www.tntextbooks.in

CHEMISTRY

HIGHER SECONDARY - FIRST YEAR

VOLUME - II

REVISED BASED ON THE RECOMMENDATIONS OF THE
TEXT BOOK DEVELOPMENT COMMITTEE

A Publication Under
Government of Tamilnadu
Distribution of Free Textbook Programme
(NOT FOR SALE)

Untouchability is a sin
Untouchability is a crime
Untouchability is inhuman

TAMILNADU
TEXTBOOK CORPORATION
College Road, Chennai - 600 006

www.tntextbooks.in

© Government of Tamilnadu

First Edition - 2005
Revised Edition - 2007

CHAIRPERSON & AUTHOR
Dr. V.BALASUBRAMANIAN
Professor of Chemistry (Retd.)
Presidency College, (Autonomous), Chennai - 600 005.

REVIEWERS

Dr. M.KRISHNAMURTHI
Professor of Chemistry
Presidency College (Autonomous)
Chennai - 600 005.

Dr. M.KANDASWAMY
Professor and Head
Department of Inorganic Chemistry
University of Madras
Chennai - 600 025.

Dr. M. PALANICHAMY
Professor of Chemistry
Anna University
Chennai - 600 025.

DR. J. SANTHANALAKSHMI
Professor of Physical Chemistry
University of Madras
Chennai - 600 025.

Mr. V. JAISANKAR,
Lecturer in Chemistry
L.N.Government Arts College,
Ponneri - 601 204.

AUTHORS

Dr. S.P. MEENAKSHISUNDRAM
Professor of Chemistry,
Annamalai University,
Annamalai Nagar 608 002.

Dr. R. RAMESH
Senior Lecturer in Chemistry,
Bharathidasan University
Trichirapalli 620 024.

Mrs. T. VIJAYARAGINI
P.G. Teacher in Chemistry,
SBOA Mat. Higher Secondary School
Chennai - 600 101.

Dr. S.MERLIN STEPHEN,
P.G.Teacher in Chemistry
CSI Bain Mat. Hr. Sec. School
Kilpauk, Chennai - 600 010.

Dr. K. SATHYANARAYANAN,
P.G. Teacher in Chemistry,
Stanes Anglo Indian Hr. Sec. School,
Coimbatore - 18.

Dr. M. RAJALAKSHMI
P.G. Teacher in Chemistry,
Chettinad Vidyashram
Chennai - 600 028.

Price : Rs.

This book has been prepared by the Directorate of School Education on behalf of the Government of Tamilnadu.

This book has been printed on 60 G.S.M paper

Printed by Offset at :

www.tntextbooks.in

PREFACE

Where has chemistry come from ? Throughout the history of the human race, people have struggled to make sense of the world around them. Through the branch of science we call chemistry we have gained an understanding of the matter which makes up our world and of the interactions between particles on which it depends. The ancient Greek philosophers had their own ideas of the nature of matter, proposing atoms as the smallest indivisible particles. However, although these ideas seems to fit with modern models of matter, so many other Ancient Greek ideas were wrong that chemistry cannot truly be said to have started there.

Alchemy was a mixture of scientific investigation and mystical quest, with strands of philosophy from Greece, China, Egypt and Arabia mixed in. The main aims of alchemy that emerged with time were the quest for the **elixir of life** (the drinking of which would endue the alchemist with immortality), and the search for the **philosopher's stone**, which would turn base metals into gold. Improbable as these ideas might seem today, the alchemists continued their quests for around 2000 years and achieved some remarkable successes, even if the elixir of life and the philosopher's stone never appeared.

Towards the end of the eighteenth century, pioneering work by Antoine and Marie Lavoisier and by John Dalton on the chemistry of air and the atomic nature of matter paved the way for modern chemistry. During the nineteenth century chemists worked steadily towards an understanding of the relationships between the different chemical elements and the way they react together. A great body of work was built up from careful observation and experimentation until the relationship which we now represent as the periodic table emerged. This brought order to the chemical world, and from then on chemists have never looked back.

Modern society looks to chemists to produce, amongst many things, healing drugs, pesticides and fertilisers to ensure better crops and chemicals for the many synthetic materials produced in the twenty-first century. It also looks for an academic understanding of how matter works and how the environment might be protected from the source of pollutants. Fortunately, chemistry holds many of the answers !

www.tntextbooks.in

Following the progressing trend in chemistry, it enters into other branches of chemistry and answers for all those miracles that are found in all living organisms. The present book is written after following the revised syllabus, keeping in view with the expectations of National Council of Educational Research & Training (NCERT). The questions that are given in each and every chapter can be taken only as model questions. A lot of self evaluation questions, like, choose the best answer, fill up the blanks and very short answer type questions are given in all chapters. **While preparing for the examination, students should not restrict themselves, only to the questions/problems given in the self evaluation. They must be prepared to answer the questions and problems from the entire text.**

Learning objectives may create an awareness to understand each and every chapter.

Sufficient reference books are suggested so as to enable the students to acquire more informations about the concepts of chemistry.

Dr. V. BALASUBRAMANIAN
Chairperson
Syllabus Revision Committee (Chemistry)
& XI Std Chemistry Text Book Writing Committee

www.tntextbooks.in

CONTENTS

www.tntextbooks.in

Syllabus : Higher Secondary - First Year Chemistry

INORGANIC CHEMISTRY

Unit I - Chemical Calculations

Significant figures - SI units - Dimensions - Writing number in scientific notation - Conversion of scientific notation to decimal notation - Factor label method - Calculations using densities and specific gravities - Calculation of formula weight - Understanding Avogadro's number - Mole concept-mole fraction of the solvent and solute - Conversion of grams into moles and moles into grams - Calculation of empirical formula from quantitative analysis and percentage composition - Calculation of molecular formula from empirical formula - Laws of chemical combination and Dalton's atomic theory - Laws of multiple proportion and law of reciprocal proportion - Postulates of Dalton's atomic theory and limitations - Stoichiometric equations - Balancing chemical equation in its molecular form - Oxidation reduction-Oxidation number - Balancing Redox equation using oxidation number - Calculations based on equations. - Mass/Mass relationship - Methods of expressing concentration of solution - Calculations on principle of volumetric analysis - Determination of equivalent mass of an element - Determination of equivalent mass by oxide, chloride and hydrogen displacement method - Calculation of equivalent mass of an element and compounds - Determination of molar mass of a volatile solute using Avogadro's hypothesis.

