or four times that of the noise fluctuation (i.e., a signal-to-noise ratio of three or four). This requirement places a lower limit on the intensity of observable signals.

Concept Check

- What are the differences between an absorption spectrum and emission spectrum?
- What is the significance of signal-to-noise ratio?

5.4 Infrared Spectroscopy

Infrared (IR) spectroscopy is one of the most powerful analytical techniques, which is based on the fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiations, the molecules of a chemical substance vibrate at different rates of vibration, giving rise to closely packed absorption bands called IR absorption spectrum, which may extend over a wide range of wavelength. Various bands will be present in this spectrum corresponding to the characteristic functional groups and bonds present in a chemical substance. Thus, an IR spectrum of a chemical substance is a fingerprint for its identification.

Interaction between Infrared Radiations and Molecular Vibrations

When IR radiation, whose energy is comparable to the spacing of vibrational levels, is allowed to fall on a sample of heteronuclear diatomic molecules, the vibrating molecules can absorb energy from the radiation beam and thereby increase their vibrational energy. These molecules are therefore infrared active. The mechanism of this transfer of energy between the radiation and the vibrating molecules is as follows. The vibrating molecule has a fluctuating dipole moment, and hence interacts with the electromagnetic radiation. The energy of vibration is given by

$$e_{\text{vib}} = \left(v + \frac{1}{2} \right) b\nu \quad (5.9)$$

where v is the vibration quantum number having values 0, 1, 2, and ν is the frequency in cycles/s and is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{F}{\mu}} \quad (5.10)$$

where F is the force constant, which gives the idea of toughness or the strength of the bond and μ is the reduced mass which is equal to $(m_1 m_2)/(m_1 + m_2)$; where m_1 and m_2 are the masses of the atoms of the bond. The energy difference between successive vibrational levels is given by

$$\Delta E_{\text{vib}} = \frac{b}{2\pi} \sqrt{\frac{F}{\mu}} \quad (5.11)$$

At room temperature, the value of kT is sufficiently small compared to typical values of ΔE_v so that most of the molecules are in the lowest allowed vibrational state. Electromagnetic radiation can induce transitions among the vibrational energy levels only when the vibration of a molecule leads to an oscillating dipole and a vibrational spectrum can be expected. Homonuclear molecules due to their symmetry, will not give infrared spectrum; whereas molecules such as HCl, H₂O, NO₂, etc., will give infrared spectrum.

Band positions may be expressed in terms of the wave number $\bar{\nu} = 1/\lambda$ whose unit is cm⁻¹. Band intensities may be expressed either as transmittance (T) or absorbance (A).

Modes of Vibration

A diatomic molecule has a single vibration whereas polyatomic molecules have much more complex vibrations. A molecule has as many degrees of freedom as total degrees of freedom of its individual atoms. Each atom in a molecule has three degrees of freedom corresponding to the Cartesian coordinates (x, y, z) necessary to describe its position relative to other atoms in the molecule. So a polyatomic molecule containing n atoms has a total of $3n$ degrees of freedom, that is, $3n$ coordinates are necessary to specify the positions of all nuclei. This means out of $3n$ degrees of freedom, 3 are translational associated with transition of center of mass and 3 (or 2 if the molecule is linear) are rotational degrees of freedom. The remaining $3n - 6$ ($3n - 5$ for a linear molecule) degrees of freedom are vibrational. There are, therefore, $3n - 6$ (or $3n - 5$ for linear) energy level patterns, each with its own spacing. If, corresponding to all these patterns, vibrating molecule possesses oscillating dipole moments, then there will be $3n - 6$ ($3n - 5$ for linear) observed bands. Thus, water molecule H₂O ($n = 3$) being non-linear has 3 vibrational degrees of freedom, each giving an absorption band centered at 1595 cm⁻¹, 3652 cm⁻¹ and 3756 cm⁻¹. Carbon dioxide molecule CO₂ ($n = 3$) being linear has 4 vibrational degrees of freedom, but only 2 absorption bands are visible in the infrared region.

Normal Coordinates and Normal Modes of Vibration

If the vibration does not alter any of the symmetrical properties of the molecule, it is said to be a symmetric vibration. On the other hand, if the vibration is such that reflection of the molecule in any plane of symmetry results in a change of sign of the displacement, it is called as antisymmetric vibration.

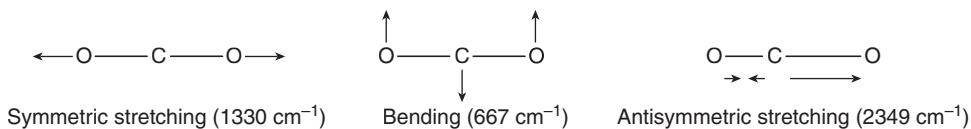


Figure 10 Fundamental vibrations of carbon dioxide molecule.

The presence of symmetry in a molecule simplifies the study of its modes of vibration. In fact, each of $3n - 6$ or $3n - 5$ vibrations are symmetric or antisymmetric with respect to any of symmetric element of the molecule. Consider the linear triatomic molecule CO_2 which has $3 \times 3 - 5 = 4$ vibrational modes. The symmetry of the 3 modes of vibrations of the CO_2 molecule is shown in Figure 10. The wave numbers 1330 cm^{-1} and 667 cm^{-1} correspond to symmetric vibrations, whereas 2349 cm^{-1} , the highest one, corresponds to an antisymmetric mode. In the spectrum (Figure 11), we can see only two vibrational frequencies at 667 cm^{-1} and 2349 cm^{-1} . This is because

1. Symmetrical stretch does not bring about any change in the dipole moment.
2. There is no energy difference in the above two bending vibrations, that is, they are degenerate. Both are equivalent and require the same energy to vibrate.

The study of vibration spectra of a molecule also determines its shape and symmetry. Let us consider the case of H_2O molecule and find out whether it has linear or bent structure.

1. The linear structure will have symmetrical bending and symmetrical stretching; the vibration involving symmetrical stretching cannot lead to absorption of energy because its symmetry does not give rise to any change in dipole moment. For the other two symmetrical bending structures, vibration will give rise to an oscillating dipole. Consequently, only two absorption bands are expected to appear in the vibrational spectra for linear structures, and thus the molecule is infrared active.
2. In the case of bent structure, all the three vibrations shown in Figure 12(a-c) are infrared active and they give rise to three absorption bands in vibrational spectra. Therefore, for bent molecule or non-linear molecule, three absorptions are expected to appear in the vibrational spectra of the molecule. For H_2O , three absorption bands at 750 cm^{-1} , 1323 cm^{-1} and 1616 cm^{-1} are observed in the IR spectrum corresponding to three modes of vibration (Figure 13).

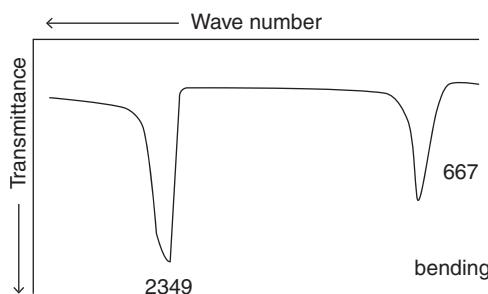


Figure 11 IR spectrum of carbon dioxide.

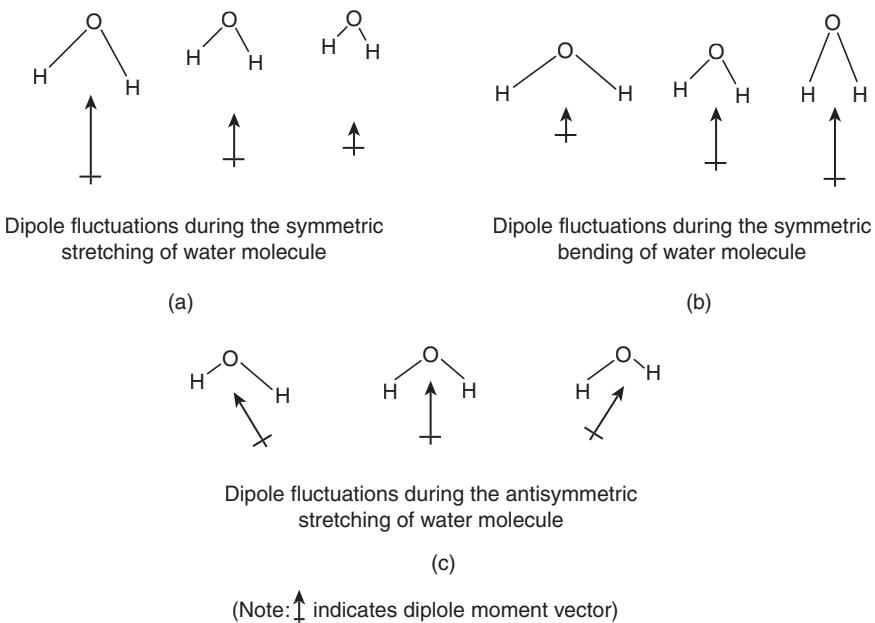


Figure 12 Fundamental vibrations of water molecule.

In the spectrum (Figure 13), we observe that

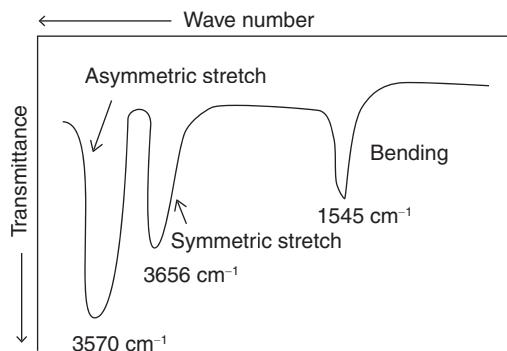


Figure 13 IR spectrum of water molecule.

- The intensities of the three bands are different because it depends upon the change of dipole moment. In asymmetric vibrations, change of dipole moment is much higher as compared to symmetric stretching and bending.
- Stretching absorption of a bond appears at higher frequency in the IR spectrum than the bending absorption of the same bond. Therefore, band at 3570 cm^{-1} corresponds to an asymmetric stretch, 3656 cm^{-1} to a symmetric stretch and 1545 cm^{-1} to bending.

Hence, it is understood that if there is no change in the dipole moment accompanying the vibrations, the molecule will be inactive in the infrared spectrum. On the other hand, if the dipole moment is altered, the change may be in the direction parallel or perpendicular to the symmetric axis. The former vibration is referred to as the parallel vibration and the latter vibration is referred to as the perpendicular vibration.

Energy of Diatomic Molecule

When two atoms combine to form a stable covalent molecule (e.g., HCl gas), it is possibly because of some internal electronic rearrangement. On the one hand there is a repulsion between the positively charged nuclei of atoms and between the negative electron clouds. On the other hand, there is an attraction between the nucleus of one atom and the electrons of the other, and vice versa. The two atoms settle at a mean inter-nuclear distance such that these forces are just balanced and the energy of the whole system is at a minimum. Attempt to distort the bond requires an input of energy. If energy is plotted against internuclear distance, the minimum intermolecular distance is referred to as the equilibrium distance r_{eq} or more simply as the bond length (Figure 14). It resembles the parabolic curve of energy plotted against the extension or compression of a spring obeying Hooke's law.

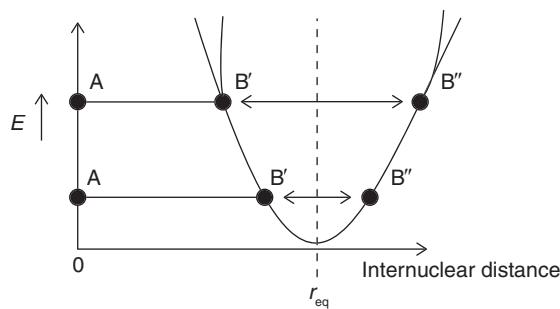


Figure 14 Plot of energy vs. internuclear distance.

The plot is similar to the parabolic curve of energy plotted against extension or compression of a spring obeying Hooke's law. Such a system is considered as a simple harmonic oscillator (Figure 15) that obeys Hooke's law.

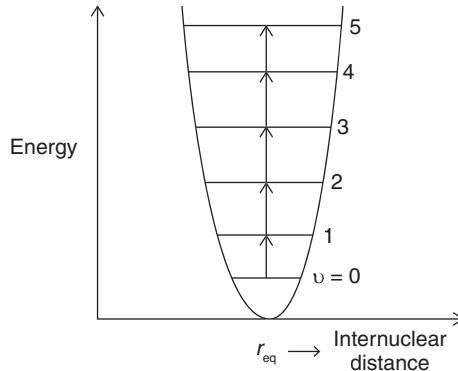


Figure 15 The simple harmonic oscillator.

Figure 14 shows that if one atom (A) is considered to be stationary on the $r = 0$ axis, the other will oscillate between B' and B'' . If the energy is increased to E_2 , the oscillation will become more vigorous – that is to say, the degree of compression or extension will be greater – but the vibrational frequency will not change. An elastic bond, like a spring, has a certain vibration frequency dependent upon the mass of the system and the force constant, but independent of the amount of distortion classically, the oscillation frequency is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

We know that frequency is given by

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

where $\frac{1}{\lambda} = \bar{\nu}$. Therefore,

$$\nu = c \times \bar{\nu} \Rightarrow \bar{\nu} = \frac{\nu}{c}$$

In terms of wave numbers, we must divide by the velocity of light, c expressed in cm^{-1} . Therefore, oscillation frequency is

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{m}} \text{ cm}^{-1}$$

The simple selection rule derived from Schrodinger wave equation, for the simple harmonic oscillator, undergoing vibrational changes (obeying Hooke's law) is

$$\Delta\nu = \pm 1 \quad (5.12)$$

The Anharmonic Oscillator

Real molecules do not obey exactly the laws of SHM because though elastic, are not homogeneous enough. So, for real molecules, if the bond between atoms is stretched, there comes a point at which it will break and the molecule will dissociate into atoms. So even though for small compressions and extensions the bond may be taken as perfectly elastic, for larger amplitudes, say greater than 10% of the bond length, a much more complicated behavior is observed. Figure 16 depicts diagrammatically, the shape of the energy curve for a real diatomic molecule together with simple harmonic parabola (dashed line) expected for an ideal diatomic molecule.

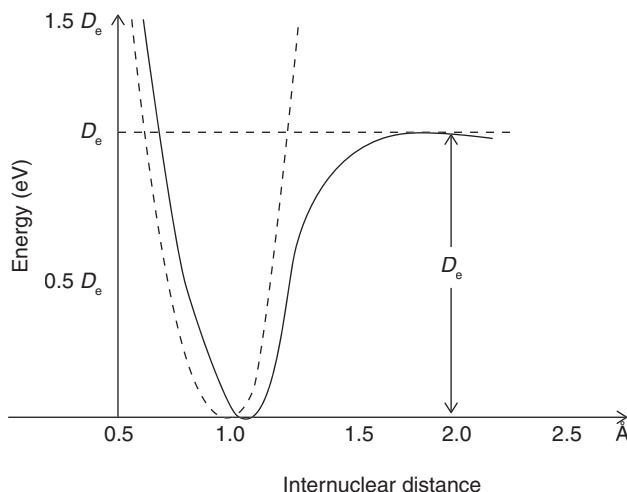


Figure 16 Morse curve of the energy of a diatomic molecule undergoing anharmonic oscillations.

The selection rules for the anharmonic oscillator are found to be

$$\Delta\nu = \pm 1, \pm 2, \pm 3 \dots$$

These are the same as for the harmonic oscillator, with the additional possibility of larger jumps. However, these are predicted by theory but actually observed with decreasing probability and generally only the lives of $\Delta\nu = \pm 1, \pm 2$ and ± 3 , at the most, have observable intensity.

1. For transition $\nu = 0 \rightarrow \nu = 1; \Delta\nu = +1$. It has considerable intensity and is known as fundamental absorption.
2. For transition $\nu = 0 \rightarrow \nu = 2; \Delta\nu = +2$. It has small intensity and is known as first overtone with small intensity known as first overtone.
3. For transition $\nu = 0 \rightarrow \nu = 3; \Delta\nu = +3$. It generally has negligible intensity and is known as second overtone.

For example, the spectrum of HCl, shows a very intense absorption at 2886 cm^{-1} , a weaker one at 5668 cm^{-1} and a very weak one at 8347 cm^{-1} .

Overtones and Combination Frequencies

The spectrum of a polyatomic molecule consists essentially of an absorption band at each of the $3n - 6$ (or $3n - 5$ for linear) fundamental frequencies. This is based on the assumption that each vibration is simple harmonic. If however this restriction is lifted, the possibility of overtone transitions arises. Corresponding to each of the fundamental modes ν_1, ν_2, ν_3 , etc., there is now a possibility of first, second and further overtones of diminishing intensities, occurring approximately at frequencies twice the fundamental frequencies or at sum of fundamental frequencies or overtones. Thus, bands may occur at

a combination of frequencies such as $\nu_1 + \nu_2$, $2\nu_1 + \nu_2$, $\nu_1 + \nu_2 + \nu_3$, etc., frequencies and are known as combination bands. Similarly, difference bands may occur at frequencies such as $\nu_1 - \nu_2$, $\nu_1 + \nu_2 - \nu_3$, etc. These bands are normally weak but often occur in a complex spectrum.

Further, it may happen that in a particular molecule two different modes of vibration, more commonly a fundamental and some overtones or combination, have the frequencies very close to each other. Then just as two pendulums of similar frequencies resonate and exchange energy, the two close molecular vibrational frequencies may also resonate, resulting in two new frequencies one higher and one lower than the original frequencies. Such a resonance phenomenon, when it occurs between a fundamental and overtone is known as Fermi resonance. A simple example of such resonance is found in CO_2 where $\nu_1 (1330 \text{ cm}^{-1})$ is very close to $2\nu_2 (1134 \text{ cm}^{-1})$; the two bands observed at frequencies 1285 cm^{-1} and 1385 cm^{-1} (whose average is 1330 cm^{-1}) are therefore attributed to a resonance between $\nu_1 + 2\nu_2$.

Calculation of Vibrational Frequencies

The frequency of a vibration can be calculated by using Hooke's law, which states that, the frequency of vibration is directly proportional to the square root of the force constant of the bond. The force constant is characteristic of a given bond. The vibrations of two atoms joined together by a chemical bond are similar to the vibrations of two balls joined by a spring. Stretching of the spring requires more energy than that required to bend it. The more we stretch the spring, the greater will be resisting force offered by the spring. Such resisting force offered by a chemical bond is known as force constant of the bond.

The frequency is also *inversely* proportional to the square root of the reduced mass $\left(\frac{m_1 m_2}{m_1 + m_2}\right)$ of the

system. So higher the value of the reduced mass, lower is the frequency of absorption. Similarly, the stronger the bond, greater will be the frequency of absorption.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{f \left(\frac{m_1 + m_2}{m_1 m_2} \right)}$$

We know that

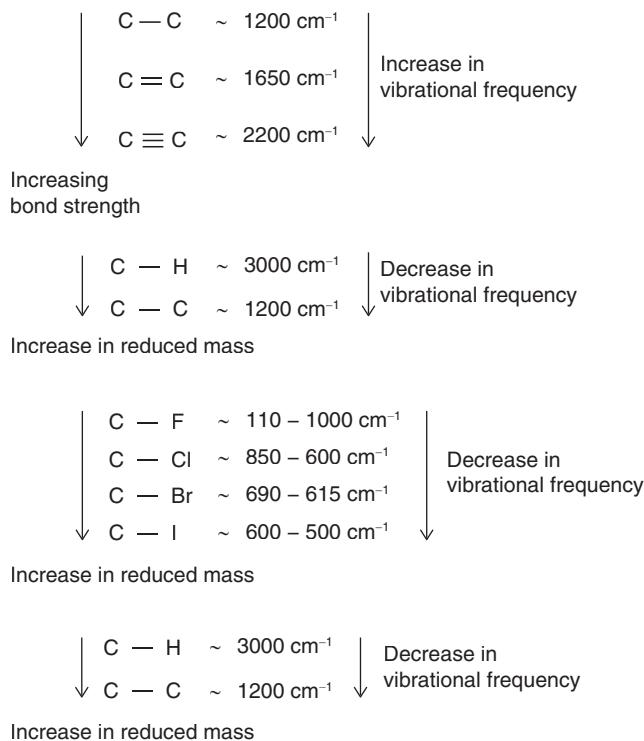
$$\nu \propto \sqrt{\frac{\text{Bond strength}}{\text{Mass}}},$$

$$\nu = \sqrt{\frac{f}{m}} = \frac{1}{2\pi} \sqrt{\frac{f}{\frac{m_1 m_2}{m_1 + m_2}}} = \frac{1}{2\pi} \left(\frac{f}{\frac{m_1 m_2}{m_1 + m_2}} \right)^{\frac{1}{2}}$$

Therefore,

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{f \left(\frac{m_1 + m_2}{m_1 m_2} \right)} \left(\because \bar{\nu} = \frac{\nu}{c} \right)$$

Consider the bonds,



In addition to fundamentals, overtones may arise, if a molecule in the lowest or first vibrational state is excited to the third vibrations level. The energy required is almost twice that required for oscillation to the second vibrational level. It is not exactly twice as much because the higher levels tend to lie closer together than the lower level. However, the intensities of overtones decrease as the order of overtone increases (i.e., second overtone is less intense than the first overtone) as shown in Figure 17.

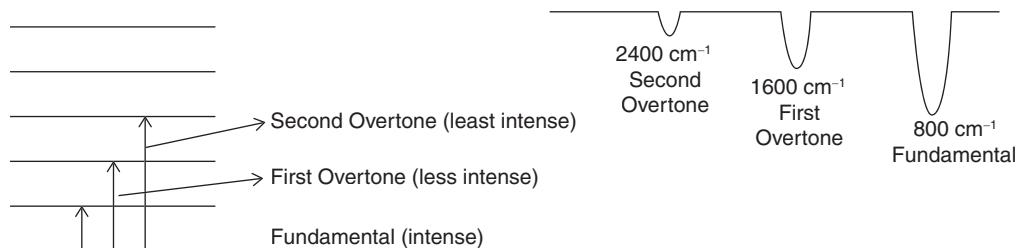


Figure 17 Intensities of overtones.

Vibrational Coupling

We have learnt that the vibrations that result from the transitions following the selection rule $\Delta\nu = +1$ are called *fundamental vibrations* and the other frequencies which can be generated by modulation of the fundamentals are known as *overtones* (harmonics). Overtones appear at integer multiples of fundamentals

vibrations, so that strong absorptions at say, 800 cm^{-1} and 1750 cm^{-1} will also give rise to weaker absorption at 1600 and 3500 cm^{-1} respectively. Two frequencies may interact to give *beats* which are combination or difference of these frequencies. Thus, absorptions at 750 cm^{-1} and 1450 cm^{-1} may interact to produce weaker beat frequency at 2200 cm^{-1} similarly the difference beat frequency appears at frequency corresponding to difference of these two frequencies. The two N–H stretch bands in the 3497 – 3077 cm^{-1} region in primary amines and primary amide spectra result from coupling. Similarly, the two C=O stretching bonds in 1818 – 1720 cm^{-1} region is carboxylic anhydride and imide spectra and the two C–H stretch bonds in the 3000 – 2760 cm^{-1} region for both methylene and methyl group result from coupling of vibrations.

Fermi Resonance

Interaction between fundamental vibrations and overtones or combination – tone vibrations is known as Fermi resonance. Enrico Fermi, who described the concept of resonance in vibration coupling, later stated that it is a feature characteristic of AX_2 groups.

Some examples where Fermi resonance can be observed are discussed as follows:

- In aldehydes:** Aldehydes show aldehydic C–H stretching absorption in the 2830 – 2780 cm^{-1} region. Two moderately intense bands are observed in this region which can be attributed to Fermi resonance between the fundamental aldehydic C–H stretch and the first overtone of the aldehydes C–H bending vibration that usually appears near 1390 cm^{-1} .
- In CO_2 molecule:** For CO_2 , the fundamental bending vibration occurs near 666 cm^{-1} and the first overtone near 1334 cm^{-1} . So, the IR spectrum, if no Fermi resonance was taking place would be as shown in Figure 18(a). However, the spectrum of CO_2 molecule observed is as shown in Figure 18(b). The symmetrical stretching of CO_2 (zero dipole moment) appears in Raman spectrum near 1340 cm^{-1} . On closer examination, two bands are observed, one at 1286 cm^{-1} and one at 1388 cm^{-1} . The splitting results from coupling between the fundamental C=O stretching; vibrations, near 1340 cm^{-1} and the first overtone of the bending vibration near 1334 cm^{-1} .

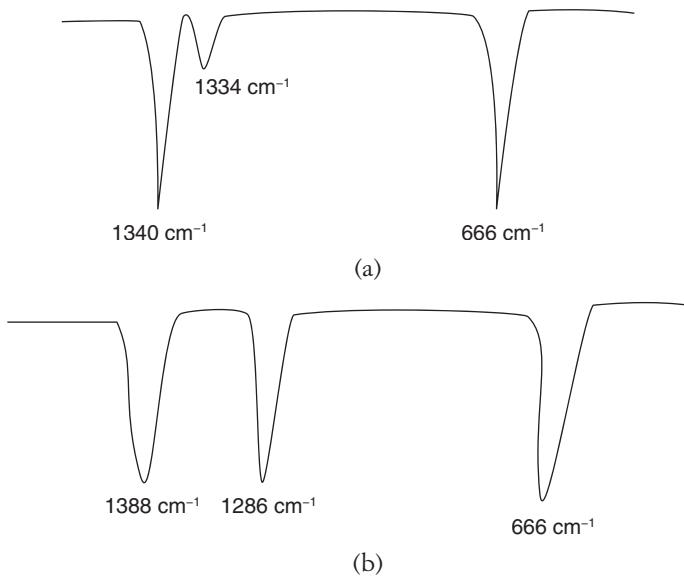


Figure 18 IR spectrum for CO_2 : (a) Without Fermi resonance (\times) and (b) with Fermi resonance (\backslash).

The overtone acquired intensity at the expense of fundamental because both are in a state of mutual exchange and coupling and the band at lower frequency is shifted to still lower frequency region, while the band at higher frequency is shifted to still higher region.

Recording of IR spectrum (Instrumentation for IR Spectroscopy)

IR Spectrometer

The spectrophotometer (Figure 19) consists of a source of infrared light, generally rods made of Nernst glower or Nernst filament containing mixtures of the oxides of Zr, Th, Ce, Y, Er, etc., silicon carbide and other ceramic materials. When they are heated to 1800°C, they emit radiation throughout the whole frequency range of the instrument.

Diffraction grating, containing a series of microscopically close parallel triangular grooves engraved on a reflecting surface is used as a monochromator. Light reflected from the grating is diffracted to get the light of specific wavelengths and is split into two beams of equal intensity. Then one beam is passed through the sample to be examined. If the frequency vibration of the sample of molecule falls within the range of the instrument, the molecule may absorb energy of this frequency from the light. The spectrum is therefore scanned by comparing the intensities of the two beams after one has passed through the sample to be examined. The wavelength range over which the comparison is made spreads out in the usual way with a grating.

The detection is made by using two types of detectors. First type is the one sensing the heating effect of the radiation (Golay cell), and the second is the one which depends on photoconductivity (indium antimonide and mercury cadmium telluride). In both the detectors, when the effect, that is, temperature or conductivity rise at a given frequency is greater, the transmittance of the sample at that frequency is also greater.

The whole operation is done automatically in such a way that the usual finished spectrum consists of a chart showing downward peaks corresponding to absorption plotted against *wavelength* of frequency. To allow for variations in the spectrophotometer, the spectra are often calibrated against accurately known bands of the spectrum of polystyrene; the peaks of one or more of the bands being superimposed on the spectrum which is to be taken.

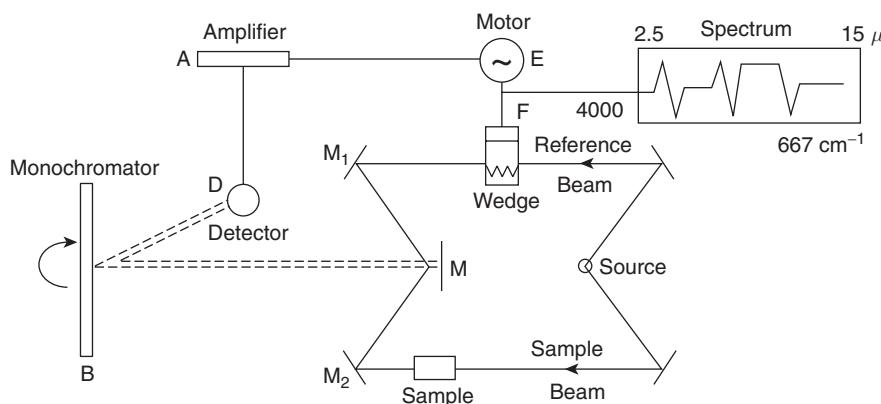


Figure 19 IR spectrophotometer.

Sampling

When the sample is in vapor form, it is introduced into a special cell usually about 10 cm long, which can then be placed directly in the path of one of the infrared beams. The end walls of the cell are usually made of sodium chloride which is transparent to IR.

If the sample is liquid, a drop of the liquid is squeezed between two flat plates of sodium chloride. If the sample is solid, about 1 mg of the solid is finely ground in a small agate mortar with a drop of a liquid hydrocarbon (nujol) or if C—H vibrations are to be examined with hexachlorobutadiene. The mull thus obtained is then pressed between two flat plates of sodium chloride. Alternatively, the solid is ground with 10–100 times its quantity of pure KBr and the mixture is pressed into a disk using a special mould or embedded in a special cardboard frame; in either case by means of a hydraulic press to give a KBr pellet. The use of KBr eliminates the problem of appearance of bands due to mulling agent and also KBr pellet gives better spectra.