Unit 2 - General Introduction to Metallurgy

Ores and minerals - Sources from earth, living system and in sea - Purification of ores-Oxide ores sulphide ores magnetic and non magnetic ores - Metallurgical process - Roasting-oxidation - Smelting-reduction - Bessemerisation - Purification of metals-electrolytic and vapour phase refining - Mineral wealth of India.

Unit 3 - Atomic Structure - I

Brief introduction of history of structure of atom - Defects of Rutherford's model and Niels Bohr's model of an atom - Sommerfeld's extension of atomic structure - Electronic configuration and quantum numbers - Orbitals-shapes of s, p and d orbitals. - Quantum designation of electron - Pauli's exclusion principle - Hund's rule of maximum multiplicity - Aufbau principle - Stability of orbitals - Classification of elements based on electronic configuration.

Unit 4 - Periodic Classification - I

Brief history of periodic classification - IUPAC periodic table and IUPAC nomenclature of elements with atomic number greater than 100 - Electronic configuration and periodic table - Periodicity of properties Anomalous periodic properties of elements.

Unit 5 - Group-1s Block elements

Isotopes of hydrogen - Nature and application - Ortho and para hydrogen - Heavy water - Hydrogen peroxide - Liquid hydrogen as a fuel - Alkali metals - General characteristics - Chemical properties - Basic nature of oxides and hydroxides - Extraction of lithium and sodium - Properties and uses.

Unit 6 - Group - 2s - Block elements

General characteristics - Magnesium - Compounds of alkaline earth metals.

Unit 7 -p- Block elements

General characteristics of p-block elements - Group-13. Boron Group - Important ores of Boron - Isolation of Born-Properties - Compounds of Boron- Borax, Boranes, diboranes, Borazole-preparation. properties - Uses of Boron and its compounds - Carbon group - Group -14 - Allotropes of carbon - Structural difference of graphite and diamond - General physical and chemical properties of oxides, carbides, halides and sulphides of carbon group - Nitrogen - Group-15 - Fixation of nitrogen - natural and industrial - HNO_3-Ostwald process - Uses of nitrogen and its compounds - Oxygen - Group-16 - Importance of molecular oxygen-cell fuel - Difference between nascent oxygen and molecular oxygen - Oxides classification, acidic basic, amphoteric, neutral and peroxide - Ozone preparation, property and structure - Factors affecting ozone layer.

www.tntextbooks.in

Physical Chemistry

Unit 8 - Solid State - I

Classification of solids-amorphous, crystalline - Unit cell - Miller indices - Types of lattices belong to cubic system.

Unit 9 - Gaseous State

Four important measurable properties of gases - Gas laws and ideal gas equation - Calculation of gas constant ‘‘R” - Dalton’s law of partial pressure - Graham’s law of diffusion - Causes for deviation of real gases from ideal behaviour - Vanderwaal’s equation of state - Critical phenomena - Joule-Thomson effect and inversion temperature - Liquefaction of gases - Methods of Liquefaction of gases.

Unit 10 - Chemical Bonding

Elementary theories on chemical bonding - Kossel-Lewis approach - Octet rule - Types of bonds - Ionic bond - Lattice energy and calculation of lattice energy using Born-Haber cycle - Properties of electrovalent compounds - Covalent bond - Lewis structure of Covalent bond - Properties of covalent compounds - Fajan’s rules - Polarity of Covalent bonds - VSEPR Model - Covalent bond through valence bond approach - Concept of resonance - Coordinate covalent bond.

Unit 11 - Colligative Properties

Concept of colligative properties and its scope - Lowering of vapour pressure - Raoul’s law - Ostwald - Walker method - Depression of freezing point of dilute solution - Beckmann method - Elevation of boiling point of dilute solution - Cotrell’s method - Osmotic pressure - Laws of Osmotic pressure - Berkley-Hartley’s method - Abnormal colligative properties Van’t Hoff factor and degree of dissociation.

Unit 12 - Thermodynamics - I

Thermodynamics - Scope - Terminology used in thermodynamics - Thermodynamic properties - nature - Zeroth law of thermodynamics - Internal energy - Enthalpy - Relation between ‘‘H and “E - Mathematical form of First law - Enthalpy of transition - Enthalpy of formation - Enthalpy of combustion -

Enthalpy of neutralisation - Various sources of energy-Non-conventional energy resources.

Unit 13 - Chemical Equilibrium - I

Scope of chemical equilibrium - Reversible and irreversible reactions - Nature of chemical equilibrium - Equilibrium in physical process - Equilibrium in chemical process - Law of chemical equilibrium and equilibrium constant - Homogeneous equilibria - Heterogeneous equilibria.

Unit 14 - Chemical Kinetics - I

Scope - Rate of chemical reactions - Rate law and rate determining step - Calculation of reaction rate from the rate law - Order and molecularity of the reactions - Calculation of exponents of a rate law - Classification of rates based on order of the reactions.

ORGANIC CHEMISTRY

Unit 15 - Basic Concepts of Organic Chemistry

Catenation - Classification of organic compounds - Functional groups - Nomenclature - Isomerism - Types of organic reactions - Fission of bonds - Electrophiles and nucleophiles - Carbonium ion Carbanion - Free radicals - Electron displacement in covalent bond.

Unit 16 - Purification of Organic compounds

Characteristics of organic compounds - Crystallisation - Fractional Crystallisation - Sublimation - Distillation - Fractional distillation - Steam distillation - Chromotography.

Unit 17 - Detection and Estimation of Elements

Detection of carbon and hydrogen - Detection of Nitrogen - Detection of halogens - Detection of sulphur - Estimation of carbon and hydrogen - Estimation of Nitrogen - Estimation of sulphur - Estimation of halogens.

Unit 18 - Hydrocarbons

Classification of Hydrocarbons - IUPAC nomenclature - Sources of alkanes - General methods of preparation of alkanes - Physical properties -

www.tntextbooks.in

Chemical properties - Conformations of alkanes - Alkenes - IUPAC nomenclature of alkenes - General methods of preparation - Physical properties - Chemical properties - Uses - Alkynes - IUPAC Nomenclature of alkynes - General methods of preparation - Physical properties - Chemical properties - Uses.

Unit 19 - Aromatic Hydrocarbons

Aromatic Hydrocarbons - IUPAC nomenclature of aromatic hydrocarbons - Structure of Benzene - Orientation of substituents on the benzene ring - Commercial preparation of benzene - General methods of preparation of Benzene and its homologues - Physical properties - Chemical properties - Uses - Carcinogenic and toxic nature.