A typical IR spectrum is shown in Figure 20.

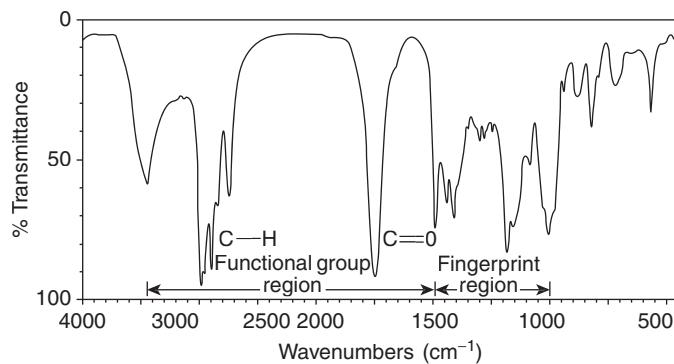


Figure 20 IR spectrum.

Analysis of IR Spectra

With an increase in the number of atoms in a molecule, the number of normal modes of vibration increases rapidly and a detailed analysis of spectrum becomes difficult. When interpretation of IR spectrum is taken up, one can qualitatively assign the strongest bands and can identify some of the weaker ones as overtones and combinations. For practical purposes, some generalizations may be made for analysis of IR spectra. These are discussed as follows:

- Group vibrations:** Absorption at a frequency that is characteristic of a particular group can be taken as indication of the presence of that group in the compound being studied. This means that a particular group gives rise to characteristic absorption bands at certain frequencies which remain much the same from compound to compound.
- Fingerprint region:** The spectral region, $1430\text{--}910\text{ cm}^{-1}$ is called fingerprint region. It contains many absorption bands caused by bending vibrations and also the absorption bands caused by several stretching vibrations. Since in a molecule, bending vibrations are in general more numerous than stretching vibrations, this region of the spectrum is particularly rich in absorption bands. It

is seldom possible to assign each of these bands to a particular mode of vibration. The complex combination of bands as a whole is highly typical of the given molecular structure, and hence is extremely useful in establishing conclusively the identity of the two samples. Similar molecules may show very similar spectra at frequencies higher than 1430 cm^{-1} , but in the fingerprint region there will usually be discernible differences.

The characteristic frequencies of some of the important groups are given in Table 2. Characteristic frequencies are useful for interpreting the IR spectrum of unknown molecules. For example, if a spectrum contains strong absorption at around 3600 cm^{-1} , it indicates that the compound contains an $-\text{OH}$ group.

Table 2 Characteristic frequencies of some of the important groups

Group	Nature of Vibration	Type of Compound	Wave Number (cm^{-1})	Intensity
O—H	Stretch, (H-bonded)	Primary, secondary alcohols	3200–3600	Strong, broad
O—H	Stretch, (free)	Phenol	3500–3700	Strong, sharp
C—O	Stretch	Esters, alkyl ketones	1050–1150	Strong
C—H	Stretch	Alkane	2850–3000	Strong
—C—H	Bending		1350–1480	Variable
=C—H	Stretch	Alkene	3010–3100	Medium
=C—H	Bending		675–1000	Strong
C=C	Stretch		1620–1680	Variable
C—F	Stretch		1000–1400	Strong
C—Cl	Stretch	Alkyl halide	600–800	Strong
C—Br	Stretch		500–600	Strong
C—I	Stretch		500	Strong
C—H	Stretch	Alkyne	3300	Strong, sharp
—C≡C—	Stretch		2100–2260	Variable, not present in symmetrical alkynes

(Continued)

Table 2 Continued

<i>Group</i>	<i>Nature of Vibration</i>	<i>Type of Compound</i>	<i>Wave Number (cm⁻¹)</i>	<i>Intensity</i>
N—H	Stretch	Amine	3300–3500	Medium (primary amines have two bands; secondary have one band, often very weak)
C—N	Stretch		1080–1360	
N—H	Bending		1600	Medium
C—H	Stretch	Aromatic hydrocarbon	3000–3100	Medium
C=C	Stretch		1400–1600	Medium weak, multiple bands
C=O	Stretch	Carbonyl compounds	1670–1820	Strong
(Conjugation moves absorptions to lower wave numbers)				
C—O	Stretch	Ether	1000–1300 (1070–1150)	Strong
C≡N	Stretch	Nitrile	2210–2260	Medium
N—O	Stretch	Nitro	1515–1560 and 1345–1385	Strong, two bands
(Conjugation moves absorptions to lower wave numbers)				
C=O	Stretch		1700–1725	Strong
O—H	Stretch	Acid	2500–3300	Strong, very broad
C—O	Stretch		1210–1320	
C=O	Stretch		1740–1720	Strong
=C—H	Stretch	Aldehyde	2820–2850 and 2720–2750	Medium, two peaks
C=O	Stretch		1640–1690	
N—H	Stretch	Amide	3100–3500	Unsubstituted have two bands
N—H	Bending		1550–1640	
C=O	Stretch	Anhydride	1800–1830 and 1740–1775	Two bands

(Continued)

Table 2 Continued

<i>Group</i>	<i>Nature of Vibration</i>	<i>Type of Compound</i>	<i>Wave Number (cm⁻¹)</i>	<i>Intensity</i>
C=O	Stretch		1735–1750	Strong
C—O	Stretch	Ester	1000–1300	Two bands or more
Acyclic	Stretch		1705–1725	Strong
Cyclic	Stretch		3-membered (1850); 4-membered (1780); 5-membered (1745); 6-membered (1715); 7-membered (1705)	Strong
α, β -Unsaturated	Stretch		1665–1685	Strong
Aryl	Stretch	Ketone	1680–1700	Strong

Interpretation of IR Spectrum

An absorption band in the IR spectra refers to an absorption of an IR radiation of a frequency characteristic of a bond or a group and indicates the presence of that bond or group in the molecule. For example, the absorption band at 3300 cm^{-1} is indicative of the presence of $-\text{OH}$ group in the molecule. The absence of characteristic bands for a bond or group can generally be considered as an evidence for the absence of these bands or groups in the molecule. Thus, the absence of absorption in region $1850\text{--}1640\text{ cm}^{-1}$ indicates the absence of carboxyl group in the molecule.

For the purpose of interpretation, IR spectra may be divided into the following regions, which show up more clearly in the spectrum and are uncomplicated by other absorptions. These are collectively known as functional group region.

1. **Frequency range $4000\text{--}2200\text{ cm}^{-1}$:** Absorption bands appearing in this region are due to bonds formed with hydrogen, that is, $\text{X}-\text{H}$, where $\text{X}=\text{C}, \text{N}, \text{O}, \text{S}$. The band for $\text{O}-\text{D}$ also appears in the same region.
2. **Frequency range $2200\text{--}2000\text{ cm}^{-1}$:** Absorption bands in this region indicate the presence of triple bonds such as $-\text{C}\equiv\text{C}-$, $-\text{C}\equiv\text{N}-$ or conjugated double bonds $-\text{C}=\text{C}=\text{C}-$ as these require high frequency and high energy.
3. **Frequency range $1800\text{--}1550\text{ cm}^{-1}$:** This is double bond region and absorption bands in this region indicate the presence of double bonds such as $-\text{C}=\text{C}-$, $-\text{C}=\text{O}$, $-\text{C}=\text{N}-$, $-\text{N}=\text{N}-$, etc.
4. **Frequency range $1600\text{--}1300\text{ cm}^{-1}$:** Strong skeletal bands for aromatic compounds and heterocyclic aromatics fall in the region of the spectrum. The lack of strong absorption bands in region generally indicates a non-aromatic structure.
5. **Frequency range $1400\text{--}900\text{ cm}^{-1}$:** This region is usually referred to the fingerprint region. The absorption pattern in this region is quite complex, with the bands arising from interactions between vibrational modes of bonds. This region of the spectrum is very important because the pattern of

absorption in this region is unique for a particular compound and hence can be used for identification of unknown compounds. For this purpose, the IR spectrum obtained for the unknown compound is compared with available reference of standard spectra recorded for compounds under identical conditions.

Thus, for interpretation purpose, the frequency range of IR spectrum can be represented as shown in Figure 21 in terms of both absorbance and transmittance.

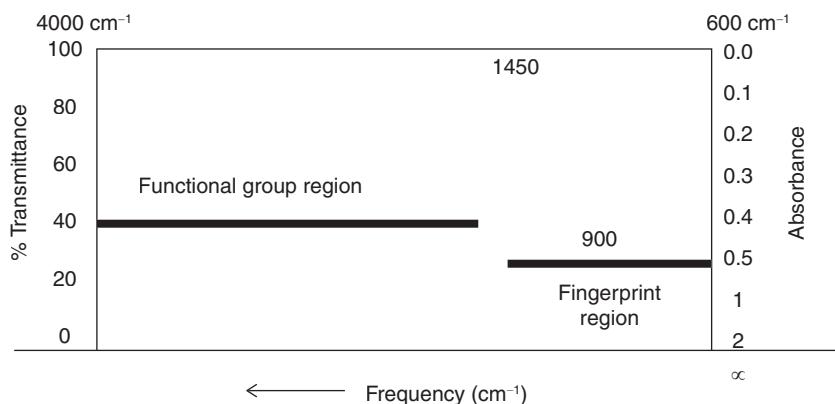


Figure 21 Important regions for interpretation of IR spectrum.

Applications of IR Spectroscopy

- Identification of functional groups:** Most of the functional groups have characteristic IR absorption frequencies. The functional groups present in an unknown compound can be identified by correlating the absorption frequency with the data.
- Identification of substances:** If the IR of two substances is found to be identical under similar conditions then they must be the same compound. Similar conditions here mean that the compounds are in the same physical state and the concentration of solution and solvent used are also the same, as are other experimental conditions.
- Determination of the purity:** IR spectroscopy has been used for establishing the purity of the compound. Whenever a compound has an impurity, it reduces the sharpness of individual bands. It also causes the appearances of extra bands and a general blurring of the spectrum. Thus, fairly sharp and well resolved absorption bands indicate pure compounds and broad and poorly resolved absorption bands are obtained for compounds containing impurity. For example, small quantities of ketones in a hydrocarbon can be detected because the latter has no absorption near 1720 cm^{-1} , which is a characteristic frequency of the carbonyl group. IR spectroscopy method of detection of impurities is used for quality control of many chemicals or drugs on an industrial scale.
- Study of chemical reactions:** Majority of the organic reactions involve changes in functional groups, IR spectroscopy is very useful in following the progress of such reactions. Practically, a

small amount sample is withdrawn from time to time, and spectrum is taken to determine to what extent the reaction has progressed. For example, in the oxidation of secondary alcohol, the disappearance of hydroxyl group stretching near 3570 cm^{-1} and the appearance of carbonyl stretching near 1725 cm^{-1} will reveal the extent of reaction.

5. **Presence of water in a sample:** Presence of moisture (water) in any compound can be identified using IR spectroscopy. Further, if water is found to be present in a compound, IR gives information about the nature of water (whether it lattice water or coordinated water) present in the compound. If a sample contains lattice water, its IR spectrum will contain three characteristic bands, one in the $3600\text{--}3200\text{ cm}^{-1}$ region, second in the 1650 cm^{-1} region and the third in the $600\text{--}300\text{ cm}^{-1}$ region. On the other hand, if water is coordinated to a metal ion, an additional band in the $880\text{--}650\text{ cm}^{-1}$ region is observed.
6. **Shape or symmetry of a molecule:** IR spectroscopy is used to deduce the shape or symmetry of a molecule. IR spectrum of NO_2 molecule gives three peaks at 750 cm^{-1} , 1323 cm^{-1} and 1616 cm^{-1} . The formula for non-linear molecules, $3n - 6$ also predicts three fundamental vibrations. This proves that NO_2 is a bent molecule and not a linear molecule which should give four peaks according to the formula for linear molecules, $3n - 5$.
7. **Geometrical isomers can be distinguished by their IR spectra:** *Trans* isomers are more symmetric than *cis* isomers. Hence the *trans* isomer has little change in dipole moment in the presence of IR radiation, and shows a simpler spectrum than the *cis* isomer. This characteristic property leads to their easy identification.

Fourier Transform (FT)

Fourier transform IR spectrometry was developed to overcome the limitations in the use of the dispersive instrument. The main difficulty is that it is a slow scanning method.

Fourier transformation is used to produce spectroscopic methods that are much faster than conventional frequency domain methods. Data are rapidly collected in the time domain and then converted by FT to the conventional frequency domain. The time required for a single scan is greatly reduced, and the time required for a group averaging is also decreased. Transformations of conventional signals may be multiplied by appropriate conditioning functions to achieve digital filtering and other useful signal modifications. A second mathematical operation, an inverse Fourier transformation, is required to restore the conditional signal to its original form. A new computer software algorithm, known as a fast Fourier transformation (FFT) has reduced the execution time considerably over previous transform algorithms software. Two methods of data representation are the frequency amplitude function $F(\nu)$ and the less common time amplitude function, $F(t)$ as shown in Figure 22. They are represented as

$$\begin{aligned} F(\nu) &= \int_{-\infty}^{\infty} f(t)e^{-i(2\pi)\nu t} dt \\ F(t) &= \int_{-\infty}^{\infty} f(\nu)e^{-i(2\pi)\nu t} d\nu \end{aligned} \tag{5.13}$$

If for example, $F(t) = A \cos 2\pi\nu_0 t$ then $f(\nu)$ is a single line at ν_0 with amplitude A .

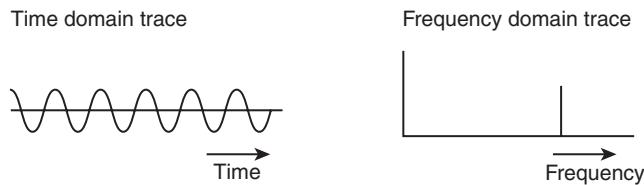


Figure 22 Data representation for FTIR in (a) time domain; (b) frequency domain.

In FTIR spectroscopy, the data are rapidly generated in the time domain [$F(t)$] form by an interferometer. The resulting data are in the form of superimposed waves and include all the frequencies of the spectral range of the instrument.

The IR radiation can be analyzed by using a scanning Michelson interferometer (Figure 23). This consists of a moving mirror, a fixed mirror and a beam splitter. Radiation from the infrared source is collimated by a mirror, and the resultant beam is then divided at the beam splitter. Half the beam passes to a fixed mirror and the half is reflected to a moving mirror. After reflection, the two beams recombine at the beam splitter and for any particular wavelength, constructively or destructively interfere depending on the difference in optical paths between the two arms of the interferometer.

With constant mirror velocity, the intensity of the emerging radiation at any particular wavelength modulates in a regular sinusoidal manner. In the case of a broadband source, the merging beam is a complex mixture of modulation frequencies which, after passing through the sample compartment, is focused on the detector. This detector signal is sampled at precise intervals during the mirror scan. Both the sampling rate and the mirror velocity are controlled by a reference signal incident upon a detector, which is produced by a modulation of the beam from the helium–neon laser.

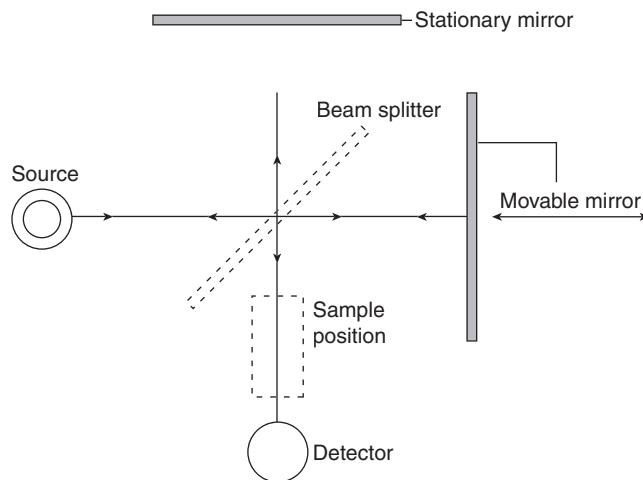


Figure 23 Michelson interferometer.

The resulting signal from the detector is known as an interferogram and contains all the information required to reconstruct the spectrum via mathematical process known as Fourier transformation.

Concept Check

- How many normal vibrational modes can be expected for ethane and carbon dioxide?
- How many fundamental vibrational frequencies can be observed in IR spectrum of water?
- What are the detectors used in IR spectrophotometer?
- How is sampling done in IR spectrophotometer?
- Why can water not be used as solvent for IR spectrophotometer?
- What are the sources of IR spectrophotometer light?
- Explain with any one example how we differentiate geometrical isomers using IR spectrophotometer?
- What do you understand by Fourier transformation? What is its significance in spectroscopy?

5.5 NMR Spectroscopy

Concepts and Theory

Nuclear magnetic resonance spectroscopy (NMR) is an absorption spectroscopy in which certain magnetic nuclei under the influence of a static external magnetic field are subjected to a second oscillating electromagnetic field in the form of radiofrequency radiation which induces the nucleus to resonate. NMR spectroscopy is the study of NMR phenomenon to examine the physical and chemical properties of a molecule.

Many atomic nuclei have mechanical spin and angular momentum which is described in terms of nuclear spin quantum number I . It has values of 0, $\frac{1}{2}$, 1, $\frac{3}{2}$ and so on ($I = 0$ denotes no spin). For the nuclei to be magnetic, they should have either odd number of protons or odd number of neutrons or both. Only the nuclei that have spin quantum number greater than zero can exhibit NMR phenomenon (e.g., ^1H , ^{11}B , ^{13}C , ^{14}N , ^{15}N , ^{17}O , ^{19}F , ^{31}P , etc.).

The criteria for magnetic nuclei are listed in Table 3.

The spin quantum number I determines the number of quantum mechanical states an isolated nucleus may assume in external uniform magnetic field, in accordance with the formula $(2I + 1)$. Hence

the nucleus of ^1H has the spin quantum number $I = \frac{1}{2}$ and has two allowed spin states $\left(2 \times \frac{1}{2} + 1 = 2\right)$

for its nucleus which are $-\frac{1}{2}$ and $+\frac{1}{2}$. In the absence of applied magnetic field, the energy of all the spin states of a nucleus are equivalent (degenerate).

Table 3 Characteristics of magnetic nuclei

Spin Quantum Number (I)	Number of Protons	Number of Neutrons	Atomic Mass	Examples Atom(I)
Half integer	Odd	Even	Odd	$^1\text{H}(1/2)$, $^3\text{H}(1/2)$, $^{15}\text{N}(1/2)$, $^{19}\text{F}(1/2)$, $^{31}\text{P}(1/2)$
Half integer	Even	Odd	Odd	$^{13}\text{C}(1/2)$, $^{17}\text{O}(5/2)$, $^{29}\text{Si}(1/2)$
Integer	Odd	Odd	Even	$^2\text{H}(1)$, $^{14}\text{N}(1)$, $^{10}\text{B}(3)$
Zero	Even	Even	Even	$^{12}\text{C}(0)$, $^{16}\text{O}(0)$, $^{34}\text{S}(0)$

Because of the spin and charge, a nucleus can behave like a magnet. NMR Spectroscopy involves application of magnetic field to nuclei and then measuring the amount of energy necessary to put various nuclei of the sample into resonance. Nuclei in different electronic environments (shielded and unshielded) require different amounts of energy to bring them into resonance. An NMR spectrum provides a signal or peak representing the energy necessary to bring each nucleus into resonance.

The Phenomenon of Nuclear Magnetic Resonance

The magnetic nuclei (^1H , ^{13}C , etc.) under the influence of external magnetic field behave as a spinning bar magnet as they possess both electric charge and mechanical spin (Figure 24). The proton like a magnet tends to align itself with the external magnet (parallel) with the magnetic field, called α -orientation (low energy state) or opposed (anti-parallel) to the field, called β -orientation (higher energy state). In these α and β states (Figure 25), the proton also spins around the axis of an applied magnetic field. This is called precessional motion.

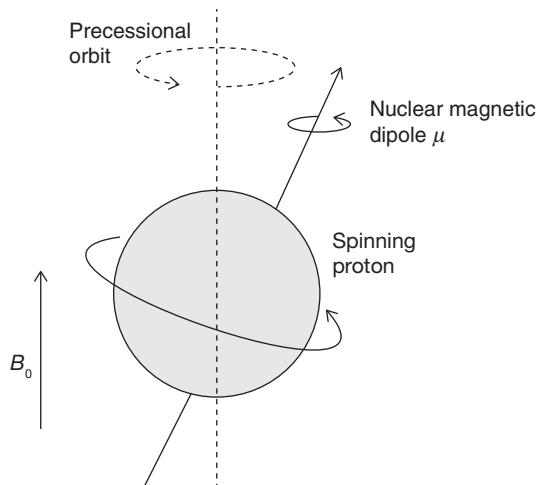


Figure 24 Proton spinning in a magnetic field B_0 .

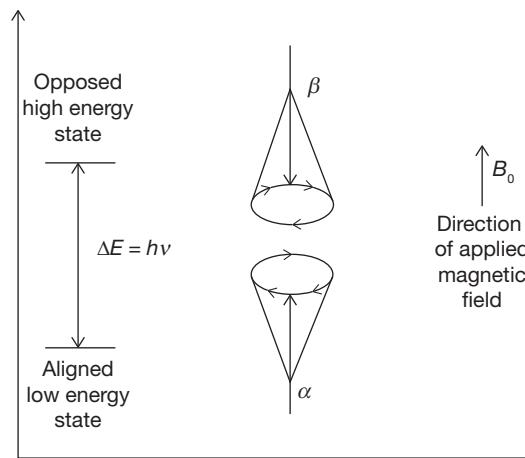


Figure 25 The α and β orientations of the precessing nuclei.

Precessional Frequency

A transition from the lower energy state to the higher energy state can be brought about by applying radiation of exactly the required frequency (in the radiofrequency region) for a given stationary magnetic field of strength B_0 . The fundamental NMR equation correlates to a particular value of the applied radio-frequency known as Larmor frequency ν , which is directly proportional to the magnetic field strength. Thus,

$$\nu \propto B_0$$

$$\nu = \left(\frac{\gamma}{2\pi} \right) B_0$$

Since $\Delta E = h\nu$ using above equation, we have

$$\Delta E = \left(\frac{h\gamma}{2\pi} \right) B_0 \Rightarrow \Delta E \propto B_0 \text{ (}\because b, \gamma \text{ and } \pi \text{ are constants)}$$

Here h is Planck's constant, γ is gyromagnetic ratio and B_0 is the strength of the magnetic field.

The radiofrequency ν is typically in the order of megahertz (MHz). A frequency of 300 MHz is needed at a magnetic field strength B_0 of 7.05 T for the proton (¹H) or a proton subjected to an external field of strength 1.4 T (14000 gauss) will precess 60 million times per second or at 60 MHz. At this ratio, the system is said to be in resonance, hence the name *nuclear magnetic resonance*. Figure 26 shows a spinning nucleus precessing about the direction of the applied magnetic field B_0 .

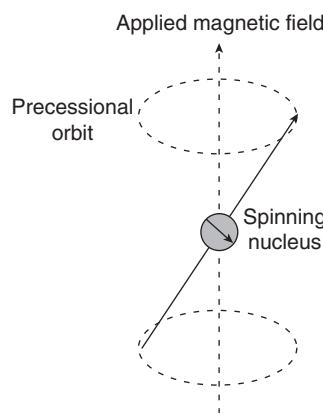


Figure 26 A spinning nucleus precesses about the direction of the applied magnetic field H , with a constant angle.

The frequencies of protons in ¹H and ¹³C as a function of field of applied magnetic field is shown in Table 4.

Table 4 Precessional frequencies as a function of applied magnetic field

B_o (Tesla)	Precessional Frequency (MHz)	
	^1H	^{13}C
1.4	60	15.1
1.9	80	20.1
2.3	100	25.1
4.7	200	50.3
7.1	300	75.5
11.7	500	125.7
14.1	600	151

The constant γ (gyromagnetic ratio) is a fundamental constant unique to each nucleus. It is the proportionality constant between the magnetic moment μ and the spin magnetic number I , that is,

$$\gamma = \frac{2\pi\mu}{hI}$$

Relaxation

The magnetic nuclei in the lower energy state undergo transitions to the higher energy state. When the population of the two states approach equality, no further absorption of energy takes place. The condition is referred to as saturation. However, the higher energy nuclei will constantly return back to the lower energy spin state by two radiation-less processes. The high energy nuclei may lose their energy to the surroundings (solvent, other atoms in the molecule, etc.) in a process called spin-lattice relaxation. A second relaxation process involves transferring ΔE to neighbouring magnetic nuclei in a process called spin-spin relaxation.

Instrumentation of NMR Spectroscopy

The early NMR instruments for proton magnetic resonance were built using permanent magnets or electromagnets, generally with field strengths of 1.4, 1.87, 2.20 or 2.35 tesla and corresponding frequencies of 60, 80, 90 or 100 MHz, respectively. The basic components, a detection system to measure the energy being absorbed by the nuclei from the radiofrequency beam and a display monitor. This is schematically represented in Figure 27.

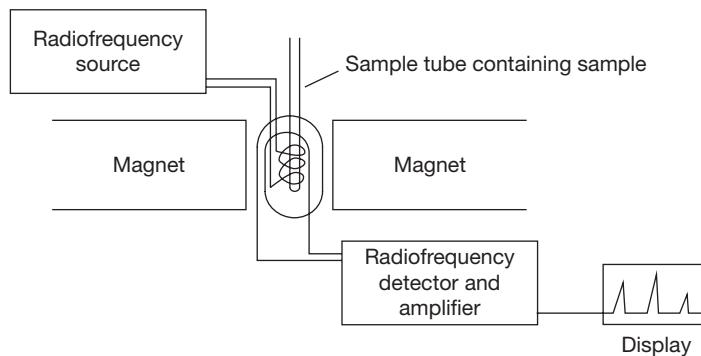


Figure 27 Schematic representation of NMR spectrophotometer.

The high-resolution spectrometers currently in use are 300 to 800 MHz instruments and have ability to resolve or differentiate between different spectral peaks along the frequency axis. The commercial NMR instruments available with highest resolution are with 1000 MHz (1GHz) or higher (1.1–1.2 GHz) frequencies. These are based on helium-cooled superconducting and operated in pulsed FT mode. The diagrammatic representation of high-resolution NMR spectrum is shown in Figure 28.

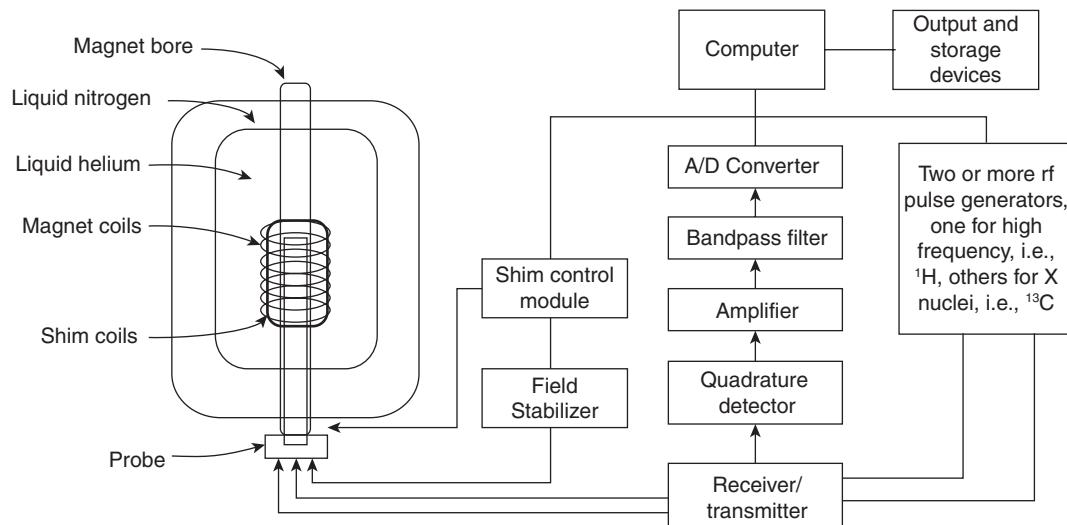


Figure 28 Schematic diagram of FT NMR with superconducting magnet.

The sample under investigation is dissolved in a deuterated solvent and the solution taken in a glass tube is placed in the probe with a spinner that spins the tube so that the non-homogenous components of the magnetic fields are averaged out. The transmitter and receiver coils also form part of the probe. The computer interface acquires the data, carries out the Fourier transform and further processes to deliver the NMR spectrum, which appears as a series of peaks (corresponding to protons in different chemical environment) whose area are proportional to the number of protons they represent. The peak areas are also calculated by the computer and displayed in the spectrum as a series of steps with heights proportional to the peak area. The NMR spectrum obtained is useful for identification of organic compounds as well as quantitative analysis and determination of purity of the sample.

Solvent Selection and Sample Preparation

The important requirements related to solvent selection and sample preparation are listed as follows:

1. The sample must be completely soluble in the chosen solvent.
2. The ideal solvent should be inexpensive, inert and low boiling. Most importantly, the solvent should not contain any protons.
3. Typically, deuterated solvents are used. For these solvents, ideally the isotopic purity should be as high as possible but this factor adds to the cost of the solvent. To strike a balance, generally, purity approaching 100% is used. So, a small sharp proton peak is observed at 7.26 ppm corresponding to the impurity of CHCl_3 when CDCl_3 is used as the solvent but this causes no difficulty or ambiguity in the interpretation of spectra.

4. Deuterated chloroform (CD_3Cl) is generally used as a solvent for NMR analysis of organic compounds. Other solvents commonly used are common organic solvents in which hydrogen has been replaced with deuterium or those not containing hydrogen atoms. For example, C_6D_6 , D_2O , $(\text{CD}_3)_2\text{SO}$, $(\text{CD}_3)_2\text{CO}$, CCl_4 , CS_2 , etc.