Unit 20 - Organic Halogen Compounds

Classification of organic hydrogen compounds - IUPAC nomenclature of alkyl halides - General methods of preparation - Properties - Nucleophilic substitution reactions - Elimination reactions - Uses - Aryl halide - General methods of preparation - Properties - Uses - Aralkyl halides - Comparison arylhalides and aralkyl halides - Grignard reagents - Preparation - Synthetic uses.

www.tntextbooks.in

CHEMISTRY PRACTICALS FOR STD XI

I. Knowledge of using Burette, Pipette and use of logarithms is to be demonstrated.

II. Preparation of Compounds.

1. Copper Sulphate Crystals from amorphous copper sulphate solutions
2. Preparation of Mohr's Salt
3. Preparation of Aspirin
4. Preparation of Iodoform
5. Preparation of tetrammine copper (II) sulphate

III. Identification of one cation and one anion from the following. (Insoluble salt should not be given)

Cation : Pb^{++}, Cu^{++}, Al^{++}, Mn^{2+}, Zn^{++}, Ca^{++}, Ba^{++}, Mg^{++}, NH_4^+.

Anions : Borate, Sulphide, Sulphate, Carbonate, Nitrate, Chloride, Bromide.

IV. Determination of Melting point of a low melting solid.

V. Acidimetry Vs Alkalimetry

1. Preparation of Standard solution of Oxalic acid and Sodium Carbonate solution.
2. Titration of HCl Vs NaOH
3. Titration of HCl Vs Na_2CO_3
4. Titration of Oxalic acid Vs NaOH

www.tntextbooks.in

www.tntextbooks.in

10. CHEMICAL BONDING

OBJECTIVES

- *To know about bonding as binding forces between atoms to form molecules.*
- *To learn about Kossel-Lewis approach to chemical bonding, the octet rule, its limitations and Lewis representations of simple molecules.*
- *To know about ionic bond, lattice energy and Born-Haber cycle.*
- *To understand covalent bond, directional character.*
- *To learn about VSEPR model and predict the geometry of simple molecules.*
- *To understand the concepts of hybridisation, σ and π bonds, resonance and coordinate covalent bonds.*

10.1 Elementary theories on Chemical Bonding

The study on the "nature of forces that hold or bind atoms together to form a molecule" is required to gain knowledge of the following-

i) to know about how atoms of same element form different compounds combining with different elements.

ii) to know why particular shapes are adopted by molecules.

iii) to understand the specific properties of molecules or ions and the relation between the specific type of bonding in the molecules.

Chemical bond

Existence of a strong force of binding between two or many atoms is referred to as a **Chemical Bond** and it results in the formation of a stable compound with properties of its own. The bonding is permanent until it is acted upon by external factors like chemicals, temperature, energy etc. It is known that, a molecule is made up of two or many atoms having its own characteristic properties which depend on the types of bonding present.

www.tntextbooks.in

Classification of molecules

Molecules having two identical atoms like H_2, O_2, Cl_2, N_2 etc. are called as **homonuclear diatomic molecules**. Molecules containing two different atoms like CO, HCl, NO, HBr etc., are called as **heteronuclear diatomic molecules.** Molecules containing identical but many atoms bonded together such as P_4, S_8 etc., are called as **homonuclear polyatomics.** In most of the molecules, more than two atoms of different kinds are bonded such as in molecules like NH_3, CH_3COOH, SO_2, HCHO and they are called as **heteronuclear polyatomics.**

Chemical bonds are basically classified into three types consisting of (i) ionic or electrovalent bond (ii) covalent bond and (iii) coordinate-covalent bond. Mostly, valence electrons in the outer energy level of an atom take part in the chemical bonding.

In 1916, W.Kossel and G.N.Lewis, separately developed theories of chemical bonding inorder to understand why atoms combined to form molecules. According to the electronic theory of valence, a chemical bond is said to be formed when atoms interact by losing, gaining or sharing of valence electrons and in doing so, a stable noble gas electronic configuration is achieved by the atoms.

Except Helium, each noble gas has a stable valence shell of eight electrons. The tendency for atoms to have eight electrons in their outershell by interacting with other atoms through electron sharing or electron-transfer is known as the **octet rule** of chemical bonding.

10.1.1 Kossel-Lewis approach to Chemical Bonding

W.Kossel laid down the following postulates to the understanding of ionic bonding:

- In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases. Therefore one or small number of electrons are easily gained and transferred to attain the stable noble gas configuration.
- The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms.

- The negative and positive ions so formed attains stable noble gas electronic configurations. The noble gases (with the exception of helium which has two electrons in the outermost shell) have filled outer shell electronic configuration of eight electrons (octet of electrons) with a general representation $ns^2\ np^6$.
- The negative and positive ions are bonded and stabilised by force of electrostatic attraction.

Kossel's postulates provide the basis for the modern concepts on electron transfer between atoms which results in ionic or electrovalent bonding.

For example, formation of NaCl molecule from sodium and chlorine atoms can be considered to take place according to Kossel's theory by an electron transfer as:

(i) $\underset{[Ne]\ 3s^1}{Na} \xrightarrow{\text{loss of e}} \underset{[Ne]}{Na^+} + e$

where [Ne] = electronic configuration of Neon $= 2s^2\ 2p^6$

(ii) $\underset{[Ne]3s^2\ 3p^5}{Cl + e} \xrightarrow{\text{gain of e}} \underset{[Ar]}{Cl^-}$

[Ar] = electronic configuration of Argon

(iii) $Na^+ + Cl^- \xrightarrow[\text{attraction}]{\text{electrostatic}} NaCl(or)Na^+\ Cl^-$

NaCl is an electrovalent or ionic compound made up of sodium ions and chloride ions. The bonding in NaCl is termed as electrovalent or ionic bonding. Sodium atom loses an electron to attain Neon configuration and also attains a positive charge. Chlorine atom receives the electron to attain the Argon configuration and also becomes a negatively charged ion. The coulombic or electrostatic attraction between Na^+ and Cl^- ions result in NaCl formation.