Chemical Shift

Chemical shift is defined as the relative difference in the nuclear magnetic resonance frequency of a nucleus depending on its electronic environment expressed with reference to a standard compound which is defined to be at 0 ppm. The position and number of chemical shifts are diagnostic of the structure of a molecule.

An important property of NMR technique is its ability to distinguish between protons in different magnetic environments in a molecule. If the resonance frequency of all protons in a molecule were the same, then NMR spectrum would show only one peak for the compound. The field strength experienced by the protons in the sample is not the same as the strength of the applied field. Protons are surrounded by an electronic charge cloud of approximately spherical symmetry. A magnetic field induces electron circulations in the charge cloud in a plane perpendicular to the applied field, and in such a direction so as to produce a field opposing the applied field as represented in Figure 29. The induced field is directly proportional to the applied field H . It is represented by σH , where σ is constant. The effective magnetic field experienced by the proton is

$$H_{\text{eff}} = H - \sigma H = H(1 - \sigma) \quad (5.14)$$

Thus, the proton is shielded from the applied field by a diamagnetic electronic circulation depending on the electron density around it in a molecule. A molecule may contain protons in different chemical environments. The average electron concentration in these environments is different and so are the shielding effects on the protons.

For example, consider the C–H and O–H bonds. O is more electronegative than C, therefore electron density around C–H proton is considerably greater than that around O–H proton. Therefore, the shielding effect is greater for C–H than O–H proton. For an applied field, the effective field at the O–H proton is greater than that C–H proton. Consequently, as the applied field is increased, O–H proton will come into resonance before the C–H proton.

The separation between the nuclear resonance for the same nucleus in different chemical environments is known as chemical shift. This chemical shift is directly proportional to strength of the applied

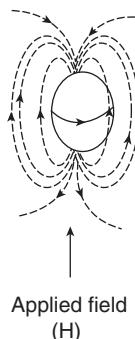


Figure 29 Diamagnetic circulation of an electron about the nucleus producing a field opposing the applied field H .

field. It gives an idea about the different types of protons in a molecule. Intensity of absorption is directly proportional to the number of protons in a given environment in the molecule.

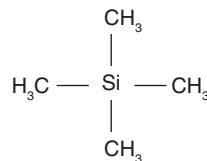
Consider NMR spectrum of ethanol (Figure 30), the spectrum shows three absorption peaks of intensity (given by area under the peak) 1:2:3. The smallest peak is assigned to the single proton in the OH group, the next peak assigned to the two protons in the CH_2 group and largest peak assigned to the three protons in the methyl group. CH_2 peak occurs in between OH and CH_3 peaks.

Chemical shifts are very small as compared to the strength of the applied field. Their magnitude is a 10^{-4} T at a field strength of about 1T. Further, a chemical shift is directly proportional to applied field. It varies with H and hence, it is expressed on a relative scale independent of H .

Chemical shift for a given environment may be expressed as

$$\delta = \frac{H_r - H_s}{\nu} \times 10^6 \quad (5.15)$$

where H_r is the resonance field strength of reference and H_s is the resonance field strength of sample. The reference compound is dissolved in the same solution as the sample (internal reference) so that both experience the same magnetic field. Here δ is a dimensionless quantity and 10^6 is included to express it as parts per million. The compound generally used as reference for proton resonance is tetramethylsilane (TMS).



Tetramethylsilane (TMS)

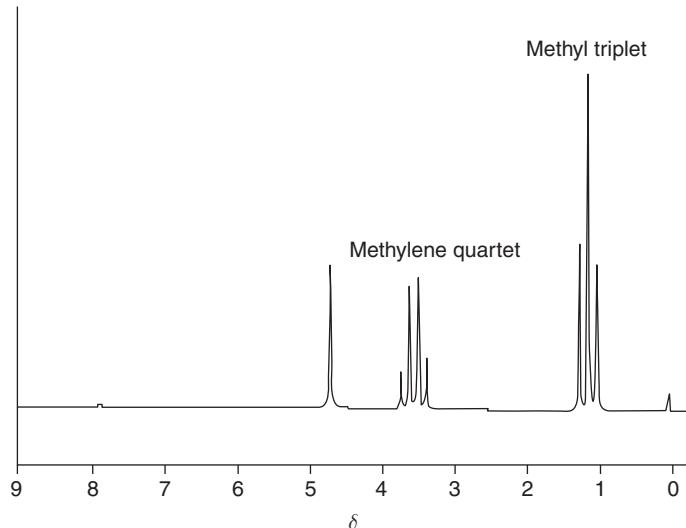


Figure 30 NMR spectrum of ethanol under high resolution.

Advantages of using TMS are as follows:

1. Gives single peak since all 12 protons are equivalent.
2. It is a resonance peak that occurs at an exceptionally high field, higher than almost all protons in different chemical environments.
3. It is chemically inert, magnetically isotropic and has low boiling point (27°C) which makes it recoverable from most samples.

The area under each NMR signal in the spectrum is proportional to the number of hydrogen atoms which are chemically and magnetically equivalent. The number of signals in the NMR spectrum gives us the data of such protons having the same environment. For example, the NMR spectrum of toluene (Figure 31) show two signals in the ratio 5:3.

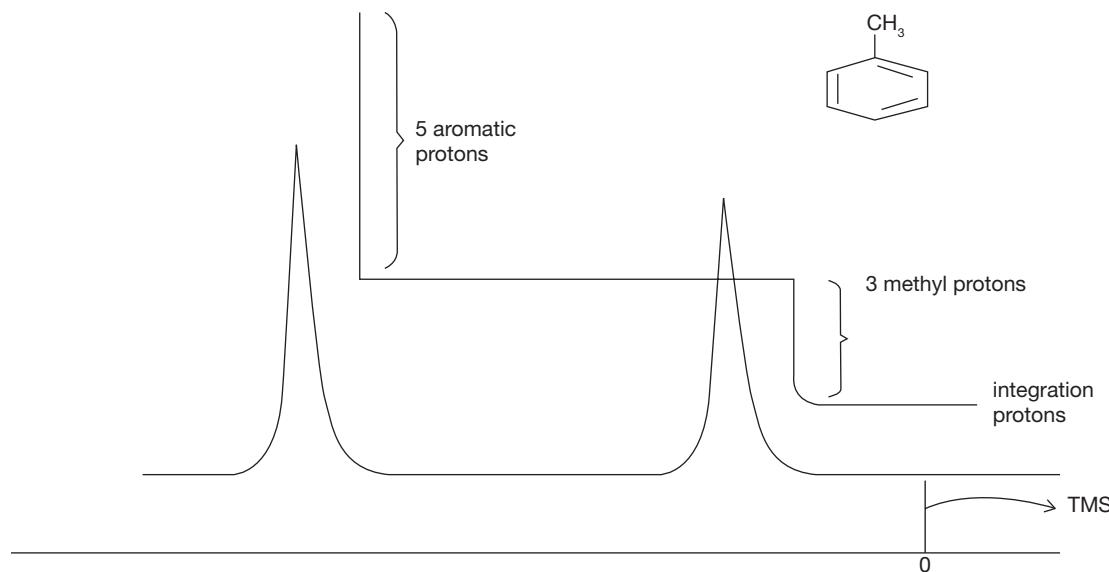


Figure 31 ^1H NMR spectrum of toluene.

The NMR spectrum is plotted with TMS on the right side. Chemical shift positions are normally expressed in δ (delta) units which are defined as proportional differences in parts per million (ppm) from an appropriate reference. Since δ unit is a dimensionless number, it is independent of the field strength. For instance, a peak at δ 2.1 in 60 MHz spectrum will be found at exactly the same position in 100 MHz or on a 400 MHz instrument. The relation between δ values and frequency in Hz is

$$\delta_x = \frac{\nu_x - \nu_{\text{TMS}}}{\nu_0}$$

Here, δ_x is the chemical shift in ppm, ν_x and ν_{TMS} are the frequencies of group X and TMS respectively and ν_0 is the operating frequency of the instrument. Chemical shifts are independent of the value of the Larmor frequency and magnetic field strength of the spectrophotometer. The frequencies of the various peaks are not independent of these values.

Table 5 δ values of protons in various environments

<i>Compound</i>	δ <i>Value</i>
CH_4	0.23
CH_3I	2.16
CH_3Br	2.68
CH_3Cl	3.25
CH_3F	4.26
H attached to C	0.9
H attached to N	2.2
H attached to O	3.5

Resonance positions are also indicated on τ scale. In the τ scale, τ is 10 at the resonance peak of TMS and decreases downfield as $\tau = 10 - \delta$.

The degree of electronic shielding of a proton is dependent on the electron density around it. Hence, higher the electron density, higher is the field and the lower is the δ value at which proton absorbs. The δ values of protons in different chemical environments are given in Table 5.

Factors Affecting Chemical Shift

The various factors that affect the chemical shift are discussed as follows.

Electronegativity

The protons in the methyl group ($-\text{CH}_3$) attached to a carbon atom resonate around 0.8 to 0.9 δ . When $-\text{CH}_3$ group is attached to a more electronegative atom, the chemical shift (δ value) of the protons is increased. Table 6 shows the impact of electronegativity of the element attached to methyl group on the chemical shift.

Table 6 Effect of electronegativity of the element bonded to carbon on the chemical shift of methyl protons

<i>Compound</i>	<i>Electronegativity (Pauling scale) of the Element Attached to $-\text{CH}_3$</i>	<i>Chemical Shift (δ)</i>
$\text{CH}_3 - \overset{ }{\text{Si}} -$	1.8	0.0
$\text{CH}_3 - \overset{ }{\text{C}} -$	2.55	0.9
$\text{CH}_3 - \text{I}$	2.66	2.16
$\text{CH}_3 - \text{Br}$	2.8	2.65
$\text{CH}_3 - \text{Cl}$	3.0	3.10
$\text{CH}_3 - \text{F}$	4.0	4.26

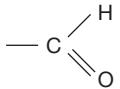
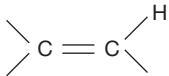
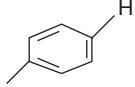
Hydrogen nuclei are surrounded by electron density which shields the nucleus from the influence of the external magnetic field B_0 . Hence, it also influences the precessional frequency of the nucleus, that is, greater the shielding, the lower will be the precessional frequency. In a magnetic field, the electrons around the proton are induced to circulate which generates a small secondary magnetic field, in the direction opposite to the external magnetic field. The greater the electron density circulating around the proton, the greater is the induced *shielding effect* or *diamagnetic effect* and lower will be the precessional frequency of the proton. Silicon is electropositive and furnishes electrons towards methyl groups of TMS due to $+I$ effect. Due to this powerful shielding effect, TMS protons resonate at low frequency and hence lower δ values. In contrast, fluorine in $\text{CH}_3\text{-F}$ draws electrons towards itself due to $-I$ effect and results in deshielding. The protons resonate at higher frequency and hence higher δ value.

Anisotropic Effect

We could predict the δ values of various protons using the concept of electronegativity and acidity of the proton. However, there are some anomalies that can be best explained by anisotropic effect. The chemical shifts of protons attached to different anisotropic groups are listed in Table 7.

Consider the example of acetylene molecule to understand the effect of diamagnetic anisotropy. The molecule is linear and has a triple bond about the axis. On application of an external magnetic field, if the axis aligns with the magnetic field, the electrons of the triple bond will circulate at right angles to the applied field, inducing their own magnetic field in the direction opposite to the applied field. The magnetic lines of force induced by the circulating electrons shield the protons and hence the NMR peak is observed at lower frequency than that expected from electronegativity effect [Figure 32(a)]. On the other hand, consider the example of aldehydic proton, where the effect of the applied magnetic field is the greatest along the transverse axis of the $-\text{C=O}$ bond (in the plane of the paper). The magnetic lines of force induced by circulating electrons, deshield the protons and the resonance occurs at lower frequency than expected on the basis of electronegativity [Figure 32(b)]. Thus, under diamagnetic anisotropy, the instantaneous orientation of the molecule with respect to the applied magnetic field determines the shielding or deshielding effect.

Table 7 Chemical shifts of protons due to anisotropic effect

Structure	Approximate Chemical Shift (δ)
	9.5–10
	4–8
$\text{H}-\text{C}\equiv\text{C}-\text{H}$	6–9
	1.5–35

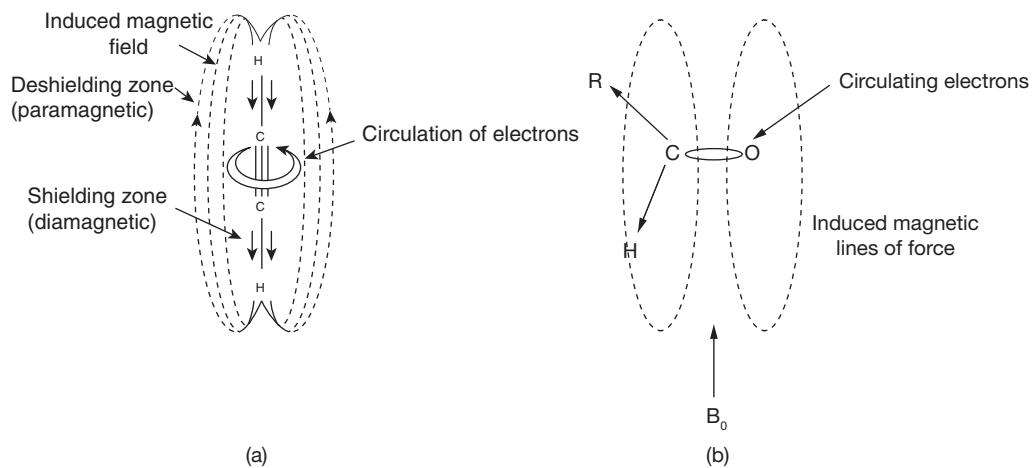


Figure 32 Diamagnetic anisotropy. (a) Alkyne protons. (b) aldehydic protons.

The anisotropy cones for shielding and deshielding effects around the double bond in alkenes and carbonyl group, resulting from diamagnetic anisotropy are depicted in Figures 33(a) and (b), respectively.

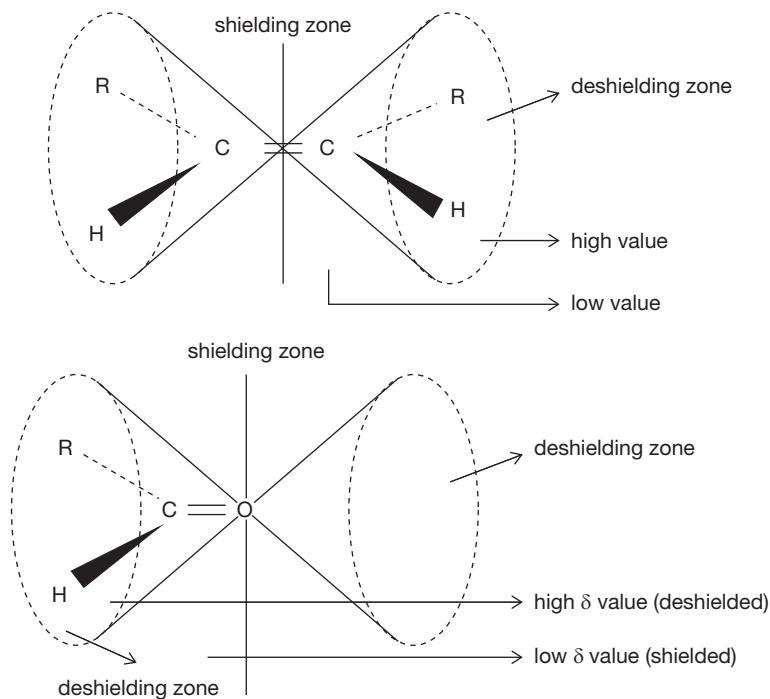


Figure 33 Anisotropic shielding and deshielding in (a) alkenes and (b) carbonyl groups.

Another example of diamagnetic anisotropy is the ring-current effect that is observed in benzene ring protons and accounts for their large deshielding effect (Figure 34).

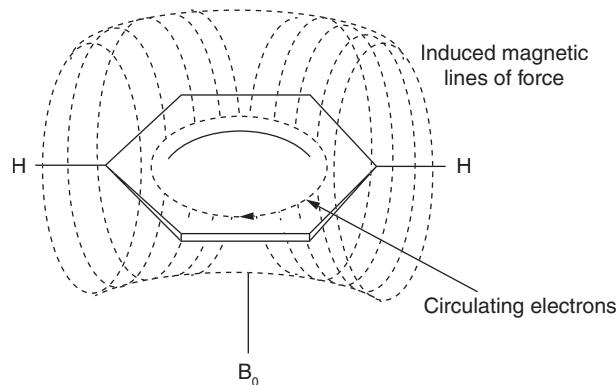
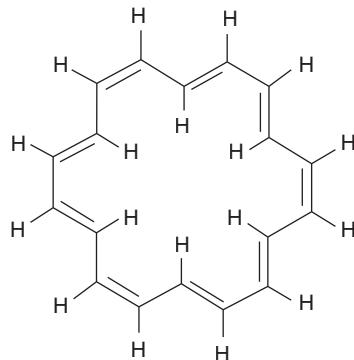


Figure 34 Ring-current effect in benzene.

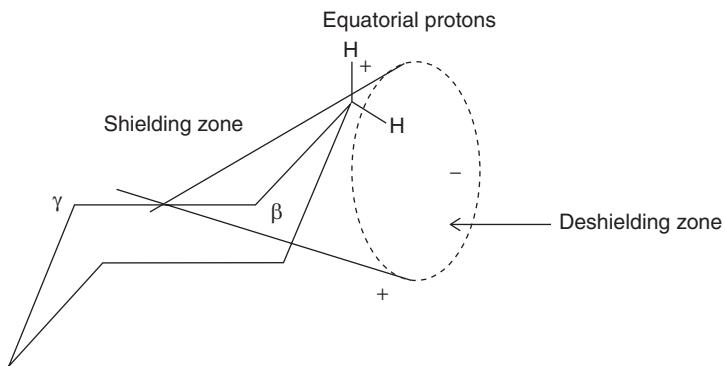
Let us consider some examples to understand anisotropy due to ring-current.

1. In the presence of an applied magnetic field, the protons held directly above and below the aromatic ring are shielded and hence resonate at lower frequency. So, the methylene protons in 1,4-poly-methyl benzenes are more shielded than those of ethylbenzene.
2. In acetophenone, the ring protons are deshielded due to ring current effect. The protons at the *ortho* position are deshielded more than the *meta* and *para* protons due to additional shielding effect of the carbonyl group. The carbonyl bond and the benzene ring are coplanar, so if the molecule is oriented such that the applied magnetic field is perpendicular to the plane of molecule, the circulating electrons of the carbonyl bond shield the conical zones above and below them (*meta* and *para* protons) and deshield the protons in the lateral zone (*ortho* protons).
3. Some annulenes exhibit both shielding and deshielding effects due to ring currents. In [18]-annulene, the protons inside the ring are strongly deshielded and those inside the ring are strongly shielded and have resonance at frequency (-3.0 ppm) lower than that of TMS (0.0 ppm).



[18]annulene

4. Unlike the electrons in π orbitals of C–C bonds in cyclic compounds, the σ electrons of C–C bonds show much lesser anisotropic effects. For example, in cyclohexane equatorial protons are found at higher chemical shifts than axial protons on the same carbon atom in a rigid six-membered ring.



Spin-Spin Interaction

The splitting of signal lines in the spectrum into two or more components is called spin–spin splitting. When the high resolution spectrum of ethanol is considered, the signal line for methyl is split into a triplet with areas of the components in the ratio, 1:2:1 approximately and the line for methylene protons is split into quartet having relative areas, 1:3:3:1. *The spacing of the component lines in spin–spin splitting is called coupling constant, J .* It is independent of the applied field, which means that it is purely an intramolecular effect.

The splitting of resonance absorption is due to the effect of the nuclei of other magnetic nuclei in the same molecule. It can be explained by assuming that the magnetic field of the protons in a group is influenced by the spin arrangements of the protons in the adjacent group. The methyl group in the ethanol molecule is adjacent to the methylene group with two equivalent protons. For the two protons, there are three possible combinations of spin orientations indicated as + and – signs, as shown in Figure 35.

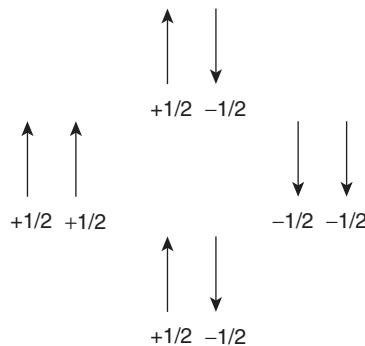


Figure 35 Possible spin orientations of a methylene group.

One of these values can be obtained in two ways. If the effect of the instantaneous spin arrangements of the methylene protons can be transmitted to protons of the methyl group, the magnetic fields of the protons in the methyl group will have three different values. One of them will occur twice as often as either of the two. The resonance absorption of the methyl protons would, therefore, be split into three peaks having relative areas 1:2:1.

Similarly, for the three peaks of the methyl group, there are four different values of the total spin, which may affect the resonance of the protons of the methylene group, and two of these four values can be obtained in three different ways (Figure 36). The methylene proton resonance will, therefore, be split into four peaks having relative areas of 1:3:3:1.

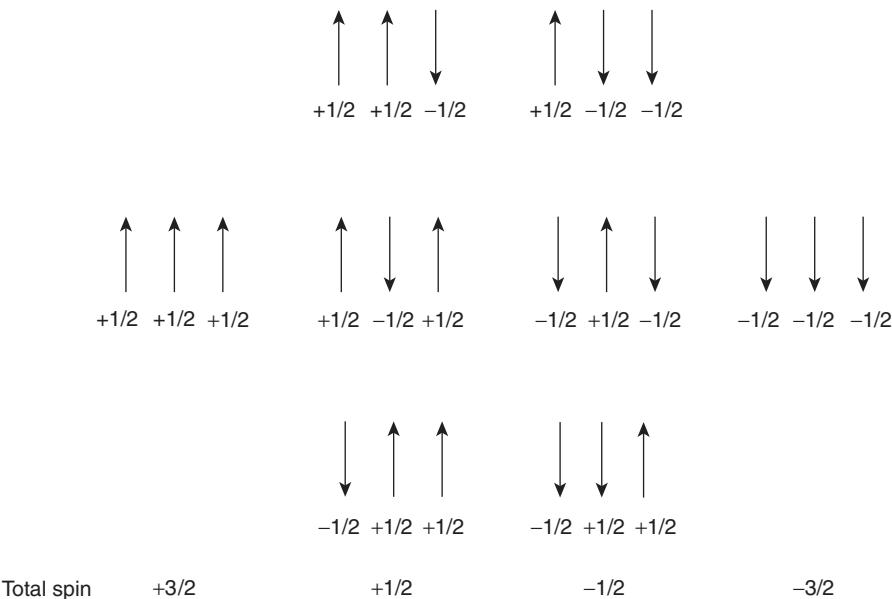


Figure 36 Possible spin orientations of the protons of a methyl group.

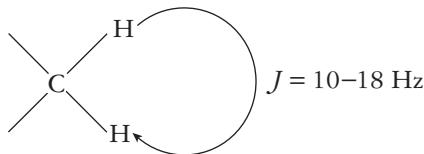
It should be noted that a hydroxyl group is not held up in a single molecule. In fact, it is exchanged among the different ethanol molecules over a period of time. The rate of this exchange is relatively slow in pure ethanol, but it is markedly increased by acidic or basic impurities that are ordinarily present in ethanol. If the rate of chemical exchange is rapid, the hydroxyl proton experiences an average effect of the spin orientations of the methylene protons and its absorption peak therefore shows only a singlet. Similarly, the hydroxyl group proton does not cause splitting of the methylene proton absorption, if there is rapid chemical exchange. The methylene proton absorption thus occurs as a quartet due to the effect of methyl group alone. In a highly purified sample of ethanol on the other hand, the OH proton will experience spin orientations of the methylene group. This will result in a triplet for the OH proton absorption. For the same reason, the absorption of the methylene protons will be influenced by the spin of the OH protons in addition to the spins of the methyl protons, as a result the absorption peak will be split into four components.

The multiplicity of the signal for any group of equivalent protons is clearly related to the number of protons of the adjacent atoms. As a simple rule the multiplicity of a given group is $(n + 1)$, where n is the number of protons of the adjacent atoms. In simple cases of interacting nuclei, the component peaks of a multiplet are symmetric about a midpoint and their relative areas are numerically proportional to the coefficients of the terms in the expansion. $(1 + r)^n$. Accordingly, n -propyl iodide ($\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$) has three different types of protons. Therefore, the NMR spectrum will show 3 H triplet (1:2:1), 2 H sextet (1:5:10:10:5:1) and 2 H triplet (1:2:1). Isopropyl iodide $\{(\text{CH}_3)_2\text{CHI}\}$ has two different types of protons. Therefore, the NMR spectrum will show 6 H doublet (1:1) and 1 H septet

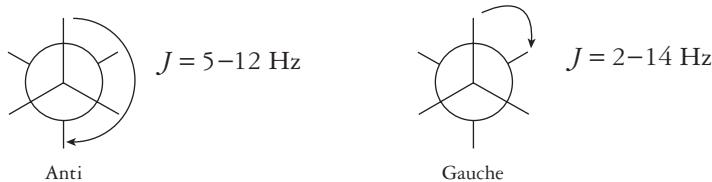
(1:6:15:20:15:6:1). Ethyl methyl ether $[(\text{C}_2\text{H}_5)\text{O}(\text{CH}_3)]$ has three different types of protons. Therefore, the NMR spectrum will show 3 H singlet, 2 H quartet (1:3:3:1) and 3H proton triplet (1:2:1).

Factors Influencing the Coupling Constant

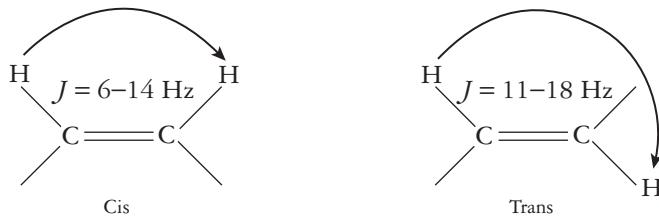
- Number of bonds between the coupling nuclei and type of the intervening bonds influence the size of the coupling constant.
- For protons attached to the same carbon atom, that is, for geminal protons, J varies from 10 Hz to 18 Hz depending on the bond angle and the overall structure of the molecule.



- For protons attached to adjacent carbon atoms, that is, vicinal protons, J varies from 2 Hz to 18 Hz depending upon the spatial positions of protons and the structure of the molecule as a whole. For example, in cyclohexane with *anti* conformation protons have $J = 5–12$ Hz while one with *gauche* conformation has $J = 2–14$ Hz.



In the case of vinylic protons, where restricted rotation due to double bonds is involved, the *cis* protons have $J = 6–14$ Hz whereas *trans* protons have $J = 11–18$ Hz.



- Aromatic coupling depends on whether the coupling protons are *ortho*, *meta* or *para* to each other. $J_{\text{ortho}} = 7–10$ Hz, $J_{\text{meta}} = 2–3$ Hz, $J_{\text{para}} = 0–1$ Hz
- Other nuclei with spins of 1/2 interact with protons and cause observable spin–spin coupling. The direct coupling of ^{13}C –H is noticed as sidebands in a proton NMR spectrum. These are called satellite signals. These sidebands do not vary as the sample spinning rate is changed, unlike the spinning sidebands.

Interpretation of NMR Spectra

The NMR spectra can be used for determining the structure of unknown compounds. Several rules are used for this and are discussed as follows:

1. The number of the main NMR signals are equal to the number of groups of equivalent protons in the proposed structure.
2. The peaks at different chemical shifts can be assigned to protons in various groups based on the values given in Table 8.

Table 8 Characteristic proton chemical shifts

Type of Proton	Structure	Chemical Shift (ppm)
Cyclopropane	C_3H_6	0.2
Primary	$\text{R}-\text{CH}_3$	0.9
Secondary	R_2-CH_2	1.3
Tertiary	$\text{R}_3-\text{C}-\text{H}$	1.5
Vinylic	$\text{C}=\text{C}-\text{H}$	4.6–5.9
Acetylenic	Triple bond, $\text{C}\equiv\text{C}-\text{H}$	2.0–3.0
Aromatic	$\text{Ar}-\text{H}$	6.0–8.5
Benzyllic	$\text{Ar}-\text{C}-\text{H}$	2.2–3.0
Allylic	$\text{C}=\text{C}-\text{CH}_3$	1.7
Fluorides	$\text{H}-\text{C}-\text{F}$	4.0–4.5
Chlorides	$\text{H}-\text{C}-\text{Cl}$	3.0–4.0
Bromides	$\text{H}-\text{C}-\text{Br}$	2.5–4.0
Iodides	$\text{H}-\text{C}-\text{I}$	2.0–4.0
Alcohols	$\text{H}-\text{C}-\text{OH}$	3.4–4.0
Ethers	$\text{H}-\text{C}-\text{OR}$	3.3–4.0
Esters	$\text{RCOO}-\text{C}-\text{H}$	3.7–4.1
Esters	$\text{H}-\text{C}-\text{COOR}$	2.0–2.2
Acids	$\text{H}-\text{C}-\text{COOH}$	2.0–2.6
Carbonyl compounds	$\text{H}-\text{C}-\text{C}=\text{O}$	2.0–2.7
Aldehydic	$\text{R}-(\text{H})-\text{C}=\text{O}$	9.0–10.0
Hydroxylic	$\text{R}-\text{C}-\text{OH}$	1.0–5.5
Phenolic	$\text{Ar}-\text{OH}$	4.0–12.0
Enolic	$\text{C}=\text{C}-\text{OH}$	15.0–17.0
Carboxylic	RCOOH	10.5–12
Amino	RNH_2	1.0–5.0

3. The intensities are measured by the areas under the peaks and they are proportional to the number of each type of protons.
4. Where a fine structure is observed, the number of lines resulting and their separations can be analyzed on the following basis:
 - Protons on a saturated carbon ($-C-H-$) not attached to any heteroatom or unsaturated carbon atom ($=C < \text{or } \equiv C-$) absorb in the region in the region δ 0.9–1.5.
 - Protons on a saturated carbon ($H-C-$) which is attached to a hetero atom or unsaturated carbon atom absorb in the following regions indicative of the nature of group.
 - (a) Acetelenic protons $-C \equiv C-H$ absorb at δ 2.0–3.0.
 - (b) Vinylic protons $-C=C-H$ absorb at δ 4.6–5.6.
 - (c) Aromatic protons $Ar-H$ absorb at δ 6.0–8.5.
 - (d) Alcohol hydroxyl protons ($R-OH$) absorb at δ 1.0–5.5.
 - (e) Aldehyde protons $-CH=O$ absorb at δ 9.0–10.0.
 - (f) Carboxylic protons ($-COOH$) absorb at δ 10.5–12.0.