Similarly formation of MgO may be shown to occur by the transfer of two electrons as:

www.tntextbooks.in

(i) $\underset{[Ne]3s^2}{Mg} \xrightarrow{\text{loss of } e^-} \underset{[Ne]}{Mg^{2+}} + 2e$

(ii) $\underset{[He]2s^2\,2p^4}{O + 2e} \xrightarrow{\text{gain of } e^-} O^{2-}$ $[He]2s^2\,2p^6$(or) [Ne]

(iii) $Mg^{2+} + O^{2-} \xrightarrow[\text{attraction}]{\text{electrostatic}} MgO(\text{or})Mg^{2+}\,O^{2-}$

The bonding in MgO is also electrovalent or ionic and the electrostatic forces of attraction binds Mg^{2+} ions with O^{2-} ions. Thus, "the binding forces existing as a result of electrostatic attraction between the positive and negative ions", is termed as **electrovalent** or **ionic** bond. The electrovalency is considered as equal to the number of charges on an ion. Thus magnesium has positive electrovalency of two while chlorine has negative electrovalency of one.

The valence electron transfer theory could not explain the bonding in molecules like H_2, O_2, Cl_2 etc., and in other organic molecules that have ions.

G.N.Lewis, proposed the octet rule to explain the valence electron sharing between atoms that resulted in a bonding type with the atoms attaining noble gas electronic configuration. The statement is : "a bond is formed between two atoms by mutual sharing of pairs of electrons to attain a stable outer-octet of electrons for each atom involved in bonding". This type of valence electron sharing between atoms is termed as **covalent bonding.** Generally homonuclear diatomics possess covalent bonds.

It is assumed that the atom consists of a `Kernel' which is made up of a nucleus plus the inner shell electrons. The Kernel is enveloped by the outer shells that could accommodate a maximum of eight electrons. The eight outershell electrons are termed as octet of electrons and represents a stable electronic configuration. Atoms achieve the stable outer octet when they are involved in chemical bonding.

In case of molecules like F_2, Cl_2, H_2 etc., the bond is formed by the sharing of a pair of electrons between the atoms. For example, consider the formation of a fluorine molecule (F_2). The atom has electronic configuration. $[He]2s^2\ 3s^2\ 3p^5$ which is having one electron less than the electronic configuration of Neon. In the fluorine molecule, each atom

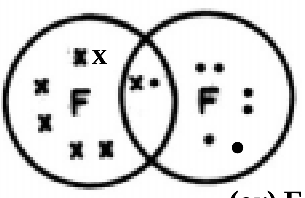
www.tntextbooks.in

contributes one electron to the shared pair of the bond of the F_2 molecule. In this process, both the fluorine atoms attain the outershell octet of a noble gas (Argon) (Fig. 10.1(a)). Dots (•) represent electrons. Such structures are called as Lewis dot structures.

Lewis dot structures can be written for combining of like or different atoms following the conditions mentioned below :

- Each bond is the result of sharing of an electron pair between the atoms comprising the bond.
- Each combining atom contributes one electron to the shared pair.
- The combining atoms attain the outer filled shells of the noble gas configuration.

If the two atoms share a pair of electrons, a single bond is said to be formed and if two pairs of electrons are shared a double bond is said to be formed etc. All the bonds formed from sharing of electrons are called as covalent bonds.



(or) F-F

8e⁻ **8e⁻**

Fig. 10.1(a) F_2 molecule

In carbon dioxide (CO_2) two double bonds are seen at the centre carbon atom which is linked to each oxygen atom by a double bond. The carbon and the two oxygen atoms attain the Neon electronic configuration.

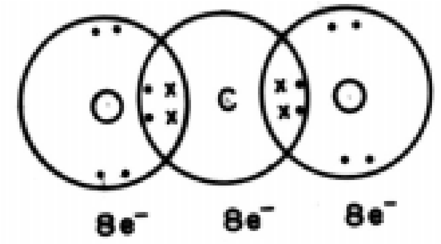


Fig. 10.1 (b) CO_2 molecule

www.tntextbooks.in

When the two combining atoms share three electron pairs as in N_2 molecule, a triple bond is said to be formed. Each of the Nitrogen atom shares 3 pairs of electrons to attain neon gas electronic configuration.

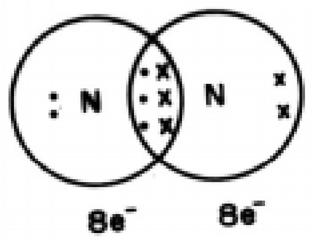


Fig. 10.1 (c) N_2 molecule

10.2 Types of Bond

There are more than one type of chemical bonding possible between atoms which makes the molecules to show different characteristic properties. The different types of chemical bonding that are considered to exist in molecules are (i) **ionic or electrovalent bond** which is formed as a result of complete electron transfer from one atom to the other that constitutes the bond; (ii) **covalent bond** which is formed as a result of mutual electron pair sharing with an electron being contributed by each atom of the bond and (iii) **coordinate - covalent bond** which is formed as a result of electron pair sharing with the pair of electrons being donated by only one atom of the bond. The formation and properties of these types of bonds are discussed in detail in the following sections.

10.3 Ionic (or) Electrovalent bond

The electrostatic attraction force existing between the cation and the anion produced by the electron transfer from one atom to the other is known as the ionic (or) electrovalent bond. The compounds containing such a bond are referred to as ionic (or) electrovalent compounds.

Ionic bond is non directional and extends in all directions. Therefore, in solid state single ionic molecules do not exist as such. Only a network of cations and anions which are tightly held together by electro-static forces exist in the ionic solids. To form a stable ionic compound there must be a net lowering of energy. That is, energy is released as a result of electovalent bond formation between positive and negative ions.

When the electronegativity difference between the interacting atoms are greatly different they will form an ionic bond. In fact, a difference of 2 or more is necessary for the formation of an ionic bond. Na has electronegativity 0.9 while Cl has 3.0, thus Na and Cl atoms when brought together will form an ionic bond.

For example, NaCl is formed by the electron ionisation of sodium atom to Na^+ ion due to its low ionisation potential value and chlorine atom to chloride ion by capturing the odd electron due to high electron affinity. Thus, NaCl (ionic compound) is formed. In NaCl, both the atoms possess unit charges.

i) $Na(g) \xrightarrow{\text{ionisation}} Na^{+}_{(g)} + e^{-}$
$2s^2 2p^6 3s^1$ $\qquad$ $2s^2 sp^6$
sodium cation

ii) $Cl(g) + e^{-} \xrightarrow{\text{affinity}} Cl^{-}$
$3s^2 3p^5$ $\qquad$ $3s^2, 3p^6$
chloride anion

iii) $Na^{+} + Cl^{-} \xrightarrow[\text{attraction}]{\text{electrostatic}} NaCl$
Sodium ion $\qquad$ Chloride ion $\qquad$ ionic/crystalline compound is formed

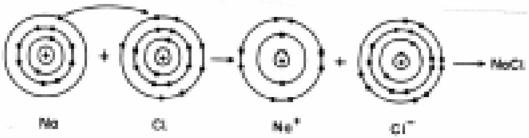


Fig. 10.2 Electron transfer between Na and Cl atoms during ionic bond formation in NaCl

In CaO, which is an ionic compound, the formation of the ionic bond involves two electron transfers from Ca to O atoms. Thus, doubly charged positive and negative ions are formed.

$Ca \xrightarrow{\text{ionisation}} Ca^{2+} + 2e^{-}$ (Calcium Cation)
$3p^6\, 4s^2$

$O + 2e^{-} \xrightarrow[\text{aaffinity}]{\text{electron}} O^{2-}$ (Oxide anion)
$2s^2\, 2p^4$ $\qquad$ $2s^2\, 2p^6$

$$Ca^{2+} + O^{2-} \xrightarrow[\text{attraction}]{\text{electrostatic}} \underset{\text{ionic compound}}{CaO}$$

Ionic bond may be also formed between a doubly charged positive ion with single negatively charged ion and vice versa. The molecule as a whole remains electrically neutral. For example in MgF_2, Mg has two positive charges and each fluorine atom has a single negative charge. Hence, Mg^{2+} binds with two fluoride (F^-) ions to form MgF_2 which is electrically neutral.

$$\underset{(2s^2\ 2p^6\ 3s^2}{Mg} \rightarrow \underset{(2s^2\ 2p^6)}{Mg^{2+}} + 2e^-$$

$$\underset{(2s^2\ 2p^5)}{2e + 2F} \rightarrow \underset{(2s^2\ 2p^6)}{2F^-}$$

i.e:- $Mg^{2+} + 2F^- \rightarrow MgF_2$
Magnesium - fluoride
(an ionic compound).

Similarly in Aluminium bromide ($AlBr_3$), Aluminium ion has three positive charges and therefore it bonds with three Bromide ions to form $AlBr_3$ which is a neutral ionic molecule.

$$\underset{2p^6\ 3s^2\ 3p^1}{Al} \rightarrow \underset{(2s^2,\ 2p^6)}{Al^{3+}} + 3e^-$$

$$\underset{(4s^2\ 4p^5)}{3\ Br + 3e^-} \rightarrow \underset{(4s^2\ 4p^6)}{3\ Br^-}$$

$Al^{3+} + 3Br^- \rightarrow AlBr_3$ (ionic bond)

10.3.1 Lattice energy and Born - Haber's cycle

Ionic compounds in the crystalline state exist as three dimensionally ordered arrangement of cations and anions which are held together by columbic interaction energies. The three dimensional network of points that represents the basic repetitive arrangement of atoms in a crystal is known as lattice or a space lattice. Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation.

Lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. That is, the enthalpy change of dissociation of MX ionic

www.tntextbooks.in

solid into its respective ions at infinity separation is taken the lattice enthalpy.

$$MX_{(s)} \rightarrow M^{+}_{(g)} + X^{-}_{(g)}$$

$$\Delta_r H^\circ = L.E$$

Lattice enthalpy is a positive value.

For example, the lattice enthaply of NaCl is 788 kJ.mol^{-1}. This means that 788 kJ of energy is required to separate 1 mole of solid NaCl into 1 mole of $Na^{+}_{(g)}$ and 1 mole of $Cl^{-}(g)$ to an infinite distance.

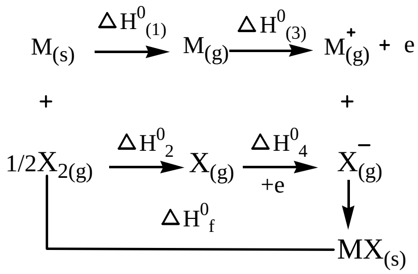
In ionic solids, the sum of the electron gain enthaply and the ionisation enthalpy may be positive but due to the high energy released in the formation of crystal lattice, the crystal structure gets stabilised.

Born Haber's Cycle

Determination of Lattice enthalpy

It is not possible to calculate the lattice enthalpy directly from the forces of attraction and repulsion between ions but factors associated with crystal geometry must also be included. The solid crystal is a three-dimensional entity. The lattice enthalpy is indirectly determined by the use of Born - Haber Cycle. The procedure is based on Hess's law, which states that the enthalpy change of a reaction is the same at constant volume and pressure whether it takes place in a single or multiple steps long as the initial reactants and the final products remain the same. Also it is assumed that the formation of an ionic compound may occur either by direct combination of elements (or) by a step wise process involving vaporisation of elements, conversion of gaseous atoms into ions and the combination of the gaseous ions to form the ionic solid.

For example consider the formation of a simple ionic solid such as an alkali metal halide MX, the following steps are considered.



ΔH^o_1 = enthalpy change for sublimation of $M_{(s)}$ to $M_{(g)}$

www.tntextbooks.in

ΔH^o_2 = enthalpy change for dissociation of 1/2 $X_{2(g)}$ to $X_{(g)}$

ΔH^o_3 = ionization energy of $M_{(g)}$ to $M^+_{(g)}$

ΔH^o_4 = electronic affinity or electron gain energy for conversion of $X_{(g)}$ to $X^-_{(g)}$

ΔH^o_5 = the lattice enthalpy for formation of solid MX (1 mole).

$\Delta_f H^o$ = enthalpy change for formation of MX solid directly from the respective elements such as 1 mole of solid M and 0.5 moles of $X_{2(g)}$.

According to Hess's law,

$\Delta H^o_f = \Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4 + \Delta H^o_5$[*]

Some important features of lattice enthalpy are:

i. The greater the lattice enthalpy the more stabler the ionic bond formed.

ii. The lattice enthalpy is greater for ions of higher charge and smaller radii.

iii. The lattice enthalpies affect the solubilities of ionic compounds.