Representative NMR Spectra of Some Organic Molecules and Their Interpretation

1. **Ethyl bromide:** In ethyl bromide molecule, there are two types of protons which are magnetically equivalent. Therefore, one can expect two signals in its NMR spectrum (Figure 37). Two signals, (a) a triplet at δ 1.7, 3H and (b) a quartet at δ 3.4, 2H are observed in addition to the signal due to the reference TMS.

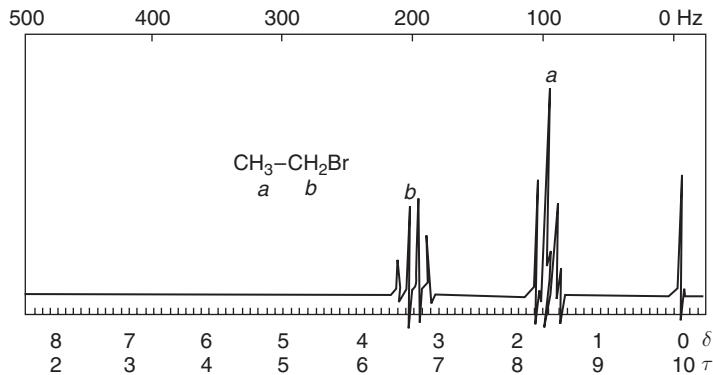


Figure 37 NMR spectrum of ethyl bromide.

The triplet at 1.7 arises from methyl protons and they are coupled with two methylene protons giving rise to upfield absorption. The quartet at δ 3.4 is from methylene protons, which are coupled with the three methyl protons to produce a downfield quartet due to deshielding influence of bromine. The relative areas under the respective signals are in the ratio 3:2 due to the respective number of protons involved.

2. **1,1-Dibromoethane:** The spectrum (Figure 38) shows two different signals (a) doublet at 2.5, 3H (CH_3) and (b) quartet at 5.85, 1H (CH) revealing the two different magnetically equivalent

protons as expected. The upfield doublet at δ 2.5 is because of the three equivalent methyl protons which are coupled with CH protons. The quartet appearing downfield at 5.85 is from the methane proton, which gets coupled with the three methyl protons. The downfield position is attributed to the attachment of two bromine atoms to the carbon carrying the protons. The relative areas under the peaks are in the ratio 3:1.

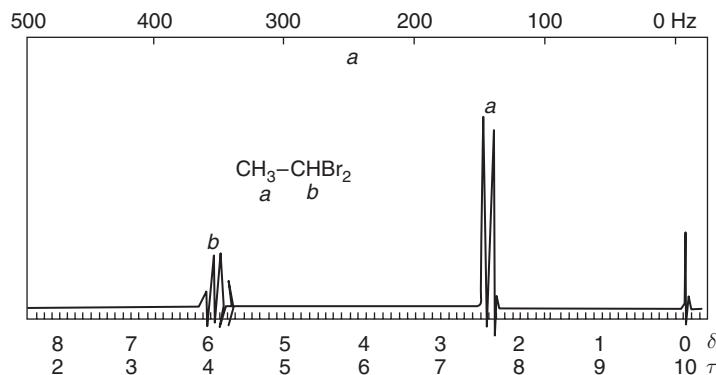


Figure 38 NMR spectrum of $\text{CH}_3\text{-CHBr}_2$.

3. Ethanol: It has three kinds of protons and three signals can be expected. The NMR spectrum (Figure 39) shows the following three signals.

- The upfield triplet at δ 1.2 is due to the three equivalent methyl protons. Evidently, its splitting is because of the two neighboring protons on the methylene group.
- The quartet at δ 3.5 is from two methylene protons. Its multiplicity of four peaks is due to the coupling with the three methyl protons; there being no coupling with hydroxyl proton.
- Finally, the downfield singlet at δ 4.8 is due to hydroxyl proton which does not show any coupling with the adjacent methylene protons.

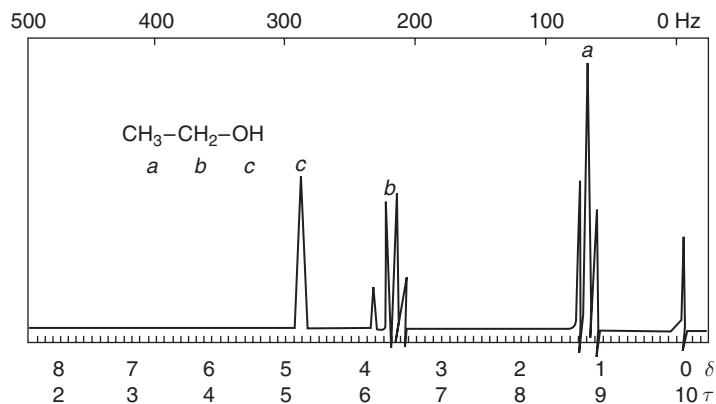


Figure 39 NMR spectrum of ethanol.

The relative area under the methyl, methylene and hydroxyl proton peaks is in the ratio 3:2:1. No splitting of signals due to the coupling of hydroxyl protons and the methylene protons on adjacent atoms is observed due to chemical exchange.

4. **Benzene:** The spectrum (Figure 40) shows only one peak at δ 7.26 because all protons on benzene ring are magnetically equivalent.

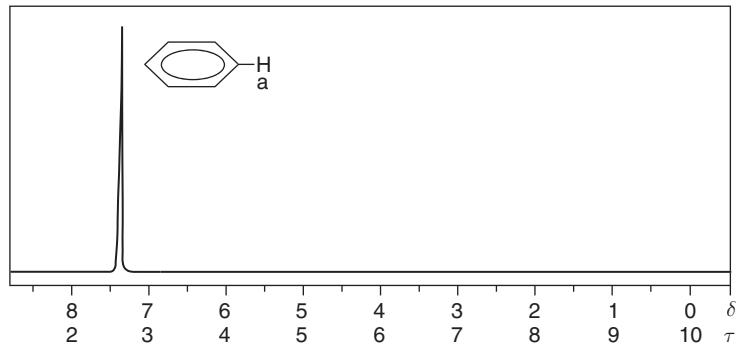


Figure 40 NMR spectrum of benzene.

5. **Toluene:** The compound has eight protons (Figure 41). The protons of type a are methyl protons which are magnetically equivalent. The signal for these protons appear at δ 2.34. The protons of type b are aromatic and are not equivalent. These protons are of three kinds, two ortho, two meta and one para with respect to the substituent methyl group. Despite being non-equivalent, all these protons give rise to only one singlet signal at δ 8.18. This implies that the methyl group has no influence magnetically on the aromatic protons. The relative areas under two signals of the spectrum are in the ratio 3:5.

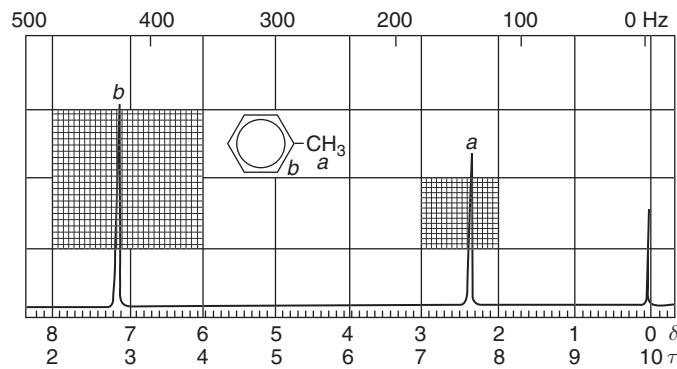


Figure 41 NMR spectrum of $\text{C}_6\text{H}_5\text{CH}_3$.

Simplification of Complex Spectra

Complicated spectra can be simplified by deuterium labeling. A deuteron has much smaller magnetic moment than a proton, and it absorbs at a much higher field. It gives no signal in the proton NMR spectra. Hence, the replacement of a proton by deuteron removes a signal from an NMR spectrum, and causes the splitting of signals of the other proton.

For example, in ethanol, we observe a triplet (3H) due to CH_3 and quartet (2H) due to CH_2 . When one proton of methyl group is replaced by deuteron, we observe a triplet (2H) due to CH_2D and triplet (2H) due to CH_2 . When the proton of methylene group is replaced, we observe a doublet (3H) for CH_3 and quartet (1H) for CHD.

CH_3 : triplet 3H and CH_2 : quartet 2H

CH_2D : triplet 2H and CH_2 : triplet 2H

CH_3 : doublet 3H and CHD: quartet 1H

One can use deuterium labeling to find out which signal is produced by which proton or protons. One observes the disappearance of a particular signal when a proton in a known location is replaced by deuterium. By use of deuterium labeling, certain set of signals can be seen more clearly in a complicated spectrum.

Concept Check

- Define chemical shift and coupling constant.
- Why nuclei Carbon-12 and Oxygen-16 do not possess a nuclear spin?
- What do you mean by chemical exchange?
- What is the use of deuteron decoupling?
- Predict the number of signals in low resolution NMR of the following: (a) *n*-propyl alcohol; (b) iso-propyl alcohol; (c) dimethyl ether and (d) ethanol.
- What are the advantages of using TMS as internal standard in NMR spectroscopy?

Applications of NMR

NMR is a sophisticated and powerful analytical tool that finds a variety of applications in different areas of research in science and medicine. Due to tremendous progress in instrumentation and its applications, NMR has become one of the most powerful and versatile spectroscopic techniques for the analysis of organic compounds and biomolecules. High-resolution NMR spectroscopy combined with X-ray crystallography, plays an important role in structure determination and molecular analysis and determination of protein function at cellular level.

Some of the key and emerging applications of NMR spectroscopy are listed as follows:

1. **Chemical analysis:** In addition to molecular structure determination, NMR is also used for conformational analysis of synthetic or naturally occurring compounds.
2. **Hydrogen bonding:** It can be used for direct detection of hydrogen bonding interactions.
3. **Drug leads and design:** It is useful for screening isolated compounds as drug leads and determining the conformations of the compounds in binding to enzymes, receptors, and other proteins. It is also a powerful technology for metabolite analysis.
4. **Material science:** It plays an important role in the research of polymer chemistry and physics.
5. **In protein biochemistry:** NMR techniques find multiple use in analysis of structure of proteins and their functions viz., protein folding and protein hydration.
6. **For biomacromolecules:** NMR techniques are used for characterization of biomacromolecules and their complexes as well as understanding their functional dynamics with reference to Molecular dynamics, Chemical properties of functional groups of biomolecules and intermolecular interactions.

Magnetic Resonance Imaging (MRI)

Magnetic resonance imaging (MRI) is an imaging technique for diagnostic purposes that uses non-ionizing radiation. It was initially called *Nuclear Magnetic Resonance Imaging* because its underlying principle of NMR phenomenon. Later the term *nuclear* was dropped and the technique became popular as MRI. It is an important application area of NMR methodology, particularly for medical diagnostics. It can be used to obtain 2-D images of almost any part of our body in any plane. Lauterbur and Mansfield received the Nobel Prize in Physiology or Medicine in 2003 for their development of MRI.

An MRI scanner consists of a large, powerful magnet in which the patient lies. A radio wave antenna is used to send signals to the body and then to receive the signals back. These returning signals are converted into images by a computer attached to the scanner. A resonant magnetic or RF field is used at the resonant frequency of the hydrogen nuclei to stimulate the magnetic moments of the nuclei. When the applied RF-excitation field is removed, the magnetic moments of the nuclei realign to the static field. This generates an RF signal at a resonant frequency determined by the magnitude of the applied field which is detected by the MRI imaging system and generates an image.

Some advantages of MRI over other diagnostic techniques such as X-ray or CT scans, include:

1. Unlike X-rays, it does not use ionizing radiation for the purpose of imaging.
2. Images may be acquired in multiple planes without repositioning the patient.
3. MRI images show better superior soft tissue contrast than CT scans and are thus better suited for examination of the brain, spine, joints and other soft tissue in the body.
4. Some angiographic images can be obtained without the use of contrast material as required for CT scan or angiography.
5. Functional MRI allows imaging of more than one active parts of the brain during certain activities and helps in understanding of the neural network.

There are also some disadvantages associated with the use of MRI scanning.:

1. MRI scans are more expensive than CT scans and the process takes longer time causing discomfort to the patient.
2. Acquiring MRI scans for patients with some metal implants and foreign bodies is not safe.
3. Tough safety and equipment protocols that require strict adherence.

5.6 UV–Visible Spectroscopy

When UV–visible light is absorbed by a molecule, it leads to a transition among its electronic energy levels. The position and intensity of absorption due to the electronic transition is characteristic of the molecular group involved. UV–visible spectroscopy is also called electronic spectroscopy. Electronic spectrum is divided into the following three regions.

1. **Visible region:** 400–750 nm (4000–7500 Å)
2. **Near UV region:** 200–400 nm (2000–4000 Å)
3. **Far UV region:** Below 200 nm (2000 Å)

Far UV region is called vacuum region, since atmospheric oxygen absorbs light in this region and spectra can be obtained for a sample only if the spectrophotometer is completely evacuated. However, absorption below this range is seldom used for general chemical analysis.

Chromophore and Auxochrome

Compounds which absorb light in the visible region appear colored and the color is due to complementary color of light absorbed. Suppose the compound absorbs violet light in visible region, it appears in the complementary color yellow/orange.

Chromophore is the term applied to any group responsible for imparting color to a compound. Generally, the presence of one or more unsaturated linkages or groups produces color. Hence these groups are called *chromophores*; the term means color carrier. Some examples of chromophores are C=C, C=O, -N=N-, etc.

Auxochrome is a substituent on a chromophore which enhances color-imparting property of the chromophore, but it itself does not impart color. Some examples of auxochromes are C-Br, C-OH, and C-NH₂, etc.

Electronic Transitions

UV-visible spectra arise from transition of electron(s) within a molecule or an ion from a lower to a higher electronic energy level. When a molecule absorbs UV radiation of frequency ν , the valence electron in that molecule undergoes transition between energy levels with the energy difference given by

$$\Delta E = h\nu$$

Three distinct types of electrons are involved in organic molecules. These are as follows:

1. **σ -electrons:** These electrons are involved in saturated bonds such as between carbon and hydrogen in *paraffins*. As the amount of energy required to excite electrons in σ bonds is much more than that available by UV light, $\sigma \rightarrow \sigma^*$ transition requires higher energy. For this reason, alkanes are useful as solvents as they do not interfere with the spectra of the compound.
2. **π -electrons:** These electrons are involved in unsaturated hydrocarbons. Typical compounds with π -electrons are alkanes, alkynes, aromatic compounds. The amount of energy required to excite these electrons falls in UV region. So, these compounds absorb UV radiation.
3. **n -electrons:** These are non-bonding electrons which are not involved in the bonding between atoms in molecules. Examples are organic compounds containing nitrogen, oxygen, sulphur or halogens. These electrons can be excited by UV radiation, so any compound that contains atoms like N, O, S or halogen will absorb UV radiation.

Electronic transitions induced by light can be explained by Morse potential curve. Consider a polyatomic molecule in which electronic transition is induced by light absorption. The Morse potential curve for the ground and excited electronic states are represented as shown in Figure 42. The excited state of the curve has a minimum that occurs at a internuclear distance larger than that of the ground state, therefore, the bond between constituting atoms is stretched but they do not fall apart in the excited state. In the excited state, there is one electron in the antibonding orbital, so the bonding is weaker and the bond length is larger. According to Franck-Condon principle, *the absorption of quantum of light will occur rapidly even with respect to molecular vibration., No changes in nuclear positions occur during the excitation process.* So, vertical excitations take place with changes in the molecular structure (bond angles and bond lengths) as the electronically excited molecule comes to thermal equilibrium with its surroundings.

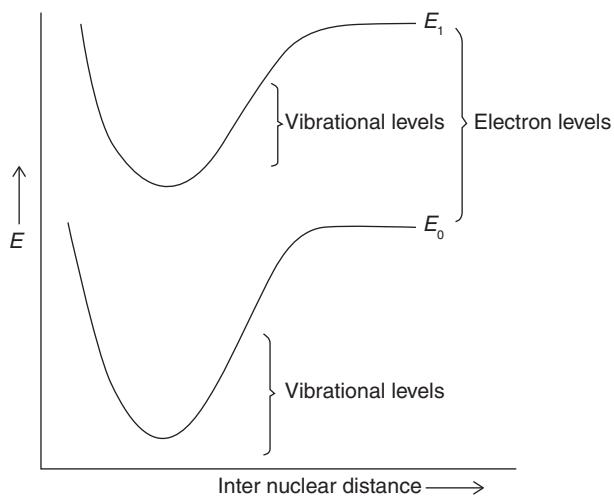


Figure 42 Morse potential curve for electronic transition.

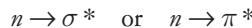
Consider the Morse potential curves for the ground state (E_0) and the first excited state (E_1). There is a series of vibrational energy levels superimposed on the potential curve for each electronic state. At room temperature, the energy available is insufficient to populate the excited vibrational levels, so most of the transitions will start from v_0 of the ground state. This transition from v_0 of the ground state may terminate in any of the several vibrational levels of the excited state. This is the reason for band spectra rather than sharp line in UV spectra. The energy of electronic excitation is measured from v_0 of the ground state to the v_0 of the excited state,

$$E_1(v_0) - E_0(v_0) = \Delta E = h\nu$$

Types of Transitions

The electronic transitions may be of the following two types:

1. Transition between bonding orbitals and antibonding orbitals, $\sigma \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$.
2. Promotion of non-bonding electron into antibonding σ or antibonding π orbitals.



The energy levels for these orbitals are shown in Figure 43. It can be seen from the figure that the energy for different transitions are in the following order:

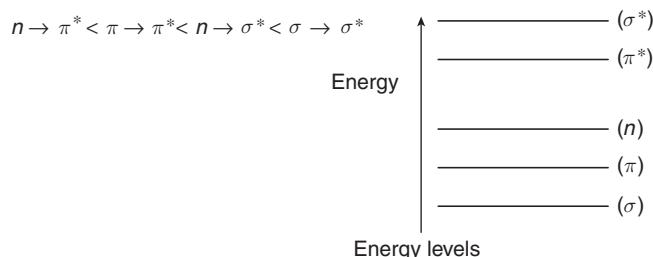


Figure 43 The energy level scheme for a molecule.

Selection Rules in UV-Visible Spectrum

The types of electronic transitions taking place between different energy levels as shown in Figure 44.

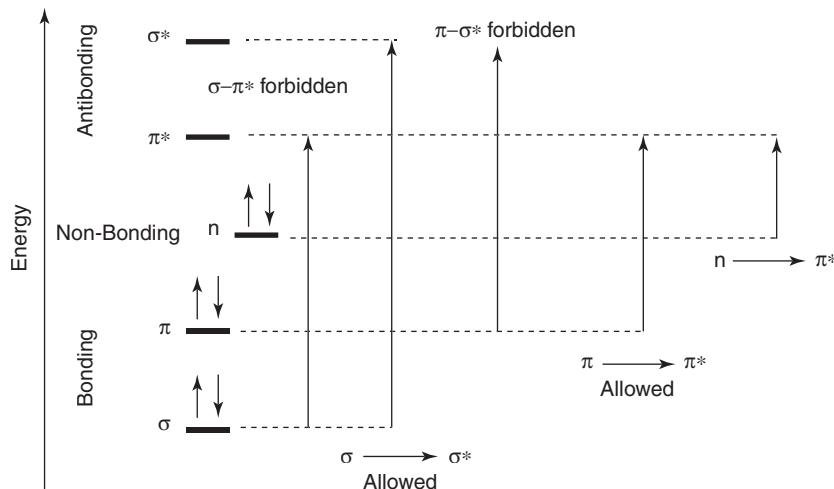


Figure 44 Types of electronic transitions

The selection rules for the transitions that are allowed (or forbidden) are listed as follows:

1. During electronic transitions, spin-inversions (less probable process) are forbidden and spin retentions (more probable process) are allowed (Figure 45).

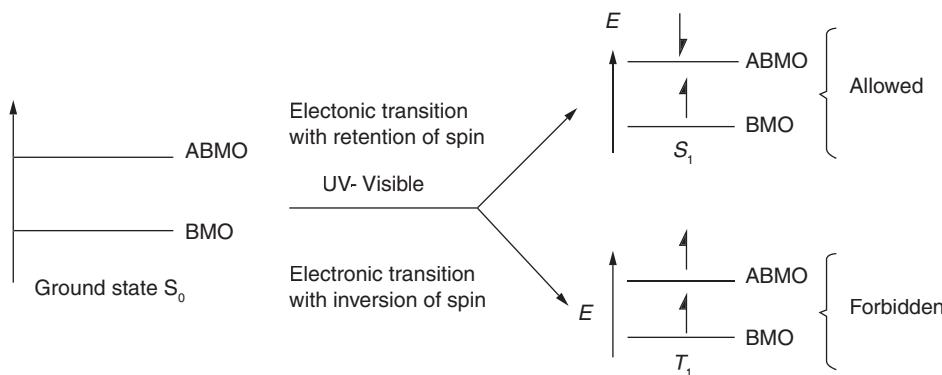
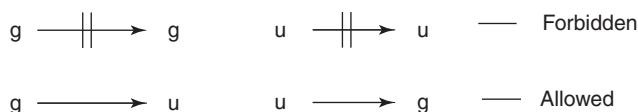


Figure 45 Electronic transitions with retention and inversion of spins.

2. Electronic transitions with retention of multiplicities are allowed, whereas electronic transitions with change in multiplicity are forbidden. This is called multiplicity exclusion principle.
3. Electronic transition between two molecular orbitals of same inversion symmetry is forbidden. Here, g stands for gerade or even and u stands for ungerade or odd.



Hence,

1. $\sigma - \sigma^*$ ($g \rightarrow u$) transition is allowed
2. $\sigma - \pi^*$ ($g \rightarrow g$) transition is forbidden
3. $\pi - \pi^*$ ($u \rightarrow g$) transition is allowed
4. $\pi - \sigma^*$ ($u \rightarrow u$) transition is forbidden
5. $n - \sigma^*$ (higher energy transition)
6. $n - \pi^*$ (low energy transition)

In transitions 5 and 6, the symmetries cannot be compared as n is atomic orbital and σ^* and π^* are molecular orbitals.

Representation of UV-Visible Spectra

The data on absorption are generally presented as absorption curves. The convention normally employed is to plot $\log E$, E , or $\log I_0/I$ against wavelength in Å or nm. The change of solvent or change in a substituent causes the wavelength of maximum absorption to shift to a longer or shorter wavelength. The shift to a longer wavelength or toward the red end of the spectrum is called Bathochromic or red shift. The shift towards the shorter wavelength is called Hypsochromic or blue shift. The intensity of the absorption if increased by any chemical factor is called hyperchromic effect, and if decreased is called hypochromic effect.

Instrumentation for UV-Visible Spectroscopy

An automatic-recording photoelectric spectrophotometer is generally used for recording the UV-visible spectrum for elucidation of organic molecular structure. The simplest of spectrometers are the single-beam instruments which are generally used for simple one-component analyses (Figure 46).

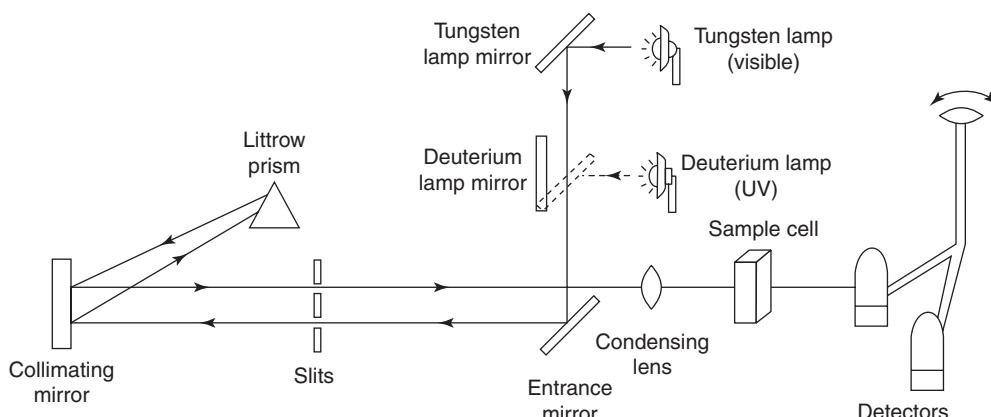


Figure 46 UV-visible single beam spectrometer.

Instruments with high-quality double-beam double-monochromator are also used in which two signals are generated by the sample and reference beams (Figure 47).

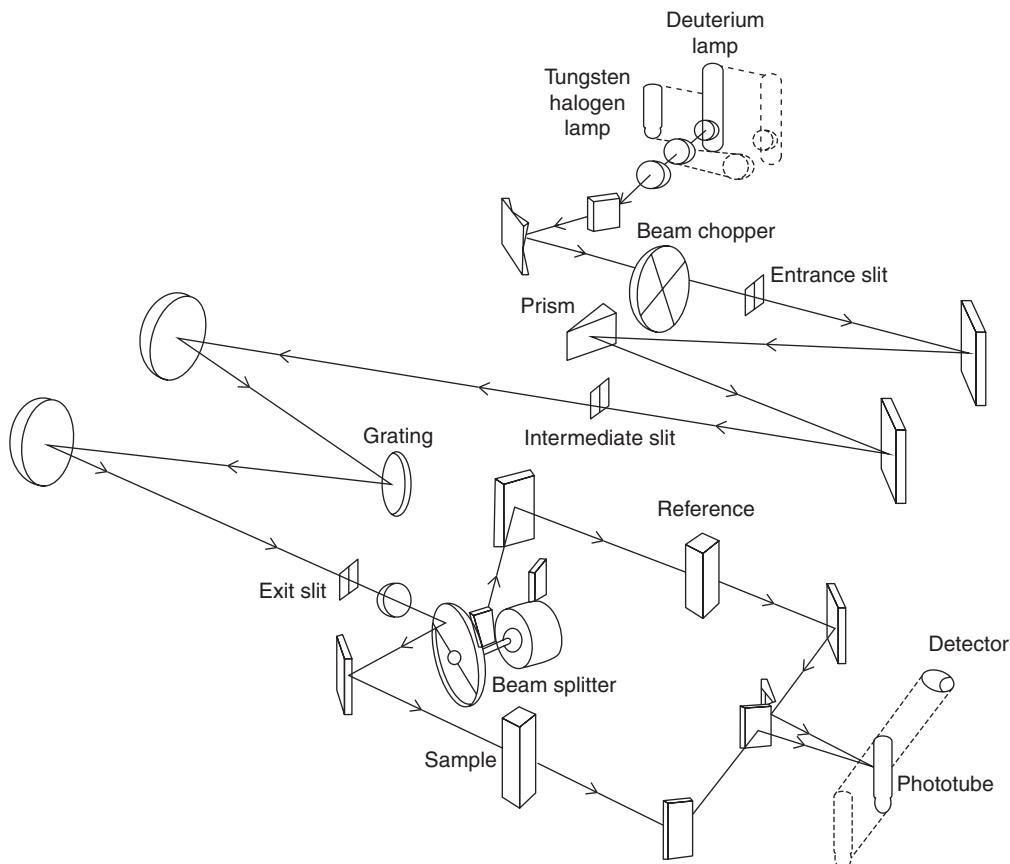


Figure 47 Schematic diagram for double-beams spectrophotometer with double-monochromator.

The main components of instrumentation are listed and discussed as follows:

- Radiation source:** The radiant energy is generated either using tungsten-halogen lamp or a deuterium discharge lamp, depending on the wavelength (frequency) of radiation required. Tungsten lamps are more suitable for measurements in the visible region. The radiations sources must meet two basic requirements: (i) to be able to emit sufficient level of radiant energy over the spectral region to be studied and (ii) Maintain constant power during the period of measurement.
- Monochromator:** The function of the monochromator is to isolate single frequency from the source band of radiation. This is accomplished by focusing the entering radiation on an entrance slit that forms a narrow image of the source. It is then collimated by reflecting off a parabolic mirror and the parallel light rays obtained are then dispersed through a quartz prism. The dispersed radiation is redirected to a collimator mirror and then refocused as an image of the source on the exit slit of the monochromator.

3. **Sample compartment:** This contains the substance to be examined in a cell with quartz windows and a reference cell which hold the pure solvent used to dissolve the sample. In UV systems, the sample container is most often placed after the monochromator to prevent exposure to the entire band of high-energy UV radiation being emitted by the source.
4. **Detector:** The detectors convert electromagnetic radiation into electric current and hence function as transducers. These operate with photocathodes that emit electrons in direct proportion to the number of photons striking the photosensitive surface with large internal amplification.
5. **Amplifier and recorder:** The beams of light in the detector are amplified and the ratio of the sample signal to the reference signal is plotted on a recorder.

Applications of UV Absorption Spectroscopy

1. **Qualitative analysis:** This technique is generally used to characterize aromatic compounds and conjugated olefins. This spectroscopic technique is useful to differentiate conjugated dienes from non-conjugated diene, conjugated dienes from conjugated trienes; and α , β -unsaturated ketones from β , γ -unsaturated ketones.
2. **Detection of impurities:** This is one of the best methods for detecting impurities in organic compounds. The main reasons for the superiority of this method are as follows:
 - The bands due to impurities are very intense.
 - The different λ_{max} values for the impurities can be easily identified. For example, a common impurity in cyclohexane is benzene. Its presence can be easily detected by its absorption at 255 nm.
3. **Quantitative analysis:** This is useful for quantitative estimation of substances in solutions. For the determination of concentration of a substance, the wavelength of maximum absorption for the compound is selected. The optical densities of the solutions of the compound are measured for different concentrations, and plotted against concentration of solute over a wide range of concentrations. The straight line obtained is used as calibration curve for determining the unknown concentration of the solute.
4. **Chemical kinetics:** UV-visible spectroscopy is used to study the kinetics of the reaction. Change in concentration in terms of absorbance values during a reaction can be measured for following the kinetics of reaction, since the concentration is proportional to absorbance.
5. **Geometry of metal complexes:** Comparing the wavelengths of maximum absorption values of complexes of unknown geometry with those of complexes with known geometry, the unknown geometry can be predicted.

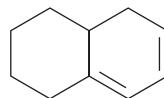
Woodward–Fieser Rules for Calculating Absorption Maximum in Dienes

According to these rules,

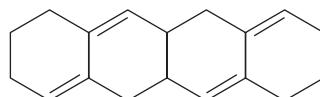
1. Longer the conjugated system, greater is the wavelength of absorption maximum.
2. The intensity of absorption also increases with the increase in the length of the chromophore.
3. The conjugated polyene system appears colored to the naked eye if there are more than five double bonds in conjugation, and absorption occurs around or above 400 nm (visible region).
4. The presence of alkyl group on the double bond also causes bathochromic shift.

Various types of double bonds in conjugation are described as follows with examples:

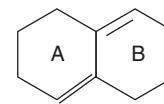
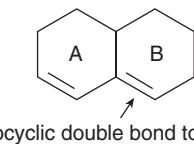
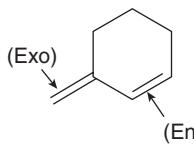
1. Alicyclic dienes or dienes contained in an open chain system. For example, butadiene system.
2. Homoannular conjugated double bonds, conjugated double bonds present in the same ring.



3. **Heteroannular conjugated double bonds:** Conjugated double bonds which are not present in same ring.



4. **Exocyclic and Endocyclic conjugated double bonds:**



The absorption maxima for various conjugated dienes based on these types of double bonds can be calculated using Woodward–Fieser rules and values of parent systems and incremental values for auxochromes are given in Table 9.

Table 9 $\pi \rightarrow \pi^*$ transition of conjugated dienes and trienes (ethanol as solvent)

Compound	Absorption Maxima (λ_{\max} nm)
Parent value for butadiene system or a cyclic conjugated diene	217
Acyclic triene	245
Homoannular conjugated diene	253
Heteroannular conjugated diene	215
Increment for each substituent	
Alkyl substituent or ring residue	5
Exocyclic double bond	5
Double bond extending conjugation	30
Auxochrome	
-OR	+6
-SR	30
-Cl*, -Br*	5
-NR ₂	+60
-OCOCH ₃	0

Problem 1

Calculate the adsorption maximum in the ultraviolet spectrum of 2,4-hexadiene.

Solution

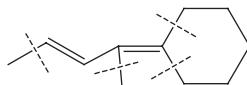
The basic unit in 2,4-hexadiene is butadiene. There are two alkyl substituents (one on each double bond) on it. Thus, for $(\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3)$

$$\begin{array}{c} \text{Basic value} = 217 \text{ nm} \\ \text{Two alkyl substituents } (2 \times 5) = 10 \text{ nm} \\ \hline \text{Calculated value} = 227 \text{ nm} \end{array}$$

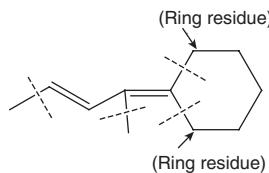
The observed value is also found to be 227 nm.

Problem 2

Calculate the adsorption maximum in the ultraviolet spectrum of the following compound:

**Solution**

It is a butadiene system. There are two alkyl substituents and two ring residues on the double bonds. Moreover, there is an exocyclic double bond.



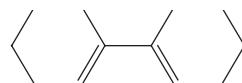
The value of absorption maximum is calculated as follows:

$$\begin{array}{c} \text{Basic value} = 217 \text{ nm} \\ \text{Two alkyl substituents } (2 \times 5) = 10 \text{ nm} \\ \text{Two ring residues } (2 \times 5) = 10 \text{ nm} \\ \hline \text{One exocyclic double bond} = 5 \text{ nm} \\ \hline \text{Calculated value} = 242 \text{ nm} \end{array}$$

Hence, the observed value is also found to be 242 nm.

Problem 3

Calculate the adsorption maximum in the UV spectrum of the following compound:

**Solution**

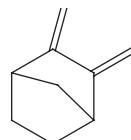
It is an example of heteroannular diene and there are four ring residues on the double bonds. Thus,

$$\begin{array}{c} \text{Basic value for butadiene system} = 215 \text{ nm} \\ \text{Four ring residues } (4 \times 5) = 20 \text{ nm} \\ \hline \text{Calculated value} = 235 \text{ nm} \end{array}$$

Hence, the observed value is also found to be 234 nm.

Problem 4

Calculate the absorption maximum in the ultraviolet spectrum of 2,3 dimethylene bicyclo (2,2,1) heptane.

**Solution**

The value of absorption maximum for this compound is calculated as:

$$\begin{array}{c} \text{Basic value} = 217 \text{ nm} \\ \text{Two ring residues } (2 \times 5) = 10 \text{ nm} \\ \text{Two exocyclic double bond} = 10 \text{ nm} \\ \hline \text{One bicyclic system(strain correction)} = 15 \text{ nm} \\ \text{Calculated value} = 252 \text{ nm} \end{array}$$

Hence, the observed value is also found to be 254 nm.

Key Terms

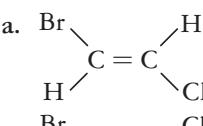
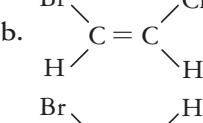
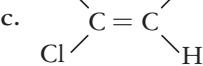
Spectroscopic techniques	Absorption of Electromagnetic radiation by organic molecules	FT IR (fourier transform infrared)
Electromagnetic spectrum		Michelson interferometer
Molecular spectroscopy	Energy of diatomic molecules	NMR spectroscopy
Radiofrequency region/radiation	Signal-to-noise ratio	Nuclear resonance
Microwave region/radiation	Infrared spectroscopy	Chemical shift
Infrared region/radiation	Molecular vibrations	Chemical exchange
Visible and UV region/radiation	Group and fundamental vibrations	Coupling constant
Lambert–Beer’s law	Overtones	UV-visible spectroscopy
Absorbance spectrum	Calculation of vibrational frequencies.	Chromophore and auxochrome
Emission spectrum	Vibration coupling	Electronic transitions
Absorbance	Fingerprint region	Woodward–Fieser rules
Transmittance		

Objective-Type Questions

Multiple-Choice Questions

1. The frequency of electromagnetic radiation of wavelength 455 nm is
 - a. 6.59×10^{14} Hz
 - b. 6.59×10^{-14} Hz
 - c. 3×10^{14} Hz
 - d. 2.0×10^6 Hz
2. What is the concentration of a solution which has an abundance of 0.975 in a cell with a 1 cm path length if the molar absorptivity of the solute is 12,500?
 - a. 8.7×10^{-4} M
 - b. 7.8×10^{-2} M
 - c. 8.7×10^{-2} M
 - d. 7.8×10^{-5} M
3. What is the molar absorptivity of a solute at 463 nm in a cell with a path length of 1.50 cm if the absorbance of a 1.20×10^{-4} M solution is 0.485?
 - a. 2.69×10^3 l/mol-cm
 - b. 3.12×10^2 l/mol-cm
 - c. 6.29×10^2 l/mol-cm
 - d. 2.13×10^2 l/mol-cm
4. The wave number of IR radiation of 500 μm is
 - a. 3000 cm^{-1}
 - b. 2000 cm^{-1}
 - c. 1500 cm^{-1}
 - d. 3500 cm^{-1}
5. The stretching frequency of OH bond in alcohols is normally observed in the range
 - a. $3640\text{--}3610 \text{ cm}^{-1}$
 - b. $1740\text{--}1720 \text{ cm}^{-1}$

- c. $1670\text{--}1660\text{ cm}^{-1}$
d. $1050\text{--}1100\text{ cm}^{-1}$
6. Among the following which is used to make plates and cells in IR?
 a. CuSO_4
 b. MgCl_2
 c. NaCl
 d. CaSO_4
7. How many types of magnetically equivalent protons are present in naphthalene molecule?
 a. 3
 b. 2
 c. 4
 d. 8
8. NMR spectra cannot be obtained from which of the following nuclei (i) ^{16}O ; (ii) ^{13}C ; (iii) ^{31}P ; (iv) ^{14}N ?
 a. (i), (ii)
 b. (ii), (iii)
 c. (iii), (iv)
 d. (i), (iv)
9. How many signals are expected in NMR for the compound $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$?
 a. 1
 b. 2
 c. 3
 d. 4
10. How many signals are expected for cyclohexane in normal conditions?
 a. 6
 b. 3
 c. 1
 d. 4
11. Which of the following parameters is not used to characterize electromagnetic radiation?
 a. Wavelength
 b. Intensity
 c. Wave number
 d. Frequency
12. Which among the following shows highest carbonyl stretching frequency?
 a. Amide
 b. Aldehydes
 c. Acid chloride
 d. Acyclic ketone
13. Which of the following molecules will show a peak infrared spectrum around 1700 cm^{-1} ?
 a. CH_4
 b. $\text{CH}_2 = \text{CH}_2$
 c. $\text{CH} \equiv \text{CH}$
 d. $\text{CH}_3 - \underset{\parallel}{\text{C}} - \text{CH}_3$
14. Which of the following compounds will show longest wavelength of UV absorption?
 a. Ethylene
 b. Naphthalene
 c. Anthracene
 d. 1, 3-Butadiene
15. Which of the following is not true for UV spectra of benzene and its derivatives?
 a. Presence of simple alkyl groups causes shift in absorption to longer wavelength.
 b. Presence of substituents with non-bonding electrons shifts the absorption to longer wavelengths.
 c. In disubstituted derivatives, ortho isomers show absorption at shortest wavelength among ortho, meta and para isomers.
 d. None of the above.
16. Which of the following nuclei will not show nuclear magnetic resonance?
 a. ^1H
 b. ^{12}C
 c. ^{15}N
 d. ^{16}O
17. For the compound with molecular formula $\text{C}_2\text{H}_2\text{BrCl}$, NMR spectra shows two doublets with $J = 16\text{ Hz}$. The structure of the compound is given by

- a. 
- b. 
- c. 
- d. None of the above
18. Which of the following compounds would exhibit a single peak in ^1H NMR spectrum?
- $\text{CH}_3 - \text{C} \equiv \text{CH}$
 - $\text{CH}_2 = \text{C} = \text{CH}_2$
 - $(\text{CH}_3)_2\text{C} = \text{CH}_2$
 - $\text{CH}_3 - \underset{\text{H}}{\text{C}} = \text{CH}_2$
19. Which of the following compounds will show spin–spin coupling in the NMR spectra?
- $\text{ClCH}_2\text{CH}_2\text{Cl}$
 - $\text{CH}_3 - \text{C}(\text{Cl}_2) - \text{CH}_3$
 - $\text{ClCH}_2\text{CH}_2\text{I}$
 - $\text{BrCH}=\text{CHBr}$
20. Which among the following unconjugated carboxylic acid derivatives will have highest carbonyl stretching frequency?
- Acid chloride
 - Amide
 - Ester
 - Acid anhydride
21. Which of the following statements is not true?
- UV–visible spectra helps in predicting the number of conjugated double bonds.
 - In UV–visible spectra, the absorption bands exist as sharp lines.
 - The substance which absorbs in visible region appears colored to human eye.
 - Electromagnetic radiation in wavelength range 780–10 nm corresponds to UV–visible region.
22. Identification of functional groups in a compound can be established by using
- UV spectroscopy.
 - chromatography.
 - NMR spectroscopy.
 - IR spectroscopy.
23. The mode of excitation of molecule in IR spectroscopy is
- electronic.
 - vibrational.
 - magnetic.
 - optical.
24. Lambert–Beer's law states that
- $A = \varepsilon Cl$
 - $A = \varepsilon / Cl$
 - $A = Cl / \varepsilon$
 - $A = \varepsilon C / l$

Fill in the Blanks

- For a molecule to give pure rotational spectrum it must possess _____.
- The absorption frequency of methane in IR region is observed at _____.
- Aldehydes can be distinguished from ketones in IR spectroscopy by absorption near 2720 cm^{-1} due to _____.
- In UV–visible spectrum toluene absorbs at _____ wavelength as compared to benzene due to presence of an _____.
- In geometrical isomers *cis* isomers absorb at _____ wavelength as compared to *trans* isomers, in UV–visible spectroscopy.
- In carbonyl compounds, substitution with an auxochrome causes a _____ shift, whereas conjugation with an ethylenic group causes _____ shift.
- The NMR spectra of the functional isomers of $\text{C}_2\text{H}_6\text{O}$ show _____ and _____ peaks, respectively.

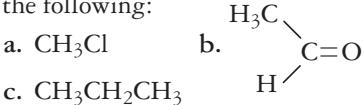
8. _____ shifts the NMR signals up field, whereas _____ shifts the signals down-field.
9. _____ is the difference in the absorption position of the proton with respect to the TMS signal.

Review Questions

Short-Answer Questions

- What are electromagnetic radiations? Give regions of electromagnetic spectrum in the order of increasing frequency.
- What are the factors that influence the width and intensity of spectral lines?
- State Beer's and Lambert's law of absorbance.
- What are the possible electronic transitions when energy is absorbed by a molecule in the UV region?
- Define the terms chromophores and auxochromes and give examples.
- Identify the chromophores in the following:
 - CH_3SH
 - $\text{C}_6\text{H}_5 - \text{CH}_3$
 - $\text{CH}_3 - \text{CH}_2 - \text{C} = \text{O} - \text{CH}_3$
 - $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_3$
- Distinguish between hyperchromic and hypochromic shift.
- Explain the terms hypsochromic (blue) shift and bathochromic (red) shift. What structural features may lead to these shifts in organic molecules?
- State Franck–Condon principle. How does it explain the appearance of electronic transitions?
- A polar solvent shifts $\pi - \pi^*$ transition to longer wavelength and $n - \pi^*$ transition to shorter wavelength. Explain?

11. Give all possible electronic transitions for the following:



12. How are UV-visible spectra used to distinguish between

- Cis-stilbene and trans-stilbene
- Benzene and anthracene
- Ortho-methyl and para-methyl acetophenone

13. Give reasons for the following:

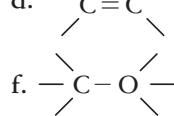
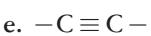
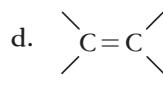
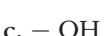
- Change of solvent from hexane to water causes a blue shift in λ_{\max} for acetone.
- Aniline shows λ_{\max} at 230 nm in neutral medium and 203 nm in acidic medium.

14. Why does conjugated butadiene require less energy for $\pi - \pi^*$ transition as compared to unconjugated ethylene?

15. What are the necessary conditions for a molecule to show IR spectrum?

16. What is the number of fundamental vibrations in a linear or non-linear molecule with n atoms?

17. Give the IR absorption frequencies of the following functional groups:



18. What is the importance of fingerprint region in IR spectroscopy?
19. Draw the vibrational modes of CO_2 molecule, stating which of the modes will be IR active.
20. On the basis of IR spectra, distinguish between the following:
 - Ethanol and dimethyl ether
 - 1-Hexyne, 1-hexene and hexane
 - Ethyl amine and acetamide
 - Propanal and propanone
21. On the basis of IR spectra, distinguish between the following:
 - Aliphatic and aromatic compounds
 - Terminal and non-terminal alkyne
 - Intermolecular and intramolecular hydrogen bonding
22. Explain the following:
 - Crotonaldehyde exhibits absorption at 1700 cm^{-1} and 1630 cm^{-1} , whereas C=O and C=C stretching is observed at $1720\text{--}1740\text{ cm}^{-1}$ and near 1650 cm^{-1} in unconjugated aliphatic aldehydes.
 - Saturated aliphatic carboxylic acids show carbonyl stretch near 1760 cm^{-1} , whereas saturated ketones give carbonyl stretching near 1720 cm^{-1} .
23. What are the relaxation processes by which nucleus in upper transition state may return to lower spin state?
24. What is the standard reference used for measuring chemical shift and why?
25. Give the number of ^1H signals for the following compounds.
 - $\text{CH}_3\text{OCH}_2\text{CH}_3$
 - $\text{CH}_3 - \text{CH} = \text{CH}_2$
 - $\text{C}_6\text{H}_5 - \text{CH}_3$
 - $\begin{array}{c} \text{H} \\ | \\ \text{d. } \text{CH}_3 - \text{C} = \text{O} \end{array}$
- e. $\begin{array}{c} \text{Cl} \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ | \\ \text{Cl} \end{array}$
26. Predict the number and multiplicity of the signals in the following:
 - $\text{Cl} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Cl}$
 - $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$
 - $\text{Cl}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3$
27. What are shielding and deshielding effects?
28. What is meant by term chemical shift? How does it arise and how is it measured?
29. What is meant by spin–spin coupling? What is coupling constant?
30. Explain the following:
 - Number, intensity and multiplicity of signals in isobutyl bromide, secondary butyl bromide and *n*-butyl bromide.
 - Presence of spin–spin coupling in 2-chloropropene and its absence in 1-chloro-2,2-dimethyl propane.
31. Explain the use of NMR spectroscopy to distinguish between
 - aldehyde and ketone
 - cis* and *trans* isomers
 - p*-xylene and ethyl benzene
32. For the following compounds, give structures consistent with NMR data:
 - $\text{C}_3\text{H}_5\text{Cl}_3$: δ 2.20 singlet 3H; δ 4.20 singlet 2H;
 - $\text{C}_9\text{H}_{11}\text{Br}$: δ 2.15 quintet 2H; δ 2.75 triplet 2H; δ 3.33 triplet 2H; δ 7.22 singlet 5H.
33. Explain the use of deuterium labeling for simplifying complex NMR spectra.
34. A gaseous hydrocarbon A on passing through a heated (600°C) quartz tube gives a liquid compound B (molecular weight 78). The latter compound undergoes electrophilic substitution reactions. The fol-

- lowing data was obtained on analysis of B. Identify compounds A and B.
- IR spectrum: Characteristic absorption at 3040 cm^{-1}
- UV absorption: $\pi-\pi^*$ transition at 204 nm
- $^1\text{H NMR}$ spectrum: Singlet (6H) at $\delta 2.7$
35. (a) The NMR spectra of $\text{C}_2\text{H}_4\text{Br}_2$ shows only one signal. What is the structure of the compound?
 (b) The compound X on mass analysis gave molecular ion peak at 44 mass units. Elemental analysis gave C = 54.55%, H = 9.09%. The $^1\text{H NMR}$ exhibited a downfield signal (quartet), which is one-third as intense as second signal (doublet). The compound responds to silver mirror test. Identify the compound.
36. How can we distinguish between the following pairs using IR spectra?
 a. Ethanol and dimethyl ether.
 b. 2-Propanol and propane.
 c. Ethylamine and acetamide.
37. Give the structure of $\text{C}_3\text{H}_5\text{Cl}_3$ consistent with the following NMR data: Singlet, $\delta 2.20$, 3H and singlet, $\delta 4.20$, 2H.
38. Define the terms chromophore and auxochrome in UV spectroscopy.
39. How many NMR signals do you expect from each of the following compounds. Also indicate the splitting pattern of the various signals: (a) CH_3OCH_3 , (b) $\text{CH}_3\text{COCH}_2\text{CH}_3$, (c) $\text{CH}_3\text{CH}_2\text{OH}$.
40. IR spectra is often characterized as molecular fingerprints. Comment on it.
41. Give examples of two applications of each of IR and UV spectrometry.
42. Give the relation between wavelength and energy of electromagnetic radiation.
43. What is the significance of signal-to-noise ratio in spectroscopy?
44. What is vacuum region? What are the advantages and disadvantages of the region in spectroscopy?
45. Butadiene in hexane solution exhibits $\lambda_{\max} = 217\text{ nm}$ with $\epsilon_{\max} = 20900$, whereas 1,3,5,7 octatetraene in hexane exhibits $\lambda_{\max} = 296\text{ nm}$ with $\epsilon_{\max} = 52900$. Give suitable reasons.
46. β -carotene is a naturally available yellow pigment. Account for its color.
47. What causes chemical shifts in NMR spectroscopy?
48. What do you understand by the terms, upfield and downfield?

Long-Answer Questions

- State Beer's and Lambert's law and derive mathematical expression for Lamber-Beer's law.
- What do you understand by UV-visible spectroscopy? What are the different types of transitions that take place on absorption of energy in UV-visible region? Explain the significance of these transitions with examples.
- With the help of a suitable example, explain how quantitative analysis is carried out using UV-visible spectrophotometer?
- Discuss the various applications of UV-visible spectroscopy.
- What are the different modes of vibration that result when a molecule absorbs infrared radiation? Describe the various vibrations using the example of XY_2 bent molecule.
- Describe the effect of the following factors on vibrational frequencies: (a) Physical state, (b) solvent effects, (c) hydrogen bonding and (d) electronic effects.
- Write notes on (a) Fourier transform IR and (b) Michelson's interferometer.

8. Explain the principle of NMR spectroscopy. Explain how the NMR spectrum of a compound is recorded?
9. What is meant by the term chemical shift? Discuss the various factors that affect the chemical shift of protons.
10. Explain the NMR spectrum of $\text{CH}_3\text{CH}_2\text{OH}$ molecule giving the significance of number of signals, relative intensity of signals and splitting of signals.
11. Discuss the application of NMR spectroscopy to (a) structural diagnosis, (b) keto-enol tautomerism, (c) hydrogen bonding and (d) geometrical isomerism.
12. Write notes on (a) spin–spin interactions; (b) shielding and deshielding of protons and (c) nuclear overhaüser effect.
13. Describe briefly two techniques used for simplification of complex NMR spectra.
14. Describe in brief the terms: (a) chromophore, (b) Bathochromic shift, (c) hyperchromic shift and (d) hypochromic shift.
15. Write informative notes on any two of the following: (a) Lambert's and Beer's law; (b) UV–visible spectroscopy and (c) IR-spectroscopy.
16. What is electromagnetic radiation? Explain the type of excitations in molecules when they interact with different regions of electromagnetic radiation.
17. Explain the principle and instrumentation of UV–visible spectrophotometry.
18. What are fundamental and overtone vibrations? Give examples.
19. Explain IR spectrophotometer with principle and instrumentation.
20. What are the advantages of FTIR? Explain the functioning of Michelson's interferometer?
21. Explain the applications of IR spectroscopy?
22. Explain the following in IR spectroscopy: (a) radiation sources and (b) sampling techniques.
23. Explain the principle of NMR spectroscopy.
24. Explain the electronic shielding effects manifested in ethylene and acetylene.
25. What is spin–spin interaction? How does it influence the protons in neighboring carbons?
26. What are the various factors that influence coupling constant? Give suitable examples for your explanation.
27. Explain the NMR spectrum of ethanol with and without the involvement of chemical exchange.
28. Explain Woodward-Fieser rules for calculating absorption maximum in dienes.

Numerical Problems

1. Convert the following wave numbers to microns and Å: (a) 1200 cm^{-1} and (b) 3600 cm^{-1} .
2. Calculate the number of molecules in a higher energy level relative to the number in a lower energy level if the levels are separated by an energy of $0.4 \times 10^{-21} \text{ J}$ and the temperature is 25°C .
3. Calculate the difference in the frequency expected for the vibrational excitation from ground level to first level of ^{35}HCl to ^{37}HCl assuming that the force constants of the two molecules are identical and equal to $4.84 \times 100 \text{ N/m}$.
4. One of the fundamental vibrational modes of H_2O occurs at 3652 cm^{-1} . What would

- be the frequency of the corresponding vibration for D_2O ?
5. Calculate the strength of the magnetic field in which protons will have a Larmor frequency of 60 MHz.
 6. A substance is known to have a molar extinction coefficient of 14000 at its wavelength of maximum absorption. Calculate the molarity of the substance using 1 cm cell in a spectrometer if the optical density is 0.850.
 7. At definite wavelength, an absorber when placed in a cell of 1 cm path length absorbs 20% of the incident light. If the absorptivity of the absorber at this wavelength is 2.0, find out its concentration.
 8. A monochromatic radiation is incident on a solution of 0.05 M concentration of an absorbing substance. The intensity of the radiation is reduced to one-fourth of the initial value after passing through 10 cm length of the solution.
 9. Calculate the molar extinction coefficient of the substance. In a cell, the aqueous solution of a substance of known concentration absorbs 10% of the incident light. What fraction of the incident light will be absorbed by the same solution in a cell five times as long?

Answers

Multiple-Choice Questions

- | | | |
|--------|--------------|---------|
| 1. (a) | 9. (c) | 17. (a) |
| 2. (d) | 10. (c) | 18. (b) |
| 3. (a) | 11. (b) | 19. (c) |
| 4. (b) | 12. (c) | 20. (d) |
| 5. (a) | 13. (a) | 21. (b) |
| 6. (c) | 14. (c) | 22. (d) |
| 7. (b) | 15. (d) | 23. (b) |
| 8. (d) | 16. (b), (d) | 24. (a) |

Fill in the Blanks

1. permanent dipole moment
2. $2850\text{--}3000\text{ cm}^{-1}$ and $1350\text{--}1480\text{ cm}^{-1}$
3. C—H_{str} vibration
4. higher, auxochrome
5. shorter
6. hypsochromic, bathochromic
7. one and three
8. shielding, deshielding
9. chemical shift

Numerical Problems

1. (a) 8.3333 microns; (b) 2.7778 microns.
5. 14084 gauss
2. $N_1/N_0 = 0.91$
6. 6.071×10^{-5} mol/l
3. 5.77 cm^{-1}
7. 0.0969 mol/l
4. $H_2O = 1.0956 \times 10^{14} \text{ s}^{-1}$; $D_2O = 1.7034 \times 10^{14} \text{ s}^{-1}$
8. $1.204 \text{ dm}^3/\text{mol}\cdot\text{cm}$
9. 0.41

Experiment 1

Determination of Total Hardness of Water by Complexometric Method using EDTA

Introduction

Water that does not form lather with soap is called hard water. It contains dissolved magnesium and calcium ions that get into the flowing water when it comes into contact with limestone and other rocks that contain calcium compounds. Hardness of water is mainly due to the presence of calcium and magnesium salts in it. Total hardness is the sum of temporary hardness (due to bicarbonates of calcium and magnesium) and permanent hardness (due to chlorides, sulphates, etc., of calcium and magnesium).

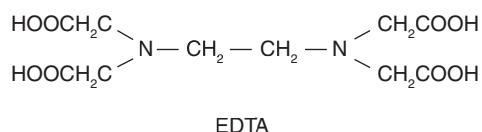
Aim

To determine the total, permanent and temporary hardness of a water sample.

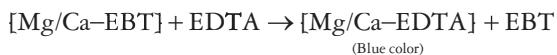
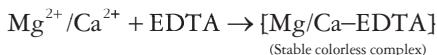
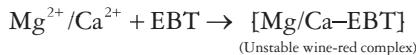
Principle

Estimation of hardness of water can be carried out by complexometric titration using ethylenediamine tetraacetic acid (EDTA) as complexing agent and Eriochrome black-T (EBT) as indicator.

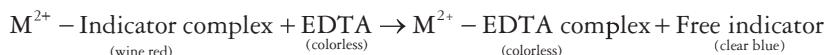
(EDTA) is a reagent, which reacts with metal ions like Ca^{2+} , Mg^{2+} forming complex compounds. Therefore, this reagent can be used to determine the concentration of hardness-causing substances.



The completion of the reaction (end point of the titration) is identified using EBT as indicator. This is an organic dye, blue in color. EBT when added to water forms an unstable wine-red colored complex with calcium and magnesium. As the solution is titrated with EDTA, free Mg^{2+} and Ca^{2+} present in water form stable colorless complex with EDTA. Once all the free Mg^{2+} and Ca^{2+} are complexed, EDTA replaces Mg^{2+} and Ca^{2+} complexed with EBT in the unstable wine-red complex. Free EBT imparts blue color to the solution, so the color change from wine-red to blue indicates the end-point of the reaction. The amount of EDTA used in the titration corresponds directly to the hardness of water.



The overall reaction can be represented as



Since the reaction involves the liberation of H^+ ions and the indicator is sensitive to the concentration of H^+ ions (pH) of the solution, a constant pH of around 10 has to be maintained. For this purpose, ammonia–ammonium chloride buffer is used.

Total hardness of water can be determined by titrating the water sample against standard EDTA solution. Permanent hardness of water can be determined by titrating the water sample against standard EDTA solution after removal of temporary hardness by boiling the water sample. The difference between total and permanent hardness gives the temporary hardness.