Calculation of lattice enthalpy of NaCl

Let us use the Born - Haber cycle for determining the lattice enthalpy of NaCl as follows :

The standard enthalpy change, $\Delta_f H^o$ overall for the reaction,

$$Na_{(s)} + 1/2\ Cl_{2(g)} \rightarrow NaCl_{(s)} \text{ is } -411.3\ kJmol^{-1}$$

$$Na_{(s)} \quad + \quad ½\ Cl_{2(g)} \xrightarrow{\Delta_f H^o} NaCl_{(s)}$$

---

[*] The value of ΔH^o_5 calculated using the equation of Born - Haber cycle should be reversed in sign

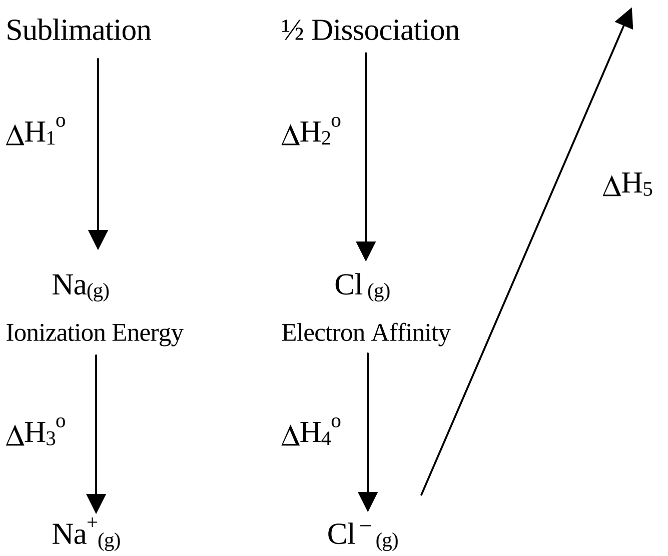


Fig. 10.3 Born-Haber cycle for Lattice enthalpy determination involving various stepwise enthalpic processes for NaCl solid formation

Since the reaction is carried out with reactants in elemental forms and products in their standard states, at 1 bar, the overall enthalpy change of the reaction is also the enthalpy of formation for NaCl. Also, the formation of NaCl can be considered in 5 steps.The sum of the enthalpy changes of these steps is considered equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

Atomisation :

ΔH°_1 for $Na(s) \rightarrow Na(g)$ is + 108.70 (kJ mol^1)

Dissociation:

ΔH°_2 for ½ $Cl_2(g) \rightarrow Cl(g)$ is + 122.0

Ionisation :

ΔH°_3 for $Na(g) \rightarrow Na^+(g) + e$ is + 495.0

Electron affinity :

ΔH°_4 for $e + Cl(g) \rightarrow Cl^-(g)$ is - 349.0

Lattice enthalpy :

ΔH°_5 for $Na^+(g) + Cl^-(g) \rightarrow NaCl(g)$ is ?

$$\Delta_f H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 + \Delta H^\circ_5$$

$-411.3 = 108.70 + 122.0 + 495 - 349.0 + \Delta H^\circ_5$

$\therefore \Delta H^\circ_5 = -788.0 \text{ kJ mol}^{-1}$

But the lattice enthalpy of NaCl is defined by the reaction $NaCl(g) \rightarrow Na^+(g) + Cl^-(g)$ only.

$\therefore$ Lattice enthalpy value from ΔH°_5 is written with a reversed sign.

$\therefore$ Lattice enthalpy of NaCl = $+788.0 \text{ kJ mol}^{-1}$.

Problem 1

Calculation of lattice enthalpy of $MgBr_2$ from the given data.

Solution

The enthalpy of formation of $MgBr_2$ according to the reaction

$Mg(s) + Br_2(l) \rightarrow MgBr_2(s); \Delta_f H^\circ = -524$ kJ/mol

ΔH°_1 for $Mg(s) \rightarrow Mg(g) = +148 \text{ kJ mol}^{-1}$

ΔH°_2 for $Mg(g) \rightarrow Mg^{2+}(g) + 2e^- = +2187 \text{kJ mol}^{-1}$

ΔH°_3 for $Br_2(l) \rightarrow Br_2(g) = 31 \text{ KJ mol}^{-1}$

ΔH°_4 for $Br_2(g) \rightarrow 2Br(g) = 193 \text{ KJ mol}^{-1}$

ΔH°_5 for $Br(g) + e^-(g) \rightarrow Br^- = -331 \text{ KJ mol}^{-1}$

ΔH°_6 for $Mg^{2+}(g) + 2Br^-(g) \rightarrow Mg\,Br_2(s) = ?$

$\Delta_f H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 + \Delta H^\circ_5 + \Delta H^\circ_6$

$$\begin{aligned} -524 \text{ kJ mol}^{-1} &= (+148 + 2187 + 31 \\ &\quad + 193 - 2(331) + \Delta H^0_6) \text{ kJ mol}^{-1} \\ &= -2421 \text{ KJ mol}^{-1} = \Delta H^0_6 \end{aligned}$$

Hence, lattice enthalpy of $Mg\,Br_2 = \Delta H^\circ_6 = 2421 \text{ kJ mol}^{-1}$

10.3.2 Properties of electrovalent (or) ionic compounds

Ionic compounds possess characteristic properties of their own like physical state, solubility, melting point, boiling point and conductivity. The nature of these properties are discussed as follows.

i. Due to strong coulombic forces of attraction between the oppositely charged ions, electrovalent compounds exist mostly as hard crystalline solids. Due to the hardness and high lattice enthalpy, low volatility, high melting and boiling points are seen.

ii. Because of the strong electrostatic forces, the ions in the solid are not free to move and act as poor conductor of electricity in the solid state. However, in the molten state, or in solution, due to the mobility of the ions electrovalent compounds become good conductor of electricity.

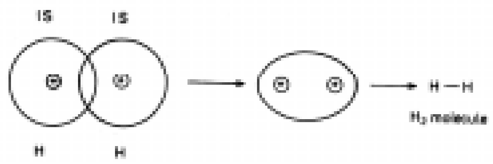
iii. Ionic compounds possess characteristic lattice enthalpies since they exist only as ions packed in a definite three dimensional manner. They do not exist as single neutral molecule or ion.

iv. Ionic compounds are considered as polar and are therefore, soluble in high dielectric constant solvents like water. In solution, due to solvation of ions by the solvent molecules, the strong interionic attractions are weakened and exist as separated ions.

v. Electrovalent compounds having the same electronic configuration exhibit isomorphism.

10.4 Covalent bond

A covalent bond is a chemical bond formed when two atoms mutually share a pair of electron. By doing so, the atoms attain stable octet electronic configuration. In covalent bonding, overlapping of the atomic orbitals having an electron from each of the two atoms of the bond takes place resulting in equal sharing of the pair of electrons. Also the interatomic bond thus formed due to the overlap of atomic orbitals of electrons is known as a covalent bond. Generally the orbitals of the electrons in the valency shell of the atoms are used for electron sharing. The shared pair of electrons lie in the middle of the covalent bond. Including the shared pair of electrons the atoms of the covalent bond attain the stable octet configuration. Thus in hydrogen molecule (H_2) a covalent bond results by the overlap of the two s orbitals each containing an electron from each of the two H atoms of the molecule. Each H atom attains '$1s^2$' filled K shell.