Apparatus and Reagents Required

Apparatus: Burette, conical flask, pipette, measuring flask

Reagents: EDTA solution, Eriochrome black T indicator, $\text{NH}_3-\text{NH}_4\text{Cl}$ buffer solution ($\text{pH } 10 \pm 0.1$), standard hard water solution and water sample

Procedure

1. A standard solution of EDTA is prepared by dissolving a known amount of EDTA (4–6 g) in 100–150 mL of deionized water and 4 mL NaOH and then making up the volume in a 250 mL volumetric flask.
2. A clean burette is washed with distilled water and then rinsed with small amount of standard EDTA solution. It is then filled with standard EDTA solution up to the zero level ensuring that no air bubbles are formed.
3. In a clean conical flask take about 25 mL of standard hard water, add 5–6 drops of EBT indicator and 3 mL of buffer solution. The color of the solution turns wine red. Titrate the solution against standard EDTA solution from the burette, till the color of the solution turns blue. Take two concordant reading and let the volume of EDTA solution used be V_1 mL.
4. About 25 mL of the given sample of hard water is taken in another clean conical flask and 3 mL of buffer solution followed by 5–6 drops of EBT indicator is added to it. Titrate similarly to find the volume of EDTA used by unknown hard water sample. Let the volume of EDTA solution used be V_2 mL.

5. Take about 100 mL of hard water sample in a beaker and boil gently for an hour. Cool and filter the water and collect in a standard 100 mL flask and makeup the volume to 100 mL. Pipette out 25 mL of this solution in a conical flask, add 3 mL of buffer solution and 5–6 drops of EBT indicator and titrate as above to calculate the permanent hardness of the water sample. Let the volume of EDTA solution used be V_3 mL.

Observations

(Titration of Standard Hard Water with EDTA) Standardization of EDTA Solution

Burette readings for volume of EDTA used for titration with standard hard water:

S. No.	Volume of Standard Hard Water (mL)	Initial Reading (x mL)	Final Reading (y mL)	Volume of EDTA Used ($V_1 = y - x$ mL)
1	25			
2	25			
3	25			

Concordant reading for volume of EDTA used (V_1)= mL

(Titration of Hard Water Sample with EDTA) (Calculation of Total Hardness of Water)

Burette readings for volume of EDTA used for titration with given hard water sample:

S. No.	Volume of Standard Hard Water (mL)	Initial Reading (x mL)	Final Reading (y mL)	Volume of EDTA Used ($V_2 = y - x$ mL)
1	25			
2	25			
3	25			

Concordant reading for volume of EDTA used (V_2)= mL

(Titration of Hard Water Sample (after Boiling) with EDTA) (Calculation of Permanent Hardness of Water Sample)

Burette readings for volume of EDTA used for titration with given hard water sample after boiling:

S. No.	Volume of Standard Hard Water (mL)	Initial Reading (x mL)	Final Reading (y mL)	Volume of EDTA Used ($V_3 = y - x$ mL)
1	25			
2	25			
3	25			

Concordant reading for volume of EDTA used (V_3) = mL

Calculations

Standardization of EDTA Solution (Titration of Standard Hard Water with EDTA)

Volume of hard water used = 25 mL

Volume of EDTA solution used for titration = V_1 mL

1 mL of standard hard water contains 1 mg of calcium carbonate (CaCO_3). Therefore, 25 mL of standard hard water contains 25 mg of CaCO_3 . Thus,

$$\begin{aligned} V_1 \text{ ml of EDTA} &= 25 \text{ mg of } \text{CaCO}_3 \\ \Rightarrow 1 \text{ ml of EDTA solution} &= \frac{25}{V_1} \text{ mg of } \text{CaCO}_3 \end{aligned} \quad (1)$$

Calculation of Total Hardness of Water (Titration of Hard Water Sample with EDTA)

Volume of hard water used = 25 mL

Volume of EDTA used for titration = V_2 mL

From Eq. (1), we have

$$25 \text{ mL of given hard water sample} = \frac{25}{V_1} \times V_2 \text{ mg of } \text{CaCO}_3$$

Therefore, 1000 mL of hard water contains

$$\begin{aligned} 1000 \text{ mL of given hard water sample} &= \frac{25}{V_1} \times V_2 \times \frac{1000}{25} \text{ mg of } \text{CaCO}_3 \\ &= \frac{V_2}{V_1} \times 1000 \text{ mg of } \text{CaCO}_3 \end{aligned}$$

Thus,

$$\text{Total hardness of water sample} = \frac{V_2}{V_1} \times 1000 \text{ ppm}$$

Calculation of Permanent Hardness of Water Sample Titration of Hard Water Sample (after Boiling) with EDTA

Volume of hard water used (after boiling) = 25 mL

Volume of EDTA used for titration = V_3 mL

From Eq. (1), we have

$$25 \text{ mL of hard water sample after boiling} = \frac{25}{V_1} \times V_3 \text{ mg of CaCO}_3$$

Therefore,

$$\begin{aligned} 1000 \text{ mL of hard water sample after boiling} &= \frac{25}{V_1} \times V_3 \times \frac{1000}{25} \text{ mg of CaCO}_3 \\ &= \frac{V_3}{V_1} \times 1000 \text{ mg of CaCO}_3 \end{aligned}$$

Thus,

$$\text{Permanent hardness of water sample} = \frac{V_3}{V_1} \times 1000 \text{ ppm}$$

Calculation of Temporary Hardness of Water Sample

$$\text{Total hardness of water} = \text{Permanent hardness} + \text{Temporary hardness}$$

Therefore,

$$\text{Temporary hardness} = \text{Total hardness of water} - \text{Permanent hardness}$$

Substituting the values of total and permanent hardness, we can calculate the temporary hardness of the water sample.

Alternate Calculation

The strength of the EDTA solution may be calculated as:

$$\text{Weight of EDTA dissolved in } 250 \text{ mL of water} = \text{_____ g}$$

$$\text{Weight of EDTA dissolved per liter} = \text{_____ g} \times 4$$

$$\text{Molarity of EDTA solution} = \frac{\text{_____ g} \times 4}{372.4} = \alpha \text{ M (say)}$$

We know that $1000 \text{ mL of } 1 \text{ M EDTA} \equiv 100 \text{ g of CaCO}_3$. So,

$$V \text{ mL of } \alpha \text{ M EDTA} = \frac{100 \times V \times \alpha}{1000} \text{ g of CaCO}_3 = y \text{ g of CaCO}_3$$

25 mL of hard water contains y g of CaCO_3

Therefore, 10^6 mL of hard water contains

$$\frac{4 \times 10^6}{25} \text{ g of } \text{CaCO}_3 = \frac{y}{25} \text{ ppm}$$

So, total hardness of water = _____ ppm.

Permanent hardness of water can be determined by titrating the water sample against standard EDTA solution after removal of temporary hardness by boiling the water sample. The difference between total and permanent hardness gives the temporary hardness.

Result

The total hardness of given sample of water = _____ ppm.

The permanent hardness of given sample of water = _____ ppm.

The temporary hardness of given sample of water = _____ ppm.

Precautions and Safety Measures

1. The sharp color change at the end point using EBT as indicator is observed if both magnesium and calcium ions are present in the solution of hard water. In absence of magnesium ions, the color change at the end point is not sharp. This is because calcium ions form a relatively weak and soluble complex with the indicator. So if the hard water sample contains only calcium ions, a small amount of magnesium chloride is added to the EDTA solution before its standardization.
2. The pH for the reaction mixture during titration should be maintained between 8 and 10. At lower pH (acidic solutions), the bonding between magnesium ions and the indicator is weak so the red color of the complex between them ions is not maintained. In strongly acidic medium, the indicator EBT polymerizes to a red-brown precipitate. At higher pH (basic solutions), the magnesium ions are precipitated as Mg(OH)_2 .
3. The buffer solution should not be pitted out with the mouth because it may affect the normal pH of the blood which is about 7.4.

Related Experiments

The hardness due to calcium and magnesium ions separately can also be determined by using the following procedures:

1. The magnesium ions present in water are precipitated as Mg(OH)_2 by addition of diethylamine which raises the pH of the solution to 12.5. The precipitate is removed and the

calcium ions in the filtrate are then estimated by complexometric titration with EDTA using calcon [solochrome dark blue which is sodium 1-(2-hydroxy-1-naphthyl(azo)-2-naphthol-4-sulphonate] as the indicator. The end point is marked by color change from pink to blue. The total hardness of water is determined by complexing with EDTA using EBT as indicator, as described above. The difference between total hardness and calcium hardness gives the value of magnesium hardness of water.

2. In another method, the calcium ions present in hard water are precipitated as calcium oxalate by adding calcium precipitating buffer solution $[(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{NH}_4\text{Cl} + \text{NH}_4\text{OH}]$. The precipitate is filtered and the magnesium ions in the filtrate are estimated with standard EDTA solution using EBT as the indicator. The total hardness of water is estimated and the calcium hardness obtained as the difference between total hardness and magnesium hardness.

Viva Voce Questions

1. Distinguish between permanent and temporary hardness of water. How can temporary and permanent hardness of water be removed?

Ans: Hardness of water caused by the presence of carbonate and mainly bicarbonate salts of magnesium and calcium is called temporary hardness. It can be removed by boiling water. The hardness caused by the presence of chloride and sulphate salts of magnesium and calcium is called permanent hardness. Apart from this, the presence of iron and aluminium salts also causes permanent hardness. Permanent hardness can be removed by various chemical treatments such as lime-soda process.

2. Why does hard water not form lather with the soap?

Ans: Soaps are sodium and potassium salts of higher fatty acids. On treatment with hard water, the calcium and magnesium ions present in the hard water form insoluble complexes with soap molecules, replacing sodium and potassium. These prevent lather formation with water.

3. How is hardness of water expressed? Name three units of hardness of water.

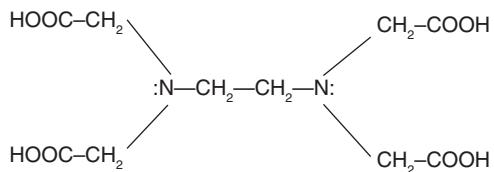
Ans: Hardness of water is expressed in terms of calcium carbonate equivalents. CaCO_3 is highly insoluble in water and is completely precipitated out during water treatment. Also, the calculations with CaCO_3 are easier because its molecular weight is 100.

Units: ppm, gpg(grains per gallon), mg/L.

4. Give the full name and structure of EDTA and explain what form of EDTA is used for its complexation reactions and why.

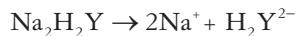
Ans: The name and structure of EDTA is:

Ethylenediamine tetraacetic acid



In abbreviated form EDTA can be written as H_4Y .

Disodium salt of EDTA is used for complexation reactions. This ionizes in aqueous solutions to form strongly chelating ions.



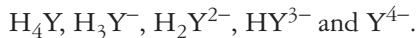
The disodium salt is used because the free acid has limited solubility in water so it cannot be used for preparation of standard solution of EDTA. Also, the disodium salt is obtained in highly pure state as a dihydrate.

5. What is the buffer used in EDTA titrations? What is the need for using a buffer?

Ans: The buffer generally used in EDTA titrations is $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ buffer. It is used to maintain the pH of the titrating mixture in the range of 8 to 10, which is the range in which the indicator is predominantly blue.

6. How does the dissociation of EDTA vary with pH of the solution?

Ans: EDTA can occur as any of the following species depending upon the extent of dissociation.



The nature of species present in the solution is determined by the pH of the solution:

At pH 5 (acidic), EDTA exists as H_2Y^{2-}

At $\text{pH} \geq 8$ (nearly neutral), EDTA exists as HY^{3-}

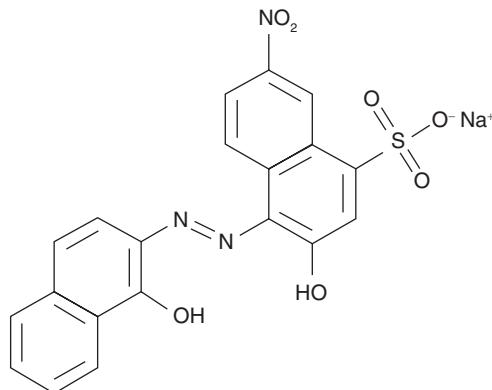
At $\text{pH} > 12$ (basic), EDTA exists as Y^{4-}

7. How can the hardness of water only due to presence of magnesium ions estimated?

Ans: The hardness of water only due to the presence of magnesium ions is estimated by first precipitating the calcium ions as calcium oxalate using a buffer solution comprising of $(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$. The white precipitate formed is filtered and the filtrate is titrated with EDTA using EBT as the indicator.

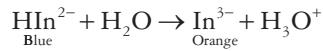
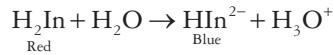
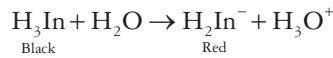
8. Name the indicator used in EDTA complexometric titrations and give its structure.

Ans: The indicator generally used in EDTA complexometric titrations is Eriochrome Black T (EBT). The structure of EBT is



9. Explain why EBT is a pH sensitive indicator.

Ans: EBT can be represented in abbreviated form as H_3In . The red color of the indicator is due to its ionized form. The phenolic groups are ionized at higher pH values as:



Thus the indicator would show different colors at different stages of dissociation which in turn would depend on the pH of the solution. So the indicator is sensitive to pH.

10. Why is the metal EDTA complex more stable than metal EBT complex?

Ans: EDTA molecule has four complexing sites and forms a stable cage like structure on complexation with metal. EBT on the other hand has two ionizable phenolic hydrogens and is hence displaced by EDTA from metal-EBT complex.

Experiment 2

Determination of Chloride Content of Water by Argentometry

Introduction

Chlorides occur widely in water and wastewaters and are usually associated with Na^+ ion. Although chlorides are not harmful, concentration beyond 250 mg/l imparts a peculiar taste to water rendering it unacceptable for drinking purpose.

Aim

To determine the amount of chlorine present in water sample using argentometric method (Mohr's method).

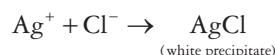
Principle

Chloride ion is determined by titration of the water sample with standard AgNO_3 in a neutral to slightly alkaline condition.

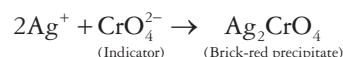
The titrations involving use of silver nitrate solution are called argentometric titrations. The indicators used in these titrations may involve formation of colored precipitate or a soluble colored compound, based on which, the two important argentometric titrations designed are Mohr's method and Volhard's method, respectively. These are described as follows:

- 1. Mohr's method:** This method, for the estimation of chlorides, involves the titration of AgNO_3 against halides in neutral medium using K_2CrO_4 as indicator.

Chloride ions react with silver ions and form a white precipitate.



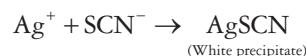
Once all the chloride ions are used up, the silver ions react with the chromate ion from potassium chromate to form a red colored silver chromate precipitate.



Formation of brick-red precipitate of Ag_2CrO_4 marks the end-point. Ag_2CrO_4 is formed only after the complete precipitation of AgCl as the solubility product of AgCl is reached earlier than that of Ag_2CrO_4 .

Neutral medium is very important as Ag_2CrO_4 is soluble in acidic medium and AgNO_3 is precipitated as AgOH in alkaline medium. This method is used for the estimation of chlorides only. It may not be used for estimation of iodides, because the precipitates formed by iodides would mask the color of the indicator.

2. **Volhard's method:** This method, for the estimation of silver, involves the titration of AgNO_3 against ammonium or potassium thiocyanate in the presence of dilute HNO_3 using ferric salt as indicator.



Appearance of a red precipitate of $\text{Fe}(\text{SCN})_3$ indicates the end-point. $\text{Fe}(\text{SCN})_3$ is formed only after the complete precipitation of silver. This method can also be used for the estimation of bromides. However, it cannot be used for the estimation of chlorides as the precipitates formed by chlorides disappear on stirring.

Apparatus and Reagents Required

Apparatus: Burette, pipettes, conical flask, beaker.

Reagents: Standard solution of silver nitrate (0.01 N), standard sodium chloride solution, potassium chromate (K_2CrO_4) as indicator.

Procedure

1. Standard silver nitrate solution is prepared by dissolving 1.698 g of silver nitrate in 1 liter of distilled water. Titrant (0.0141 M) is prepared by dissolving 2.395 g AgNO_3 in H_2O and making up to 1000 mL. Standardize against 0.0141 M NaCl.
2. Standard sodium chloride (0.01 N) is prepared by dissolving 0.584 g of NaCl (dried at 140°C) in distilled water and making up to 1000 mL.
3. A clean burette is washed with distilled water and rinsed with standard silver nitrate solution. It is then filled with the same solution up to the zero level mark.
4. Wash a clean pipette with distilled water and rinse with standard silver chloride solution. Pipette out 25 mL of the standard NaCl solution in a conical flask, add 1 mL of K_2CrO_4 indicator (2 % solution) and titrate against silver nitrate solution in the burette. The end point is indicated by color change from yellow to reddish-brown. Take two concordant readings and let the volume of silver nitrate solution used be V_1 mL.
5. To 25 mL of water sample in a graduated cylinder, add 5 drops of chromate indicator solution and titrate with silver nitrate solution until a reddish-brown color persists in the yellow

solution. Take two concordant readings and let the volume of silver nitrate solution used be V_2 mL.

- Take 25 mL of given water sample in a conical flask, add few drops of chromate indicator and titrate against standard silver nitrate solution. The end point is indicated by color change from yellow to reddish-brown. Take two concordant readings and let the volume of silver nitrate solution used be V_3 mL.

Observations

Titration of Standard Sodium Chloride with AgNO_3 (Standardization of Silver Nitrate Solution)

Burette readings for volume of AgNO_3 used for titration with standard sodium chloride:

S. No.	Volume of Standard Sodium Chloride (mL)	Initial Reading (x mL)	Final Reading (y mL)	Volume of AgNO_3 Used ($V_1 = y - x$ mL)
1	25			
2	25			
3	25			

Concordant reading for volume of AgNO_3 used (V_1) = mL

Titration of Distilled Water Sample with AgNO_3 (Blank Titration)

Burette readings for volume of AgNO_3 used for titration with distilled water sample:

S. No.	Volume of Distilled Water Sample (mL)	Initial Reading (x mL)	Final Reading (y mL)	Volume of AgNO_3 Used ($V_2 = y - x$ mL)
1	25			
2	25			
3	25			

Concordant reading for volume of AgNO_3 used = V_2 mL

Titration of Given Water Sample with AgNO_3 (Calculation of Amount of Chlorine Present in Water Sample)

Burette readings for volume of AgNO_3 used for titration with given water sample:

S. No.	Volume of Given Water Sample (mL)	Initial Reading (x mL)	Final Reading (y mL)	Volume of AgNO_3 Used ($V_3 = y - x$ mL)
1	25			
2	25			
3	25			

Concordant reading for volume of AgNO_3 used = V_3 mL

Calculations

Standardization of AgNO_3 Solution

(Titration of Standard NaCl solution with AgNO_3)

Volume of sodium chloride solution used = 25 mL

Volume of AgNO_3 solution used for titration = V_1 mL

Strength of sodium chloride solution = N_2 (Given)

Strength of AgNO_3 solution used = N_1 (To be determined)

From the law of volumetric analysis, we have

$$N_1 V_1 = N_2 V_2$$

Therefore,

$$N_1 = \frac{25 \times N_2}{V_1}$$

Substituting the given values, the strength of silver nitrate solution can be determined.

Determination of Amount of Chlorides Present

(Titration of Water Sample with Silver Nitrate)

Volume of given water solution used = 25 mL

Volume of silver nitrate used for the blank titration (with 25 mL distilled water) = V_2 mL

Volume of silver nitrate solution used for titration of water sample = V_3 mL

Actual volume of silver nitrate used for titration of chlorides in water sample = $V = V_3 - V_2$ mL

Strength of silver nitrate solution = N_1 . (Calculated in standardization experiment)

Strength of chloride given water sample = N_2 . (To be determined)

From the law of volumetric analysis, we have

$$N_1 V_1 = N_2 V_2$$

Therefore,

$$N_2 = \frac{V \times N_1}{25} = \alpha N \text{ (say)}$$

Determination of Amount of Chloride in Given Water Sample

Amount of oxygen dissolved in 1 liter of water = Strength of oxygen in water solution
 × Equivalent weight of water

Substituting the strength of oxygen solution determined (αN) and the equivalent weight of water as 8 we get

$$\begin{aligned}\text{Amount of chlorides dissolved in 1 liter of water sample} &= \alpha N \times \text{Equivalent weight of chloride ions} \\ &= \alpha N \times 35.5 \text{ g/l}\end{aligned}$$

Therefore,

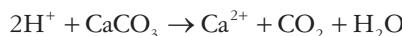
$$\text{Strength of dissolved of chlorides present in given water sample} = \alpha N \times 35.5 \times 1000 \text{ mg/l}$$

Result

The amount of dissolved chloride present in the sample of water is determined as ___ mg/l.

Precautions and Safety Measures

At pH lower than 7 to 8, the chromate indicator gets converted into dichromate and becomes ineffective. To avoid this, the pH of the water sample is checked first by adding a drop of methyl orange indicator. If the color of the solution turns pink, a pinch of calcium carbonate is added so that the color disappears. Excess CaCO_3 being insoluble does not interfere with the estimation of chloride.



1. The apparatus should be washed with distilled water.
2. The same amount of indicator should be used in all the titrations.
3. The reaction mixture should be shaken briskly during the titration and the end point should be noted when the reddish-brown color persists.

Viva Voce Questions

1. What are precipitation titrations?

Ans: These are titrations in which two solutions when brought in contact form precipitates or sparingly soluble salts in those solutions.

2. Why are argentometric titrations so called?

Ans: These are so called because they involve use of silver nitrate solution as the titrant.

3. Name two methods used in argentometric titrations. What is the difference between the two methods?

Ans: The two methods used in argentometric titrations are Mohr's method and Volhard's method. Chloride ions are estimated using Mohr's method in neutral medium with potassium chromate as indicator. Volhard method is generally used for estimation of iodide ions and silver ions are titrated with standard solution of sodium thiocyanate in acidic medium using ferric alum as indicator.

4. Why is the neutral medium required for determination of chlorides by Mohr's method?

Ans: Neutral medium is required in Mohr's method because in alkaline medium silver nitrate is precipitated as AgOH and in acidic medium chromate ion is converted to dichromate ions.

5. What is the indicator used in Mohr's method and what is the color change at the end point?

Ans: Potassium chromate; color of solution changes to reddish-brown.

6. Give the expression for the amount of chlorides present in 100 mL of water sample if the strength of chlorides is x N.

Ans: $35.5 \times x \times \frac{100}{1000}$

Experiment 3

Estimation of an HCl by Conductometric Titrations

Introduction

Conductometric titration is a type of titration in which the electrolytic conductivity of the reaction mixture is continuously monitored as one reactant is added. The equivalence point is the point at which the conductivity undergoes a sudden change. Marked increases or decrease in conductance are associated with the changing concentrations of the two most highly conducting ions—the hydrogen and hydroxyl ions. The method can be used for titrating colored solutions or homogeneous suspension, which cannot be used with normal indicators.

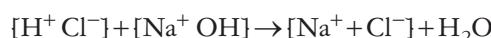
Aim

To determine the composition of a mixture of HCl acid by conductometric titrations.

Principle

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. When a mixture containing HCl is titrated against an alkali, strong acid (HCl) will be neutralized. Now, if we further add NaOH, then the solution starts having an excess of OH⁻ ions, which increases the conductivity.

Let V₁ mL be the volume of alkaline corresponding and it breaks respectively. Then V₁ mL of NaOH equivalent to HCl.



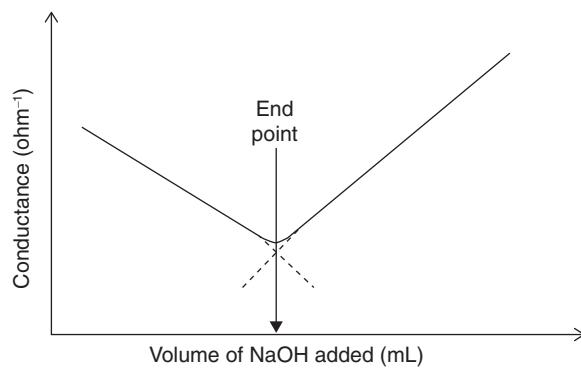
Apparatus and Reagents Required

Apparatus: Conductivity vessel, micro burette, stirrer, small beaker,

Reagents: 0.1 N HCl with 1 N NaOH

Procedure

1. Take the given mixture (25 mL of 0.1 N HCl) in a small beaker and titrate it against 1 N NaOH conductometrically.
2. Add 0.1 mL of NaOH from micro burette and stir well and note down the conductance of the solution.
3. Repeat the determination by stirring well after each adding of 0.1 mL of NaOH until the two points are obtained.
4. Plot a graph volume of NaOH vs. conductance.

**Calculations**

Preparation of 0.1 N HCl solution

$$N_1 V_1 = N_2 V_2$$

Preparation of 1 N NaOH solution for 100 mL

$$N = \text{Wt. / Mol.wt} \times 1000 / V \text{ (in mL)}$$

Volume of NaOH	Conductance of HCl
----------------	--------------------

Result

The normality of HCl is found to be _____

Precautions and Safety Measures

1. There should be provision for leaving reactions running safely overtime.
2. Separate waste bottles should be available for chlorinated and non-chlorinated solvents.
3. After switching on the instrument (Conductometer), it should be allowed to stabilize prior starting the experiment.
4. The platinum electrodes of the conductance cell must be completely immersed in the solution during the measurement of conductance.
5. The conductance cell must always be dipped either in solution or in distilled water.
6. There should be no air bubble between the two electrodes.
7. The titrant must be at least ten times more concentrate than the analyte.

Viva Voce Questions

1. What are conductometric titrations?

Ans: Conductometric titration is a type of titration in which the electrolytic conductivity of the reaction mixture is continuously monitored as one reactant is added.

2. What is quantitative analysis and qualitative analysis?

Ans: Qualitative Analysis refers to analyses in which substances are identified or classified on the basis of their chemical or physical properties, such as chemical reactivity, solubility, molecular weight, melting point, radiative properties (emission, absorption), mass spectra, nuclear half-life, etc.

Quantitative Analysis refers to analyses in which the amount or concentration of an analytes may be determined (estimated) and expressed as a numerical value in appropriate units. Qualitative Analysis may take place with quantitative analysis, but quantitative analysis requires the identification (qualification) of the analyte for which numerical estimates are given.

3. What is conductometry?

Ans: Conductometry is a measurement of electrolytic conductivity to monitor a progress of chemical reaction. Conductometry has notable application in analytical chemistry, where Conductometric titration is a standard technique. In usual analytical chemistry practice, the term conductometry is used as a synonym of conductometric titration, while the term conductometry is used to describe non-titrative applications. Conductometry is often applied to determine the total conductance of a solution or to analyze the end point of titrations that include ions.

Experiment 4

Estimation of Acetic Acid by Conductometric Titrations

Introduction

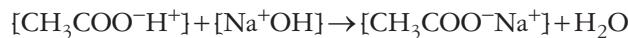
Conductometric titration is a type of titration in which the electrolytic conductivity of the reaction mixture is continuously monitored as one reactant is added. The equivalence point is the point at which the conductivity undergoes a sudden change. Marked increases or decrease in conductance are associated with the changing concentrations of the two most highly conducting ions—the hydrogen and hydroxyl ions. The method can be used for titrating colored solutions or homogeneous suspension, which cannot be used with normal indicators.

Aim

To determine the composition of a mixture of acetic acid CH_3COOH by conductometric titrations.

Principle

Let us consider the titration of acetic acid with strong base (NaOH). The conductance of the acid will be low on account of its poor dissociation. When a small amount of NaOH is added to CH_3COOH , the conductivity decreases initially then increases with the further addition of NaOH .



When the neutralization of acid is completed, further addition of alkali produces excess of OH^- ions. The conductance of solution, therefore, begins increasing more rapidly.

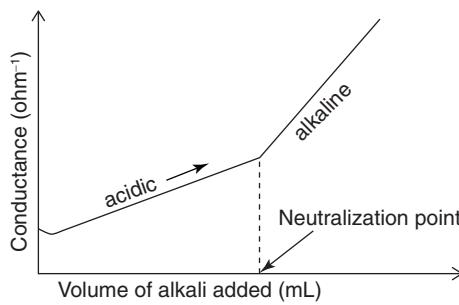
Apparatus and Reagents Required

Apparatus: Conductivity vessel, micro burette, stirrer, small beaker,

Reagents: 0.1 N CH_3COOH with 1 N NaOH

Procedure

- Take the given mixture (25 mL of 0.001 N CH_3COOH) in a small beaker and titrate it against 1 N NaOH conductometrically.
- Add 0.1 mL of NaOH from micro burette and stir well and note down the conductance of the solution.
- Repeat the determination by stirring well after each adding of 0.1 mL of NaOH until the two points are obtained.
- Plot conductance versus volume of NaOH on a graph sheet and calculate the volume of NaOH used for the neutralization of HCl and acetic acid respectively.



Result

The normality of CH_3COOH is found to be _____

Calculations

Preparation of 0.1 N CH_3COOH solution

$$N_1 V_1 = N_2 V_2$$

Preparation of 1 N NaOH solution for 100 mL

$$N = \text{Wt.}/\text{Mol.wt} \times 1000/V \text{ (in mL)}$$

Volume of NaOH Added (cm^3)	Conductance (mS)

Precautions and Safety Measures

1. After switching on the instrument (conductometer), it should be allowed to stabilize prior starting the experiment.
2. The platinum electrodes of the conductance cell must be completely immersed in the solution during the measurement of conductance.
3. The conductance cell must always be dipped either in solution or in distilled water.
4. There should be no air bubble between the two electrodes.
5. The titrant must be at least ten times more concentrate than the analyte.

Viva Voce Questions

1. Define Conductometric titration?

Ans: Conductometric titration is a type of titration in which the electrolytic conductivity of the reaction mixture is continuously monitored as one reactant is added. The equivalence point is the point at which the conductivity undergoes a sudden change.

2. What is the use of Conductometer?

Ans: An electrical conductivity meter (EC meter) measures the electrical conductivity in a solution. It is commonly used in hydroponics, aquaculture and freshwater systems to monitor the amount of nutrients, salts or impurities in the water.

3. How does the nature of electrode determine the products formed on electrolysis?

Ans: The products formed on electrolysis also depend on the electrode being inert or reactive. If the electrodes are made of inert materials such as platinum, they function only as a source or sink of electrons. However reactive electrodes, such as pure copper cathode used in electrochemical reduction of copper, participate in the reactions and affects the product of electrolysis.

4. What is normality and molarity?

Ans: Normality is defined as the number of gram equivalents of a solute dissolved per litre of the solution. Molarity is defined as the number of moles of solute per liter of solution.

Experiment 5

Potentiometric Titration of Strong Acid vs. Strong Base

Introduction

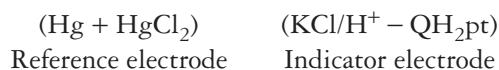
A titration in which the end or equivalence point is estimated with the help of measurement of the potentials of the reaction mixture is called potentiometric titration. Potentiometric titrations are among the most accurate known because potential follows the actual change in activity and therefore, the end point will often coincide directly with the equivalence point. Potentiometric indication is more sensitive and accurate than visual indication.

Aim

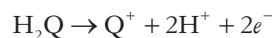
To determine the neutralization point of strong acid by titrating against strong base potentiometrically.

Principle

In potentiometric acid base titration the following cell is set up in acid solution.



Here quinhydrone is used as indicator electrode whose potential indicates the change in concentration of ions titrated. Cell reaction of quinhydrone electrode is



and its potential is given by

$$E_{\text{Quin}} = (E_{\text{Quin}} - 0.0596 \text{ pH})$$

Apparatus and Reagents Required

Apparatus: Beakers, Potentiometer, battery, standard cell, calomel electrode, platinum electrode, quinhydrone, beaker, stirrer, burette.

Reagents: 0.1N NaOH, 0.1 N HCl

Procedure

1. Take 20 mL of the acid solution in a beaker. Add a pinch of quinhydrone to saturate the solution. Dip the indicator (P^+) and reference (SCE) electrodes in the solution. Connect the two electrode leads to potentiometer and measure EMF.
2. Add the alkali solution in 1ml of lots. Shake well after each addition and measure the cell EMF at each stage. From this rough titration; find out the approximate volume needed for the end point.
3. Repeat the titration by adding 1 or 2 ml of alkali in initial steps but by adding one or two drops of alkali at a time in the ml step continue the addition take 3, 4 readings after the equivalence point. Record the volume of alkali added and EMF of the solution.
4. Plot a graph between cell EMF (y -axis) and volume of alkali used (x -axis) from this graph read the end volume of the titrate.

Observations

S. No.	Volume of alkali added (cm^3)	EMF (E) of the cell (Volts)
1.		
2.		
3.		

Calculations

From the graph, the volume of acid HCl used corresponding to the equivalence point = _____ cm^3
At the equivalence point, applying the equation

$$N_{HCl} V_{HCl} = N_{NaOH} V_{NaOH}$$

where $N_{NaOH} = 0.1$, $V_{NaOH} = x$, $V_{HCl} = 20$

$$N_{HCl} = \frac{0.1 \times x}{20} \text{ mol dm}^{-3}$$

Result

$$\text{Strength of HCl} = \text{Normality} \times \text{Equivalent weight}$$

Precautions and Safety Measures

1. Making sure the electrodes are correctly in place and functioning properly, getting the burette above the beaker and out of the way of the electrodes, making sure the stirrer bar isn't going to smash the end of the electrode.
2. Slower to get the endpoint volume – you just don't read the volume off the burette at the end (in most cases), you have to process the data in some way.

Viva Voce Questions

1. Define Potentiometric titration?

Ans: Potentiometric titration is a technique similar to direct titration of a redox reaction. It is a useful means of characterizing an acid. No indicator is used; instead the potential is measured across the analyte typically an electrolyte solution. To do this, two electrodes are used, an indicator electrode (the glass electrode and metal ion indicator electrode) and a reference electrode. Reference electrodes generally used are hydrogen electrodes, calomel electrodes, and silver chloride electrodes. The indicator electrode forms an electrochemical half-cell with the interested ions in the test solution. The reference electrode forms the other half cell.

2. What is the purpose of a potentiometric titration?

Ans: Potentiometric titration is a technique similar to direct titration of a redox reaction. It is a useful means of characterizing an acid. No indicator is used; instead the potential is measured across the analyte, typically an electrolyte solution.

3. Which electrode is used in potentiometric titration?

Ans: Reference electrodes are used in potentiometric titrations. Calomel and silver/silver-chloride electrodes are commonly used in potentiometric titration. In the case of possible interferences of chlorides (as in determination of halides), a mercurous sulphate electrode may be used.

4. What is the principle of operation of a potentiometer?

Ans: The principle of the potentiometer is that, for a wire having uniform area of cross section and uniform composition, the potential drop is directly proportional to the length of wire. The above principle is valid when potentiometer is used in comparing the EMF of two cells.

Experiment 6

Estimation of Iron Content of the Given Solution by Using Potentiometer

Introduction

Potentiometric titration is a volumetric method in which the potential between two electrodes is measured by addition of reagent volume. Various electrodes used in Potentiometric titrations are glass electrode, ion-selective electrodes, platinum redox electrode (used in redox Potentiometric titrations), reference electrodes (calomel and silver/ silver chloride), etc. The types of Potentiometric titrations for the determination of analytes include acid-base, redox, precipitation and complexometric titrations. Potentiometric titrations are preferred over manual titrations as they are more precise and accurate. A simple arrangement for Potentiometric titration is shown in Figure 1.

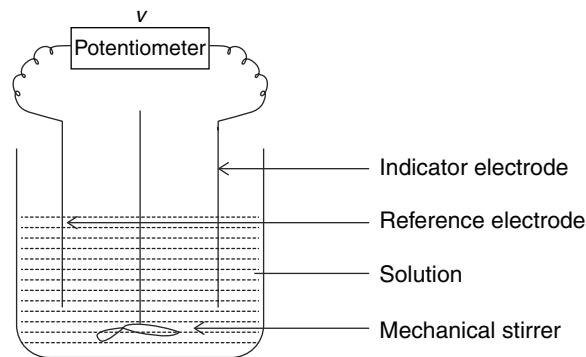


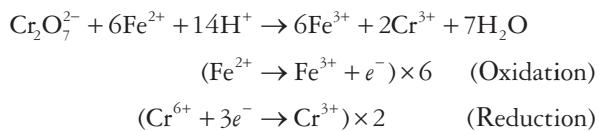
Figure 1 Potentiometric titration.

Aim

To determine the iron concentration of a given solution by titrating with potassium dichromate potentiometrically.

Principle

Gain of electrons is called reduction and loss of electrons is called oxidation. A system where oxidation and reduction occur simultaneously is called a redox system. During the oxidation of a reducing agent or reduction of an oxidizing agent, the potential changes more rapidly in the vicinity of end point of reaction. The titration of iron (II) with potassium dichromate ($K_2Cr_2O_7$) or potassium permanganate ($KMnO_4$) involves redox reactions. The equivalent point can be obtained potentiometrically due to sudden change of potential. The following reactions take place:



In this titration, small amount of $K_2Cr_2O_7$ solution converts Fe^{2+} (ferrous ions) to Fe^{3+} (ferric ions) ions and E^0 (electromotive force, emf) will rise slowly. At the end point when all Fe^{2+} ions converted to Fe^{3+} then Cr^{3+} will start converting to $Cr_2O_7^{2-}$. So there will be a sharp change in electrode potential.

Apparatus and Reagents Required

Apparatus: Potentiometer, standard cell, platinum electrode, glass electrode, beaker, burette and pipette.

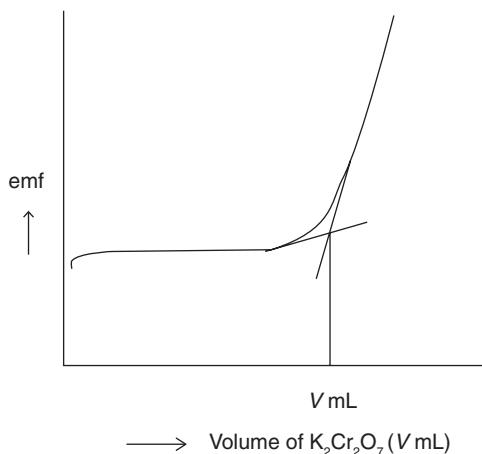
Reagents: Potassium dichromate solution, sulphuric acid, Mohr's salt (ammonium iron sulphate) solution.

Procedure

1. 0.02 M potassium dichromate solution is prepared.
2. 25 mL of ammonium iron sulphate solution (unknown concentration) is taken in a beaker and 25 mL of H_2SO_4 (2 N) is added to it.
3. Two electrodes (platinum and glass) are inserted into the beaker and connected to potentiometer instrument (already standardized).
4. 0.1 mL of potassium dichromate solution is added from burette. The solution in beaker is stirred well and allowed to stand for one minute.
5. The emf is noted from instrument.
6. Titration is continued till sudden rise in potential occurs.
7. The graph is plotted between emf vs volume of dichromate solution.

Observation

S. No.	Volume of $K_2Cr_2O_7$ (mL)	Potential emf (Volts)

Calculations

Volume of $K_2Cr_2O_7$ at equivalence point = V mL

$$N_1 V_1 = N_2 V_2$$

(Mohr salt) ($K_2Cr_2O_7$)

$$N_1 \times 25 = 0.02 \times V_2$$

$$N_1 = \frac{0.02}{25} \times V_2$$

Strength of ferrous ions in solution = $N_1 \times 56 \text{ g/L}$

Precautions and Safety Measures

1. Accurate electrodes should be used.
2. Apparatus should be cleaned properly.
3. After each addition of $K_2Cr_2O_7$ solution, the mixture should be mixed properly.
4. Keep the electrode bulb dipped in solution.

Viva Voice Questions**1. What are potentiometric titrations?**

Ans: The titrations in which the change in the electrode potential depends upon the addition of the titrant is called potentiometric titrations.

2. What are end point titrations?

Ans: End point titrations are volumetric titrations where an indicator is used to get end point, which is usually the inflection point where a change in pH is great such as going from acid to base.

3. What are the advantages of potentiometric titration?

Ans: Potentiometric titrations are generally inexpensive and reliable. These can be used for coloured solutions also.

4. What is oxidation?

Ans: Loss of electron (one or more) from an atom or ion is called oxidation. For example, $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$, $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$

5. What is reduction?

Ans: Gain of electron (one or more) by the atom or ion is called reduction.

6. What is redox reaction?

Ans: Reaction where oxidation and reduction undergoes simultaneously is called redox reaction.

Experiment 7

Determination of Rate Constant of Acid Catalyzed Hydrolysis of Methyl Acetate

Introduction

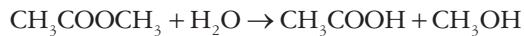
The hydrolysis reaction of an ester in pure water is a slow reaction and when a mineral acid like hydrochloric acid is added, the rate of the reaction is enhanced since the H^+ ions from the mineral acid acts as the catalyst. The acid catalysed hydrolysis of an ester follows pseudo first order kinetics. A reaction whose order is different from the actual due to large excess concentration of one of the reactants is called pseudo-order reaction.

Aim

To determine the rate constant for the acid-catalyzed hydrolysis of methyl acetate.

Principle

Methyl acetate undergoes hydrolysis, in the presence of an acid (HCl, for example), to give acetic acid and methyl alcohol.



In the presence of an acid, this reaction should be of second order, since two molecules are reacting. But, it is found to be first order. This may be explained in the following way:

The rate of the reaction is given by

$$\frac{dx}{dt} = k'[\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}]$$

where k' is the rate constant (or specific rate constant). Since water is present in large excess, its active mass (molar concentration) virtually remains constant during the course of the reaction. Therefore, its active mass gets included in the constant, and the above equation reduces to:

$$\frac{dx}{dt} = k_1[\text{CH}_3\text{COOCH}_3]$$

Thus, the rate of the reaction is determined by one concentration term only (that is, by a single power of the concentration term only). Hence, the reaction is first order. Such reactions are also referred to as pseudo first order reactions. The progress of the reaction (hydrolysis of ester) is followed by removing a definite volume of the reaction mixture, at definite intervals of time, cooling it in ice, and titrating the acetic acid formed against alkali, which has already been standardized.

The amount of alkali used is equivalent to the total amount of hydrochloric acid present originally and the amount of acetic acid formed in the reaction.

The amount of acetic acid formed (x), at definite intervals of time (t), can be obtained. The amount of acetic acid formed, at the end of the reaction, is equivalent to the initial concentration (α) of the ester.

Suppose the volumes of the sodium hydroxide solution (titrated value) required for neutralization of 5 mL of the reaction mixture are:

1. At the commencement of the reaction is V_0
2. After time (t) is V_t
3. At the end of the reaction is V_∞

Then, x (amount of acetic acid formed after time) is proportional to $(V_t - V_0)$.

α (initial concentration of ester) is proportional to $(V_\infty - V_0)$.

$[\alpha - x]$ (Concentration of ester present after time t) is proportional to

$$(V_\infty - V_0) - (V_t - V_0) = (V_\infty - V_t)$$

The first order rate expression given by $k = \frac{2.303}{t} \log \frac{\alpha}{\alpha - x}$ would correspond to

$$k = \frac{2.303}{t} \log \frac{(V_\infty - V_0)}{(V_\infty - V_t)}$$

Hence, the rate constant (k_1) could be calculated.

Apparatus and Reagents

Apparatus: Thermostat, reagent bottles, conical flask, burette, pipette (10 mL, 5 mL, 2 mL).

Reagents: Methyl acetate, HCl, NaOH, 0.1 N standard oxalic acid, phenolphthalein.

Procedure

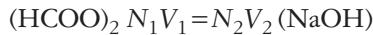
Step I: Standardization of NaOH using standard oxalic acid (0.1 N)

1. 10 mL of given 0.1 N standard oxalic acid is pipetted out into a 100 mL conical flask.
2. This solution is titrated against the given unknown concentration of NaOH using phenolphthalein indicator until the end point is colorless to pale pink.

3. Tabulate the values and repeat the titration for concurrent readings and determine the unknown concentration of supplied NaOH solution.

Table 1

S. No.	Volume of Oxalic Acid Taken (mL)	Burette Readings (mL)		Volume of NaOH Consumed (mL)
		Initial	Final	



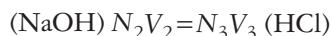
Concentration of NaOH, $N_2 = \underline{\hspace{2cm}}$

Step II: Standardization of HCl using NaOH solution.

1. 2 mL of given HCl is pipetted out into a 100 mL conical flask.
2. This solution is titrated against the NaOH using phenolphthalein indicator until the end point is colorless to pale pink.
3. Tabulate the values and repeat the titration for concurrent readings and determine the unknown concentration of supplied HCl solution.

Table 2

S. No.	Volume of HCl Taken (mL)	Burette Readings (mL)		Volume of NaOH Consumed (mL)
		Initial	Final	



Concentration of HCl, $N_3 = \underline{\hspace{2cm}}$.

Step III: Determination of rate constant (R_1) for the acid-catalyzed hydrolysis of methyl acetate.

1. 100 mL of given HCl (whose strength is determined in step II) solution is taken in a stoppered reagent bottle.

2. 5 mL of methyl acetate solution is added to the HCl solution. Note the time when half of the methyl acetate solution is added. The mixture is shaken well.
3. Pipette out 5 mL of the reaction mixture and discharge it into 50 mL of ice cold water kept in a conical flask.
4. Titrate the reaction mixture against NaOH solution using phenolphthalein as indicator. This titre value corresponds to V_0 .
5. Steps 3 and 4 are repeated at intervals of 5, 10, 15, 20, 30, 45, 60 minutes. Each titre value corresponds to V_t .
6. The remaining solution is taken in a stoppered conical flask and heated to 60°C, and kept at this temperature for 5 minutes.
7. The solution is allowed to cool to room temperature.
8. Repeat Steps 3 and 4. This titre value corresponds to V_∞ till concurrent values are obtained.
9. Plot a graph of $\log(V_\infty - V_t)$ versus time (t) and determine the slope.
10. Report the theoretical and graphical value of rate constant (k_1).

Table 3

S. No.	Time (min)	Volume of Solution Taken (mL)		Burette Readings (mL)	Volume of NaOH Consumed (mL)	$(V_\infty - V_t)$ (mL)	\log (mL)	$k_1 = \frac{2.303}{t} \log \frac{(V_\infty - V_0)}{(V_\infty - V_t)}$
		Time	Taken	Readings	Consumed	$(V_\infty - V_t)$	\log	k_1
1.	0(V_0)							
2.	5(V_{t1})							
3.	10(V_{t2})							
4.	15(V_{t3})							
5.	20(V_{t4})							
6.	30(V_{t5})							
7.	45(V_{t6})							
8.	60(V_{t7})							
9.	V_∞							

Observations and Calculations

Room Temperature= °C

 V_∞ = mL V_0 = mL $(V_\infty - V_0)$ = mL $\log (V_\infty - V_0)$ =Mean value of rate constant (k_1)= _____

Results

1. Strength of NaOH solution = _____
2. Strength of HCl solution = _____
3. Rate constant (k_1) for the acid-catalyzed hydrolysis of methyl acetate ($\text{CH}_3\text{COOCH}_3$) at _____. $^{\circ}\text{C}$ = _____ (theoretical) = _____ (graphical).

Precautions and Safety Measures

1. Safety goggles, aprons, and gloves must be worn at all times in the laboratory.
2. If you spill a solution on your skin, be sure to flush the area promptly with lots of water.
3. Take special care with acidic solutions, which is an extremely corrosive and dangerous substance.
4. If you get any on your skin or clothing, rinse it with water immediately.

Viva Voce Questions

1. What is acid hydrolysis?

Ans: In organic chemistry, acid hydrolysis is a process in which a protic acid is used to catalyze the cleavage of a chemical bond via a nucleophilic substitution reaction, with the addition of the elements of water (H_2O).

2. Define rate constant?

Ans: Chemical kinetics deals with the study of chemical reactions based on the reaction rates, effects of various variables, the atomic rearrangements and the intermediate formation. In chemical kinetics, rate law gives the mathematical representation of the rate of a reaction. The rate constant is the proportionality factor in the rate law.

3. What are the factors affecting reaction rate?

Ans: Factors that influence the reaction rates of chemical reactions include the concentration of reactants, temperature, the physical state of reactants and their dispersion, the solvent, and the presence of a catalyst.

4. What is the effect of concentration on reaction rate?

Ans: If the concentration of a dissolved reactant is increased, or the pressure of a reacting gas is increased: the reactant particles become more crowded. there is a greater chance of the particles colliding. The rate of reaction increases.

Experiment 8

Preparation of Aspirin and Paracetamol

PART A: PREPARATION OF ASPIRIN

Introduction

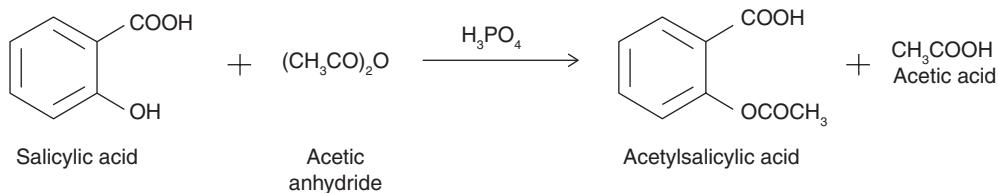
Aspirin is the common name of the compound acetylsalicylic acid. It is widely used as medicine for fever (antipyretic) and as a pain killer (analgesic). It is also used as an anti inflammatory agent and also checks blood clotting.

Aim

To prepare a pure sample of aspirin and to determine its melting point.

Principle

Aspirin is prepared by reaction of salicylic acid with an excess of acetic anhydride in the presence of small amount of a strong acid is used as a catalyst which accelerates reaction. The catalyst used in this experiment is phosphoric acid or concentrated sulphuric acid. The reaction for aspirin synthesis is shown below:



Acetic acid is water-soluble so easily separated by quenching with water.

Apparatus and Reagents Required

Apparatus: Conical flask, burner, wire gauze, beaker, Buchner funnel and glass rod.

Reagents: Salicylic acid, acetic anhydride and phosphoric acid.

Procedure

1. 5 g of salicylic acid is taken in a 250 mL conical flask.
2. 10 mL of acetic anhydride is added to it.
3. 3 drops of phosphoric acid is added and the reaction mixture is shaken well.
4. The flask is heated on water bath at a temperature of 60–70°C for 15 min.
5. The solution is allowed to cool to room temperature and 100 mL of cold water is poured in it.
6. The solution is stirred till white solid appears.
7. The solid is separated through Buchner funnel and dried in folds of filter paper.
8. Recrystallization of solid is done by dissolving solid in 20 mL of glacial acetic acid followed by heating.
9. Hot solution is filtered and filtrate is cooled to obtain crystals.
10. These crystals are then dried and weighed.
11. The melting point is checked to know the purity of aspirin obtained. (The melting point of pure aspirin is 138–140°C.)

Result

Weight of aspirin = _____ mg.

Melting point of aspirin = _____ °C.

Precautions and Safety Measures

1. Salicylic acid should be dissolved completely in acetic anhydride.
2. Acetic anhydride should be taken in excess so that it act as an acetylating agent as well as solvent.
3. The reaction mixture should be poured in water only after it has been cooled otherwise, hydrolysis of aspirin may take place.

PART B: SYNTHESIS OF PARACETAMOL

Introduction

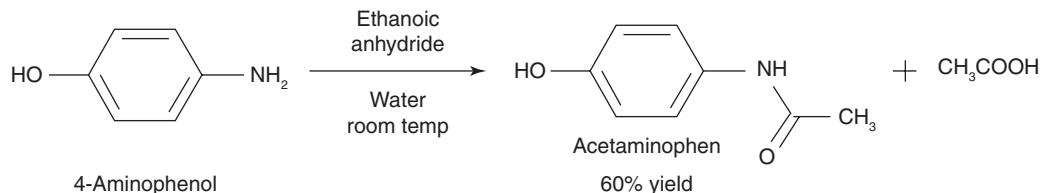
Paracetamol is also known as acetaminophen or APAP. Paracetamol is used to reduce fever and it relieves pain as well that is why it is used both as antipyretic and analgesic.

Aim

To prepare a pure sample of paracetamol and to determine its melting point.

Principle

Paracetamol can be prepared by the reaction of 4-aminophenol with ethanoic anhydride. The reaction for paracetamol synthesis is shown below:



Apparatus and Reagents

Apparatus: Buchner funnel, Conical flask, burner, wire gauze, beaker, magnetic stirrer.

Reagents: 4-Aminophenol, ethanoic anhydride, distilled water.

Procedure

- Place 2 g of the 4-aminophenol into a 50 ml conical flask, add 15 ml of water and stir the suspension vigorously (magnetic stirrer) for a few minutes.
- Add 2.2 mL of ethanoic anhydride (acetic anhydride) and continue stirring until the suspension dissolves and a precipitate (paracetamol) eventually forms.
- After 10 minutes, filter the precipitate (using a Buchner funnel), washing with small amounts of cold, distilled water.
- After drying, the crude product should be placed in a clean 100 ml conical flask and recrystallised by heating until it just dissolves in approximately 20 ml of water.
- Cool the flask in ice until crystals of the purified paracetamol appear.
- Filter the crystals under vacuum, dry in a warm oven and then record the melting point and compare with standard paracetamol tablets (~170°C).
- Repeat recrystallization process to achieve a more pure product.

Result

Weight of paracetamol = _____ mg.
Melting point of paracetamol = _____ °C.

Precautions and Safety Measures

1. Wear safety glasses or goggles at all times in the laboratory. Ethanoic anhydride is corrosive and its vapor is irritating to the respiratory system.
2. Avoid skin contact and inhalation of the vapors. In the event of skin contact, rinse well with cold water.
3. If the vapors are inhaled, move to an area where fresh air is available.

Viva Voce Questions

1. What is an acetylation reaction? Name two acetylating agents.

Ans: The process of replacement of –H atom of –OH or –NH₂ group by acyl group (–COCH₃) is called acetylation reaction. The commonly used acetylating agents are acetic anhydride (CH₃COOCH₃) and acetyl chloride (CH₃COCl).

2. What are antipyretic and anti-inflammatory drugs?

Ans: An antipyretic drug brings down the body temperature in case of high fever while an anti-inflammatory drug reduces swelling.

3. What are the important uses of aspirin?

Ans: Aspirin is used as an antipyretic, analgesic and anti-inflammatory drug.

4. What types of by-product are formed in paracetamol synthesis?

Ans: This reaction forms an amide bond and ethanoic acid as a by-product. When the reaction is complete the paracetamol is formed isolated and purified.

5. What is the pH of paracetamol?

Ans: Acetaminophen is an odorless, slightly bitter taste white crystalline powder. Its pH range is 5.5–6.5 based on saturated aqueous solution.

6. Is paracetamol a non steroidal?

Ans: Paracetamol (acetaminophen) is generally not considered an NSAID because it has only little anti-inflammatory activity.

7. What are the side effects of paracetamol?

Ans: Diarrhea, increased sweating, loss of appetite, nausea or vomiting, stomach cramps or pain, swelling, pain, or tenderness in the upper abdomen or stomach area.

Experiment 9

Thin Layer Chromatography- Calculation of R_f Values (*ortho*- and *para*-nitrophenols)

Introduction

Thin layer chromatography (TLC) is a planar form of chromatography useful for wide-scale qualitative analysis screening, reaction monitoring and can also be used for quantitative analysis.

Aim

Analysis of the given sample using thin layer chromatography and calculation of R_f values for different organic compounds present in the sample (e.g., *ortho*- and *para*-nitrophenols).

Principle

Thin layer chromatography is mainly an adsorption chromatography technique. The compound spotted on thin layer of silica gel coated on a glass plate gets adsorbed onto thin layers (stationary phase) and gets partitioned between thin layers and mobile phase, when the mobile phase percolates through the thin layer. The percolation of mobile phase is by means of capillary forces. As adsorption and partition go on simultaneously, the compound will move along the mobile phase. When more than one component/analyte is present, movement of components is according to their differential migration rates. The component, which has greater affinity towards the stationary phase, will move later than one which has relatively less affinity towards the stationary phase.

Apparatus and Reagents Required

Apparatus: Flat glass plates, Aluminum foil, UV Lamp, TLC jars with lid.

Reagents: Concentrated mixture of *ortho*- and *para*-nitro phenol and solvent.

Procedure

1. The concentrated mixture of *ortho*- and *para*-nitro is dissolved in chloroform and phenol applied on the TLC plate * with the tip of a thin capillary tube, about 2 cm above the end of the plate.
2. The plate is dipped in a covered glass jar containing the solvent (mobile phase). The solvent is allowed to travel up the plate with the sample spotted on the adsorbent just above the solvent. When the solvent front nears the top of the plate, it is removed from the jar and the position of solvent is marked on the plate. If the spot remains at the loading point or if the mobility is not satisfactory, separation of the components will not be adequate. In such case increase the polarity of solvent or solvent mixture in the following order: petroleum ether < benzene < chloroform < ethyl acetate < acetone < methyl alcohol < acetic acid < water.
3. Various common organic solvents can be used as mobile phase. The best solvent or solvent system (mixture of two different solvents) for effective separation of the two different components (organic compounds) in the given sample can be identified by hit and trial method.
4. The separation of mixture into different spots occurs. Different components of the mixture travel up to different distances with the eluent depending upon the extent of adsorption on the adsorbent as shown in the below figure 1.

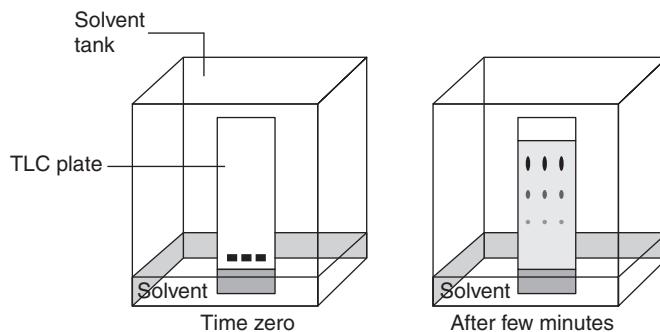


Figure 1 Different components travelling different distances.

5. The colored spots are visible on the TLC plate as such, while colorless spots are developed by placing the plate in iodine-vapor chamber. Iodine forms complex with most of the organic compounds that appear as brown spots. The sample spots can also be detected with handheld UV lamps. The TLC plates are prepared with UV-activated fluorescent indicator mixed in the silica. The components present in the given mixture quench the fluorescence induced by the

* Preparation of TLC plate: Ready to use pre-coated TLC plates or foils can be purchased. However they can be prepared by using silica gel-G, chloroform and methanol. The two solvents chloroform and methanol shall be mixed in 2: 1 ratio, that is, 66 mL : 33 mL and should be added to silica gel G (35 g) taken in glass jar while stirring with glass rod to avoid lumps. Two clean and dry TLC plates should be held together and dipped into the slurry carefully. The TLC plates should be removed from the slurry immediately wiping the excess slurry. A uniform layer of silica gel-G gets deposited on the TLC plates. Allow the TLC plates to dry to evaporate the solvent by keeping the coated slides aside for few minutes.