H_2 molecule

A covalent bond can be formed by sharing of s,p,d,f electrons also. Consider Cl_2 molecule. The outer shell electronic configuration of atom is $3s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$. When each chlorine atom mutually share the $2p_z$ unpaired electron contributed from each Cl atom of the molecule, a covalent bond is formed. By doing so, each chlorine atom attains argon electron configuration.

The Lewis dot structure will be :

More than one e^- can also be mutually shared to result in two covalent bonds between the atoms of a bond. Example in O_2 molecule (O=O) 2 covalent bonds exist.

The two unpaired electrons in $2p_y$ and $2p_z$ orbitals of each of O atom is mutually shared so that after the double bond formation stable octet electronic configuration is attained by each oxygen atom of the molecule.

In the phosphine PH_3 molecule, three hydrogen atoms combine with one phosphorous atom. Each hydrogen atom shares its 1s electron with phosphorous. So that three covalent bonds are formed in PH_3. The lewis dot structure is in Fig. 10.4.

In case of ethane molecule, the six C-H bonds and a C-C bond are covalent in nature. They are formed by mutual sharing of a pair of electrons between the two atoms of a bond. Each carbon atom completes its stable octet and each H atom has completed K shell.

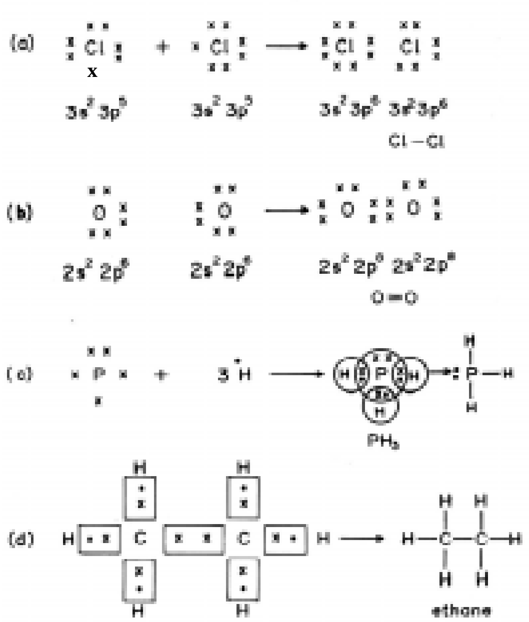


Fig. 10.4 Lewis dot structures of (a) Cl_2 (b) O_2 (c) PH_3 and (d) ethane molecules

Double bond formation

In oxygen (O_2) molecule, two pairs of electrons are mutually shared and a double bond results. The electronic configuration of O atom is $1s^2\ 2s^2\ 2p^4$. By sharing two more electrons from the other O atom, each O atom attains $2s^2\ 2p^6$, filled configuration. Thus O_2 molecule is represented as O = O. Similar to oxygen molecule in ethylene which is an organic molecule, a double covalent bond exists between the two carbon atoms due to the mutual sharing of two pairs of electrons. Each carbon atom attains the stable octet electron configuration.

10.4.1 Characteristics of covalent compounds

1. Covalent compounds are formed by the mutual sharing of electrons. There is no transfer of electrons from one atom to another and therefore no charges are created on the atom. No ions are formed. These compounds exist as neutral molecules and not as ions. Although some of the covalent molecules exist as solids, they do not conduct electricity

in fused or molten or dissolved state.

2. They possess low melting and boiling points. This is because of the weak intermolecular forces existing between the covalent molecules. Since, no strong coulombic forces are seen, some of covalent molecules are volatile in nature. Mostly covalent compounds possess low melting and boiling points.
3. Covalent bonds are rigid and directional therefore different shapes of covalent molecules are seen.
4. Most of the covalent molecules are non polar and are soluble in nonpolar (low dielectric constant) solvents like benzene, ether etc and insoluble in polar solvents like water. Carbon tetrachloride (CCl_4) is a covalent nonpolar molecule and is soluble in benzene.

10.4.2 Fajan's rules

Covalent character of ionic bonds

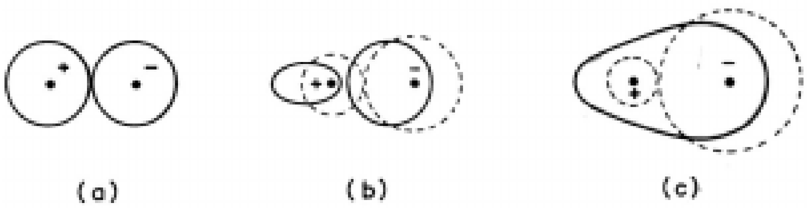


Fig. 10.5 Polarization effects : (a) idealized ion pair with no polarization, (b) mutually polarized ion pair (c) polarization sufficient to form covalent bond. Dashed lines represent hypothetical unpolarized ions

When cations and anions approach each other, the valence shell of anions are pulled towards cation nucleus due to the coulombic attraction and thus shape of the anion is deformed. This phenomenon of deformation of anion by a cation is known as **polarization** and the ability of cation to polarize a nearby anion is called as polarizing power of cation.

Fajan points out that greater is the polarization of anion in a molecule, more is covalent character in it. This is **Fajan's rule.**

Fajan also pointed out the influence of various factors on cations for polarization of anion.

(i) When the size of a cation is smaller than a cation with the same charge, then the smaller sized cation causes a greater extent of polarization on the anion than the larger sized cation.

(ii) The polarizing capacity of a cation is related to its ionic potential (which is Z^+/r) which is inversely related to the ionic radius. Therefore comparing Li^+ and Na^+ or K^+ ions, although these cations have single positive charge, Li^+ ion polarizes an anion more than Na^+ or K^+ ions can do on the same anion. This is because of the smaller size of Li^+ than Na^+ or K^+ ions.

(iii) Greater the polarization effects greater will be the covalent character imparted into the ionic bond.

The general trend in the polarizing power of cations: $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

$\therefore$ covalent character:

$$LiCl > NaCl > KCl > RbCl > CsCl.$$

a) Size of the anion

When the size of anion is larger, valence electrons are less tightly held by its nucleus. Therefore more effectively the cation pulls the valence electrons towards its nucleus. This results in more polarization effect. That is, for the same charge of the anion, larger sized anion is more polarized than a smaller sized anion.