UV lamp and appear as dark spots. The presence of some compounds on the TLC plates is also indicated by spraying with suitable reagents.

Observation and Calculation

The TLC properties of compounds are reported in terms of retardation factor or as R_f values. The R_f value is the distance traveled by the substance divided by the distance traveled by the solvent front (Figure 2).

$$R_f = \frac{\text{Distance moved by the substance from base line (}x\text{)}}{\text{Distance moved by the solvent from base line (}y\text{)}}$$

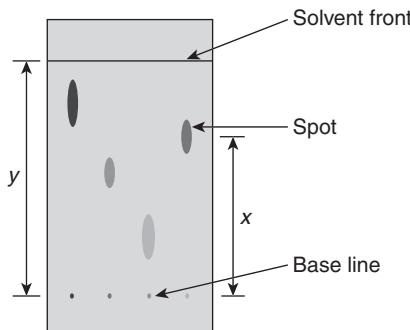


Figure 2 R_f value calculated from x and y components.

Result

R_f value for *ortho*-phenol = _____

R_f value for *para*-phenol = _____

Precautions and Safety Measures

1. The solvents used in the chromatography are highly inflammable, toxic by ingestion and inhalation.
2. This experiment should be performed only in an operating chemical fume hood or well-ventilated area, avoiding open-fire.
3. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron.

Viva Voce Questions

1. What is the basic principle chromatography?

Ans: Chromatography is based on the difference in the rate at which the component of the mixture moves through a stationary phase under the influence of moving phase.

2. What are the advantages of thin layer chromatography?

Ans: (a) A wide range of compounds can be detected using different indicators and reactive agents such as iodine vapor, sulphuric acid, etc.

(b) When non-destructive indicators like fluorescent/UV lamps are used, the separated components can be scrapped off the plate and studied by other analytical techniques.

(c) The plates used are cheap, reusable and easily disposable.

(d) Separation of larger amounts of samples can be carried out by using preparative TLC plates.

3. What is a R_f value in TLC?

Ans: The R_f value is the distance traveled by the substance divided by the distance traveled by the solvent front. It is the characteristic for a given stationary phase and solvent combination.

Experiment 10

Determination of Acid Value of Oil

Introduction

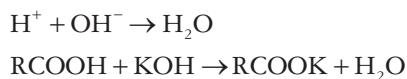
Fatty oils consist mostly of glycerol or other esters of higher fatty acids. In some cases, notable amounts of free acids are also present. The amount of free acid present depends on the source from which oil is taken. The acid content increases with time due to hydrolysis with moisture and is rough indicator of age of oil. The acid value of lubricating oil is defined as the number of milligrams of KOH required to neutralize the free acids present in 1 g of the oil sample. It gives an idea about the amount of free acids present in oil. A high acid value indicates the extent of rancidity in a stored oil sample. A low acid value is an indicator of freshness of oil sample.

Aim

To determine the acid value of the given oil.

Principle

Acid value is determined by dissolving a known weight of the oil sample in a suitable solvent and titrating with a standard alcoholic KOH solution using phenolphthalein as indicator until the appearance of pink color which is the end point.



Apparatus and Reagents Required

Apparatus: Burette, pipette, measuring cylinder, conical flask and stoppered glass bottle.

Reagents: N/10 KOH solution, standard oxalic acid solution (N/10), butanone (ethyl methyl ketone) as a solvent, phenolphthalein as an indicator and oil sample.

End Point: Appearance of permanent light pink color (KOH solution in the burette).

Procedure

Preparation of N/10 KOH solution

1. Slightly concentrated N/10 solution of KOH is titrated against standard oxalic acid (N/10) solution.
2. 20 mL of N/10 oxalic acid solution is taken in the titration flask and 2–3 drops of phenolphthalein indicator is added.
3. The burette is filled with approx. N/10 KOH solution.
4. The solution in flask is titrated with burette solution till the pink color appears which is the end point.
5. Titration is repeated to get concordant readings.

Determination of acid value

1. 6 mL of oil sample is weighed in a weighing bottle.
2. Oil is transferred in the titration flask and the empty weighing bottle is weighed again. The difference in the two weights gives the weight of the oil sample.
3. 50 mL of ethylmethyl ketone is added as a solvent with the help of measuring cylinder.
4. It is shaken vigorously to dissolve the oil.
5. 5 drops of phenolphthalein indicator is added and solution is titrated with standard alcoholic KOH slowly with constant shaking till the end point is reached, that is, light pink color appears.
6. The volume of KOH used is noted.
7. The same titration is repeated with the solvent alone and the volume of KOH used is recorded.

Observations

Volume of N/10 oxalic acid solution taken = 20 mL

<i>S. No.</i>	<i>Initial Reading (x mL)</i>	<i>Final Reading (y mL)</i>	<i>Volume of KOH used (V₁=x-y mL)</i>
1			
2			
3			

Volume of KOH solution used = V₁ mL

Weight of oil sample + weighing bottle = w₁ g

Weight of weighing bottle alone = w₂ g

Weight of oil sample = w₁ - w₂ = w g

Volume of N/10 KOH used in the sample titration = x mL

Volume of N/10 KOH used in the blank titration = y mL

Volume of N/10 KOH used against the acid present in w g of oil = (x - y) mL

Calculations

Standardization of N/10 alcoholic KOH solution

$$\frac{N_1 V_1}{(\text{KOH})} = \frac{N_2 V_2}{(\text{Oxalic acid})}$$

$$N_1 \times V_1 = \frac{1}{10} \times 20$$

$$N_1 = \frac{1}{10} \times \frac{20}{V_1}$$

Determination of acid value

$$\begin{aligned}\text{Acid value} &= \frac{\text{Volume of KOH used (mL)} \times \text{Normality} \times \text{Eq.wt. of KOH}}{\text{Weight of oil sample}} \\ &= \frac{(x - y) \times 1 \times 56}{200V_1 \times w}\end{aligned}$$

Result

The acid value of oil = _____ mg.

Precautions and Safety Measures

1. The alcoholic solution of KOH should be freshly prepared and should be standardized just before the use.
2. If, during titration with alkali, pink color disappears repeatedly then titration should be completed rapidly and first appearance of pink should be taken as the end point.
3. For pale (light colored) oils, phenolphthalein should be used as indicator and for dark colored oils such as red or orange, a smaller weight of sample should be taken and *p*-naphtholbenzoin should be used as indicator.
4. In case of alcohol as a solvent, the reaction mixture should be heated on water bath but in case of ethyl methyl ketone solvent there is no need to heat.

Viva Voce Questions

1. What is acid value of oil?

Ans: The acid value of lubricating oil is defined as the number of milligrams of KOH required to neutralize the free acids present in 1 g of the oil sample.

2. What is the significance of acid value?

Ans: Acid value gives an idea about the amount of free acids present in oil. A high acid value indicates the extent of rancidity in a stored oil sample. A low acid value is an indicator of freshness of oil sample.

3. During titration, why does the pink color disappear rapidly sometimes?

Ans: This is because of other substances apart from acids present in the oil that react with KOH. So, as soon as the pink color appears with an extra drop of KOH, the other substances react with it causing its disappearance.

Experiment 11

Verification of Freundlich Adsorption Isotherm- Adsorption of Acetic Acid on Charcoal

Introduction

The phenomenon of the assimilation of higher concentration of any species at the surface of a solid or liquid as compared to that present in the bulk of the material is known as adsorption. In the process of adsorption, substances partition in a manner that they leave the gaseous or liquid phases and form a new layer on the surface of a solid substrate.

The solid or liquid on whose surface gas or liquid is adsorbed is called adsorbent or substrate; it must be a condensed phase, that is, either liquid or solid.

The adsorbents (charcoal or a mixture of products) used in the gas mask adsorb poisonous gases and prevent their inhalation. The gas or solution which is held to this surface is called **adsorbate**; it is atomic, ionic or molecular; generally a liquid or a gas. Adsorption can be positive or negative. When the concentration of the adsorbate is more on the surface of the adsorbent than in the bulk, it is termed as positive adsorption. When the concentration of the adsorbate is less on the surface of the adsorbent than in the bulk, it is termed as negative adsorption.

Aim

To study the adsorption of acetic acid on charcoal and to verify Freundlich isotherm.

Principle

At a given temperature, the variation in the amount of solute adsorbed with change in concentration of the solution is given by an empirical relation suggested by Freundlich is known as Freundlich isotherm.

$$\frac{x}{m} = kC^{1/n}$$

where x is the mass of the adsorbate and m is the mass of the adsorbent at pressure p ; k is constant depending upon the nature of adsorbate and adsorbent.

Apparatus and Reagents Required

Apparatus: Stoppered reagent bottles, burette, pipette, conical flask, beaker, charcoal.

Reagents: Acetic acid (0.5 M), NaOH (0.1 M), distilled water, phenolphthalein indicator.

Procedure

1. Weigh accurately about 2 g of finely powdered charcoal in each of the thoroughly cleaned and dried bottles numbered 1 to 6.
2. Prepare 0.5 M acetic acid solution for 250 ml by means of a burette. Add 10, 20, 30, 40, 50 ml of acid solution and 40, 30, 20, 10 and 0 ml distilled water in bottles 1, 2, 3, 4, 5 respectively.
3. Take the given unknown solution in the bottle no. 6, shake the bottle vigorously and leave them at a desired temperature for about half an hour.
4. Prepare 0.1 M NaOH for 250 ml and standardise with standard oxalic acid solution using phenolphthalein indicator against standard NaOH then determine the concentration of acid solution.
5. Filter the solution of each bottle by means of filter paper. Collect the filtrates properly in flasks. Reject first few ml of filtrate in each case.
6. Take 10 ml from each filtrate and then titrate with standard alkali. Calculate equilibrium concentration of the acid in each bottle.

Observation and Calculation

S. No.	C_1	C_2	$\log C_1$	$\log C_2$	$x = C_1 - C_2 \times \frac{126}{10}$	$\frac{x}{m}$	$\log \frac{x}{m}$	$\log \frac{x}{m} + 2$	$\log C_2 + 2$
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Plot a graph between $\log \frac{x}{m} + 2$ values and $\log C_2 + 2$ values which will verify the Freundlich adsorption isotherm.

Precautions and Safety Measures

1. Wear your safety glasses at all times.
2. If you spill a solution on your skin, be sure to flush the area promptly with lots of water.
3. Take special care with acidic solutions, which is an extremely corrosive and dangerous substance.
4. If you get any on your skin or clothing, rinse it with water immediately.

Viva Voce Questions

1. What is an adsorption isotherm?

Ans: Adsorption isotherm determines the variation in the amount of gas adsorbed by the adsorbent at a particular temperature by varying the pressure.

2. What is the Freundlich adsorption isotherm?

Ans: Freundlich first observed the variation between extent of adsorption and pressure at constant temperature. His observation was depicted by plotting mass of gas adsorbed per gram (x/m) of the adsorbent against pressure (p) at constant temperature.

3. What are the factors that affect adsorption?

Ans: Factors that affect adsorption are as follows:

(a) Temperature (b) Pressure (c) Nature of adsorbent (d) Nature of adsorbate (e) Surface area

Experiment 12

Determination of Viscosity of Liquids by Ostwald's Viscometer

Introduction

Viscosity is a measure of a fluid's resistance to flow. It is also known as fluid friction or viscous drag because it opposes the relative motion of the different layers of a fluid. A fluid with large viscosity resists motion because its molecular arrangement gives it high internal friction. A fluid with low viscosity flows easily because its molecular arrangement results in very low friction when it is in motion. There are two types of viscosities commonly measured, kinematic and dynamic. Kinematic viscosity is the relationship between viscous and inertial forces in a fluid and dynamic viscosity is the relationship between shear stress and shear rate.

Aim

To determine the absolute viscosity of a liquid by using Ostwald's viscometer.

Principle

If a liquid flows with a uniform velocity at a rate of ' v ' in ' t ' seconds through a capillary tube of radius ' r ' and length 1cm under a driving pressure ' P ' dynes/ cm². Then, the co-efficient of viscosity is given as

$$\eta = \frac{\Pi r^4 t \Delta P}{8VL}$$

where η is the viscosity of liquid in poise, ΔP is the pressure head, that is, dynes/cm², r is the radius of inner layer of capillary tube, L is the length of capillary tube, V is the volume of capillary tube and t is the time flows in seconds.

The Poiseuille's law is applicable only to linear flow or stream line flow. For a given Ostwald's viscometer the length, radius and volume of liquids are constants and they can be combined to a single constant. Therefore, the above equation can be written as

$$\eta = kt\Delta P$$

In the above equation, ΔP depends on:

- (I) density of liquid to be measured
- (II) acceleration due to gravity

The difference due to gravity is constant. Thus, the viscosity of liquid may be expressed as

$$\eta_1 = kt_1\rho_1 \text{ and } \eta_2 = kt_2\rho_2$$

where ρ_1 is the viscosity of standard liquid, that is, water and ρ_2 is the viscosity of test liquid.

Relative viscosity can be expressed as $\frac{\eta_1}{\eta_2} = \frac{t_1\rho_1}{t_2\rho_2}$

Apparatus and Reagents

Apparatus: Ostwald's viscometer, beaker, 20–25 mL syringe, thermostat, and digital balance.

Reagents: Standard liquid (water), liquid samples.

Procedure

1. Prepare 0%, 30%, 50%, 70%, 90% and 100% solution of glycerin in pure water.
2. Set up the temperature using thermostat.
3. Put both the viscometer and thermostat into a beaker with water and make sure that viscometer is clamped vertically and check the viscometer with pure water what volume is required to fill the viscometer.
4. Measure the weight of the empty beaker.
5. Fill the beaker with each solution as mentioned in step 1 one after another and measure the weight of the beaker.
6. Heat the viscometer kept in a beaker on magnetic stirrer and note the temperature shown by thermostat to make measurements for different temperatures.
7. Now fill the viscometer with solution through arm 1 till it reaches to the mark II as shown in Figure 1 using syringe. Now pull the liquid using syringe so that liquid flow through fine capillary tube till it reaches to the mark above IV. Remove the syringe attached to arm 2 and observe the upper meniscus of the liquid. When the meniscus is aligned with mark "IV", start the stop watch to measure time. Measurement terminates when the meniscus is completely aligned with the mark III and stop the stop watch. Record the total time taken by each sample.
8. After performing each sample rinse the viscometer with pure water and waste with acetone and dry up.
9. Repeat the measurement 3–4 times for each sample for each temperature and take the average of the time.

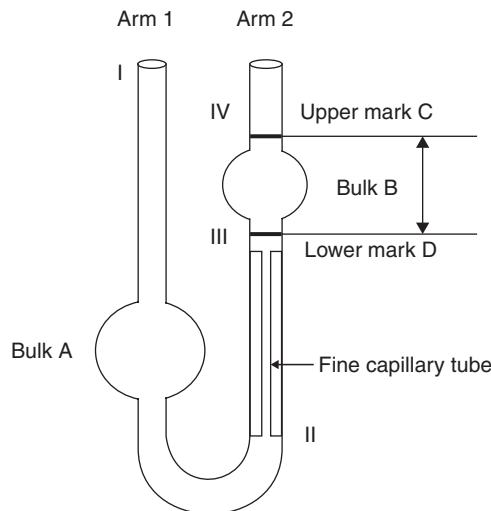


Figure 1 Ostwald viscometer.

Calculations

The viscosity of the liquid can be calculated using

$$\eta_L = \frac{\eta_w \times \rho_L t_L}{\rho_w \times t_w}$$

where η_w is the absolute viscosity of water, t_w is the time flow of water, ρ_w is the density of water, η_L is the absolute viscosity of liquid, t_L is the time flow of liquid and ρ_L is the density of liquid.

Result

Absolute viscosity of a given liquid (η_L) = _____ cps.

Precautions and Safety Measures

1. The viscometer should be held in a vertical position during the flow of the liquids.
2. While sucking the liquids, no air bubble should be formed inside the capillary tube.

Viva Voce Questions

1. What is the use of Ostwald viscometer?

Ans: Ostwald viscometer, also known as U-tube viscometer or capillary viscometer is a device used to measure the viscosity of the liquid with a known density.

2. How the viscosity is measured?

Ans: Non-Newtonian fluids exhibit a variety of different correlations between shear stress and shear rate. One of the most common instruments for measuring kinematic viscosity is the glass capillary viscometer.

3. How do you measure the viscosity of oil?

Ans: Typically, the viscosity is reported at one of two temperatures, either 40°C (100°F) or 100°C (212°F). For most industrial oils, it is common to measure kinematic viscosity at 40°C because this is the basis for the ISO viscosity grading system (ISO 3448).

4. What are the different types of viscosity?

Ans: There are two kinds of viscosity commonly reported, kinematic and dynamic. Dynamic viscosity is the relationship between the shear stress and the shear rate in a fluid. The kinematic viscosity is the relationship between viscous and inertial forces in a fluid.

Experiment 13

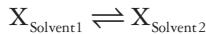
Determination of Partition Coefficient of Acetic Acid between *n*-Butanol and Water

Aim

To determine the distribution constant of acetic acid between *n*-butanol and water.

Principle

A given substance X is partially soluble in each of two immiscible solvents. If X is placed in a mixture of these two solvents and shaken, equilibrium will be established between two phases. That is, substance X will partition (distribute) itself in a manner that is a function of its relative solubility in the two solvents:



The equilibrium constant, K_d , for this equilibrium expression is known as the partition or distribution coefficient.

$$K_d = \frac{[X_{\text{solvent 2}}]}{[X_{\text{solvent 1}}]}$$

The equilibrium constant is thus the ratio of the concentrations of the species, X, in each solvent for a given system at a given temperature. The partition coefficient can be conveniently estimated as the ratio of the solubility of X in solvent 1 vs solvent 2.

$$K_d = \frac{\text{Solubility of } X \text{ in solvent 2}}{\text{Solubility of } X \text{ in solvent 1}}$$

When solvent 1 is water and solvent 2 is an organic solvent, the basic equation used to express the coefficient K_d is

$$K_d = \frac{(g / 100 \text{ mL})_{\text{organic layer}}}{(g / 100 \text{ mL})_{\text{water layer}}} \text{ or } K_d = \frac{C_2}{C_1}$$

where C_2 is the concentration of solute in organic layer and C_1 is the concentration of solute in aqueous layer.

Apparatus and Reagents

Apparatus: Separating funnels, pipette, burette, conical flask, measuring jar.

Reagents required: *n*-Butanol, distilled water, acetic acid, NaOH, phenolphthalein.

Procedure

1. Take a mixture of samples in Bottle I and II.
2. Bottle I contains 40 mL *n*-Butanol and 60 mL water and 1 to 2 mL acetic acid.
3. Bottle II contains 30 mL *n*-Butanol and 70 mL water and 1 to 2 mL acetic acid.
4. Shake the bottles vigorously after every 3 to 4 minutes for 20 minutes durations.
5. After each time of shaking, open the lid of the two bottles to release the pressure. Then wait for 5 min.
6. Pour the entire solution into a separating funnel.
7. Allow the mixture to separate into two clear layers where the upper layer is the organic layer and the lower layer is the aqueous layer.
8. The aqueous layer was collected in a clean and dry 100 mL beaker.
9. 5 mL of the solution was pipetted out into a conical flask. About 10 mL of distilled water was added and the resulting solution was titrated with supplied ~0.2 (N) NaOH using phenolphthalein indicator.
10. At end point, color of the solution is light pink.
11. The organic layer was collected into a clean and dry 100 mL beaker.
12. 5 mL of the organic layer was pipetted out into a conical flask. About 10 mL of distilled water was added and the resulting solution was titrated with supplied ~0.2 (N) NaOH using phenolphthalein indicator.
13. During titration the solution was shaken vigorously.
14. At the end point color of the solution is light pink. The process is done for the two bottles.
15. Repeat the process to take a number of readings for each titration.

Observations

Titration data for acetic acid in aqueous and organic layer:

S. No.	Bottle No	Volume of Solution	Titration of Organic Phase (mL)			Titration of Aqueous Phase (mL)		
			Initial Burette Reading		Volume Mean	Initial Burette Reading		Volume Mean
			Final Burette Reading	Reading	Volume	Final Burette Reading	Reading	Volume
1.	I							
2.	II							

Calculations

The relations involving the distribution constant and the activities of the solute in two solvents is given by the equation:

$$K_a = \frac{\alpha_2^n}{\alpha_1}$$

Here K_a is the distribution constant and α_1 and α_2 are referring to activities of the solute in two solvents, and n is computed by

$$n = \frac{\text{Mol. wt of solvent 1}}{\text{Mol. wt of solvent 2}}$$

The average molecular weight is affected by the degrees of association and dissociation. The values of n also changes with concentrations. If concentration is used instead of activities, the relationships for the distribution constant becomes

$$K_d = \frac{C_2^n}{C_1}$$

Value of K and n in concentration range:

S. No.	Concentration Range	K	n

Result

Distribution constant K_d = _____.

Precautions and Safety Measures

1. Wear your safety glasses at all times.
2. If you spill a solution on your skin, be sure to flush the area promptly with lots of water.
3. Take special care with acidic solutions, which is an extremely corrosive and dangerous substance.
4. If you get any on your skin or clothing, rinse it with water immediately.

Viva Voce Questions

1. Which layer is the aqueous layer in a separator funnel?

Ans: The denser solvent will be the bottom layer. Most halogenated solvents are denser than water; most non-halogenated solvents are less dense than water.

2. What is the boiling point of *n*-butyl alcohol?

Ans: 117.7 °C.

3. What is the process of extraction?

Ans: Extractions are a way to separate a desired substance when it is mixed with others. The mixture is brought into contact with a solvent in which the substance of interest is soluble, but the other substances present are insoluble.

Experiment 14

Determination of the Surface Tension by Stalagmometer (Drop Number Method)

Introduction

The surface tension of a liquid results from an imbalance of intermolecular attractive forces or the cohesive forces between molecules. Each molecule in the bulk of the liquid, gets pulled equally in all directions by the neighboring liquid molecules. This results in a zero net force. The molecules that are present at the surface do not have molecules on all sides unlike other molecules in the bulk of the liquid. Therefore, they are pulled inwards as shown in Figure 1. As a result of this, internal pressure is created and this forces liquid surfaces to contract to the minimal area.

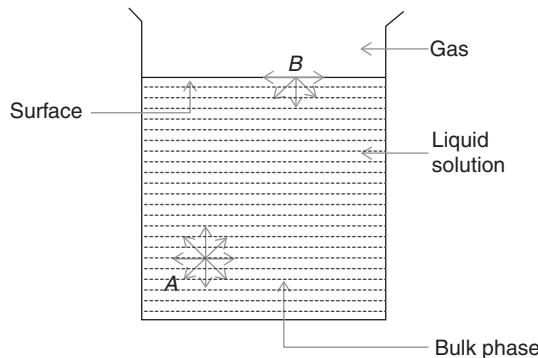


Figure 1 Force experienced by molecules at the surface and in the bulk of the liquid.

The force which acts along the surface of liquid uniformly in all directions is known as surface tension. This force is expressed in dyne/cm acting along the surface at right angles to any imaginary line in the surface and is generally represented by γ . Due to surface tension, the drops of liquid are spherical in shape as surface area of sphere is less. The rise of liquid into a capillary tube is directly proportional to the surface tension of liquid (e.g., rise of oil in the wick of lamp, rise of ground water to the twigs and leaves of the plant, etc.).

The most common method of measurement of surface tension is **drop number method**, due to its practical convenience and a good degree of reliability. It is measured by using **stalagmometer**.

Aim

To determine of the surface tension of given liquid using stalagmometer.

Principle

The method is based on the principle that when a liquid is allowed to pass through a capillary tube, held vertically, at such a slow speed that the drops fall off the tip of capillary under their own weight and are not pushed away by the kinetic force of flow or vibrations.

If n_1, n_2 are the number of drops and d_1, d_2 are the densities of water and given liquid respectively, the surface tension γ_2 of any liquid can be calculated as

$$\frac{\gamma_2}{\gamma_1} = \frac{n_1}{n_2} \times \frac{d_2}{d_1}$$

$$\gamma_2 = \frac{n_1}{n_2} \times \frac{d_2}{d_1} \times \gamma_1$$

Apparatus and Reagents Required

Apparatus: Stalagmometer, screw pinch cock, beaker, specific gravity bottle, burette, clamp stand, analytical balance and filter paper.

Reagents: Water and liquid sample.

Procedure

1. A cleaned and dried specific gravity bottle with lid is taken and its weight (w_1 g) is noted using analytical balance.
2. The specific gravity bottle is filled with water up to the rim. The lid is placed and the weight (w_2 g) of the bottle is noted.
3. The specific gravity bottle is emptied and rinsed 3 times with a given liquid. The bottle is filled with the given liquid up to the rim. The lid is placed and the weight (w_3 g) of the bottle is noted again.
4. A cleaned and dried stalagmometer fixed with a rubber tube and pinch cork is taken.
5. The lower flattened end of the stalagmometer is immersed into a beaker containing water and the water is sucked till its level reached above the bulb.
6. Two points on the stalagmometer upper mark x above the bulb and lower mark y below the bulb, are marked.
7. The stalagmometer is placed vertically on the clamp stand.
8. The pinch cork is slowly loosened so that drops start forming at countable rate.

9. The number of drops are counted from the upper mark x of water level to the lower mark y .
10. Three concordant readings are taken.
11. The same procedure with the liquid sample is repeated.

Observations

S. No.	No. of Drops of Water (n_1)	No. of Drops of Liquid (n_2)
1.		
2.		
3.		

Calculations

Determination of the density of the given liquid

Room Temperature = $T^\circ\text{C}$

Density of water at room temperature = $d_1 \text{ g/cm}^3 = 0.9982 \text{ g/cm}^3$ at 20°C

Density of given liquid at room temperature = $d_2 \text{ g/cm}^3$

Weight of empty specific gravity bottle = $w_1 \text{ g}$

Weight of specific gravity bottle filled with water = $w_2 \text{ g}$

Weight of water = $(w_2 - w_1) \text{ g} = m_1 \text{ g}$

Weight of specific gravity bottle filled with liquid = $w_3 \text{ g}$

Weight of given liquid = $(w_3 - w_1) \text{ g} = m_2 \text{ g}$

Determination of the surface tension of given liquid

If n_1 and n_2 are the number of drops and d_1 , d_2 are the densities of water and given liquid respectively, the surface tension γ_2 of any liquid can be calculated as

$$\frac{\gamma_2}{\gamma_1} = \frac{n_1}{n_2} \times \frac{d_2}{d_1}$$

$$\gamma_2 = \frac{n_1}{n_2} \times \frac{d_2}{d_1} \times \gamma_1 = \frac{n_1}{n_2} \times \frac{m_2}{m_1} \times \gamma_1$$

since $d = m/V$

(V is same in both cases so $d_1/d_2 = m_1/m_2$)

Result

The surface tension of unknown liquid is _____ dynes/cm.

Precautions and Safety Measures

1. Glass apparatus should be clean and dry.
2. The number of drops per minute should not exceed 10 otherwise they may not be properly formed.
3. Stalagmometer should be placed vertically on table. There should not be any sort of vibrations or disturbances.

Viva Voce Questions

1. Define the term surface tension.

Ans: The surface tension of a liquid is the force which acts along the surface at right angles to any imaginary line on the surface of a liquid.

2. Give CGS and SI units of surface tension.

Ans: The CGS units are dynes per cm (dyne/cm) and SI units are Newton per meter (N/m).

3. Why are liquid drops spherical in shape?

Ans: Due to surface tension, the surface of liquid tends to become minimum. The sphere shape acquires the minimum surface area.

4. Which instrument is used for measuring the density of a liquid?

Ans: Density of liquid is measured by using specific gravity bottle or a pycnometer.

5. Why is lower end of the stalagmometer flattened?

Ans: The lower end of capillary tube is flattened, ground and polished carefully to get a large dropping surface with a sharp boundary.

6. What is the function of capillary in the stalagmometer?

Ans: The capillary slows down the flow of the liquid through the tip. The final adjustment of the rate of fall of the drops however is made by regulating the screw-pinch-cock on the rubber tubing.

About the Book

The objective of textbook of **Engineering Chemistry** is to build a sound foundation in fundamentals of chemistry and an interface of theoretical concepts with their industrial/engineering applications.

This book is designed as an introductory course in Engineering Chemistry with complete coverage of topics and is in accordance with the latest syllabus of AICTE. It aims to impart students an in-depth knowledge of various aspects of chemistry as applied to engineering with a **special focus to JNTUH** syllabus. It extends the application of basic concepts of chemistry to understanding of Molecular Structure and Theories of Chemical Bonding; Water and its Treatment; Electrochemistry and Corrosion; Stereochemistry, Organic Reaction Mechanism and Synthesis of Drug Molecules; and Spectroscopic Techniques.

Precise Series

- Precise content as per syllabi
- Excellent presentation in a clear, logical and concise manner.
- Learning objectives at the beginning of each chapter.
- Focus on explanation of fundamental concepts.
- Key terms to quickly review the concepts.
- Optimum balance of objective and subjective problem set.

Highlights of the Book

- **Precise content** as per the latest **AICTE syllabus**.
- Approach to subject is **student friendly** and **non-assumptive**.
- Clearly defined **learning objectives** at the beginning of each chapter.
- Excellent correlation of **concepts** with their applications.
- Enriched with **figures, graphs** and **flowcharts** for visual understanding.
- **Key terms** to highlight the important points.
- **Topic-wise solved examples** with detailed solutions.
- Ample **practice exercises** at the end of each chapter.

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ISBN: 978-81-265-7632-6