The trend in the polarization of anions:

$$I^- > Br^- > Cl^- > F^-$$

$\therefore$ covalent character :

$$LiF < LiCl < LiBr < LiI$$

b) Charge on cation

If the oxidation state of the cation is higher the polarization of anion will be more. Thus more will be covalent nature in the bonding of the molecule.

Thus polarizing power: $Fe^{+2} < Fe^{+3}$

$\therefore$ Covalent character : $FeCl_2 < FeCl_3$.

www.tntextbooks.in

c) Presence of polar medium

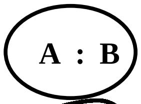
Presence of a polar medium keeps away the cations and anions from each other due to solvation. This prevents polarization of anion by the cation. Therefore $AlCl_3$ behaves as an ionic molecule in water, while it is a covalent molecule in the free state.

10.4.3 Polarity of Covalent Bonds

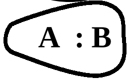
The existence of a purely ionic or covalent bond represents an ideal situation. In the covalently bonded molecules like H_2, Cl_2, F_2 (homonuclear diatomics), the bond is a pure covalent bond. In case of heteronuclear molecules like, HF, HCl, CO, NO etc, the shared electron pair gets displaced more towards the atom possessing higher electronegativity value than the other one. In HF, the shared electron pair is displaced more towards fluorine because the electronegativity of Fluorine is far greater than that of Hydrogen. This results in partial ionic character induced in the covalent bond and is represented as:

$$\overset{\delta+}{H} - \overset{\delta-}{F}$$

However, no specific charges are being found on H or F and the molecule as a whole is neutral. Thus the extent of ionic character in a covalent bond will depend on the relative attraction of electrons of the bonded atoms which depends on the electro negativity differences between the two atoms constituting the covalent bond.



a pure covalent bond

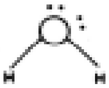


a polarised covalent bond.

Polarisation of a covalent bond causes fractional charges (δ+ or δ-) on the atoms which are separated by the bond distance. This causes a dipolar molecule formation.

Some dipolar molecules are

$\overset{\delta+}{H} - \overset{\delta-}{F}$; $\overset{\delta+}{H} - \overset{\delta-}{Cl}$,



www.tntextbooks.in

HF, HCl H_2O

As a result of polarisation, the molecule possessed a dipole moment. In a triatomic molecule like water two covalent bonds exist between the oxygen atom and the two H atoms. Oxygen with higher electronegativity attracts the shared pair of electrons to itself and thus oxygen becomes the negative end of the dipole while the two hydrogen atoms form the positive end. Thus the two covalent bonds in the water molecule possess partial ionic character.

Generally larger the electronegativity difference between the atoms consisting the bond, greater will be the ionic character. For H atom electronegativity is 2.1 and for Cl atom it is 3.0. Thus H-Cl covalent bond is polarised and it has more ionic character.

$$\overset{\delta+}{\mathrm{H}} - \overset{\delta-}{\mathrm{Cl}}$$

Consider the molecule like hydrogen cyanide HCN, the bond between hydrogen atoms and the cyanide anion is of covalent type. CN^- ion has more capacity to pull the shared pair of electrons in the H-CN bond that, partially H^+ CN^- are created. Thus in water medium this compound is ionised into H^+ and CN^- ions.

$$\mathrm{H} - \mathrm{C} \equiv \mathrm{N} \rightarrow \overset{\delta+}{\mathrm{H}} - \overset{\delta-}{\mathrm{CN}}$$

10.5 Valence Shell Electron Pair Repulsion Theory (VSEPR) Theory

Molecules exist in different shapes. Many of the physical and chemical properties of molecules arise due to different shapes of the molecules.

Some of the common geometrical shapes found among the molecules are: linear, trigonal, planar, tetrahedral, square planar, trigonal bipyramidal, square pyramidal, octahedral, pentagonal-bipyramidal etc. The VSEPR theory provides a simple treatment for predicting the shapes of polyatomic molecules. The theory was originally proposed by Sigdwick and Powell in 1940. It was further developed and modified by Nyholm and Gillespie (1957).

The basic assumptions of the VSEPR theory are that:

i) Pairs of electrons in the valence shell of a central atom repel each other.

ii) These pairs of electrons tend to occupy positions in space that minimize repulsions and maximise the distance of separation between them.

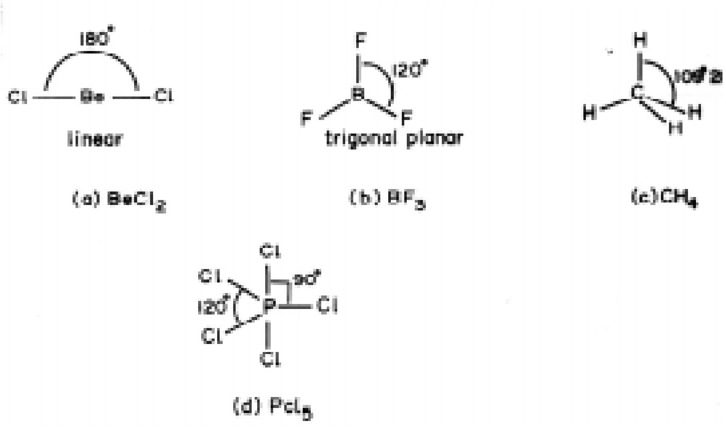
iii) The valence shell is taken as a sphere with electron pairs localising on the spherical surface at maximum distance from one another.

iv) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.

v) Where two or more resonance structures can depict a molecule the VSEPR model is applicable to any such structure.

It is convenient to divide molecule into two categories (i) molecules in which the central atom has no lone pairs of electrons and (i) molecules in which the central atom has one or more lone pairs.

Table 10.1 shows the different geometries of molecules or ions with central atom having no lone pair of electrons and represented by general type AB_x. In compounds of AB_2, AB_3, AB_4, AB_5, AB_6, types the arrangement of electron pairs (bonded pairs) as well as the B atoms around the central atom A are, linear, trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral respectively. Such arrangements are present in $BeCl_2$ (AB_2); BF_3 (AB_3); CH_4 (AB_4) and PCl_5 (AB_5) molecules with geometries as shown below in Fig.10.6.



(a) $BeCl_2$ (b) BF_3 (c) CH_4

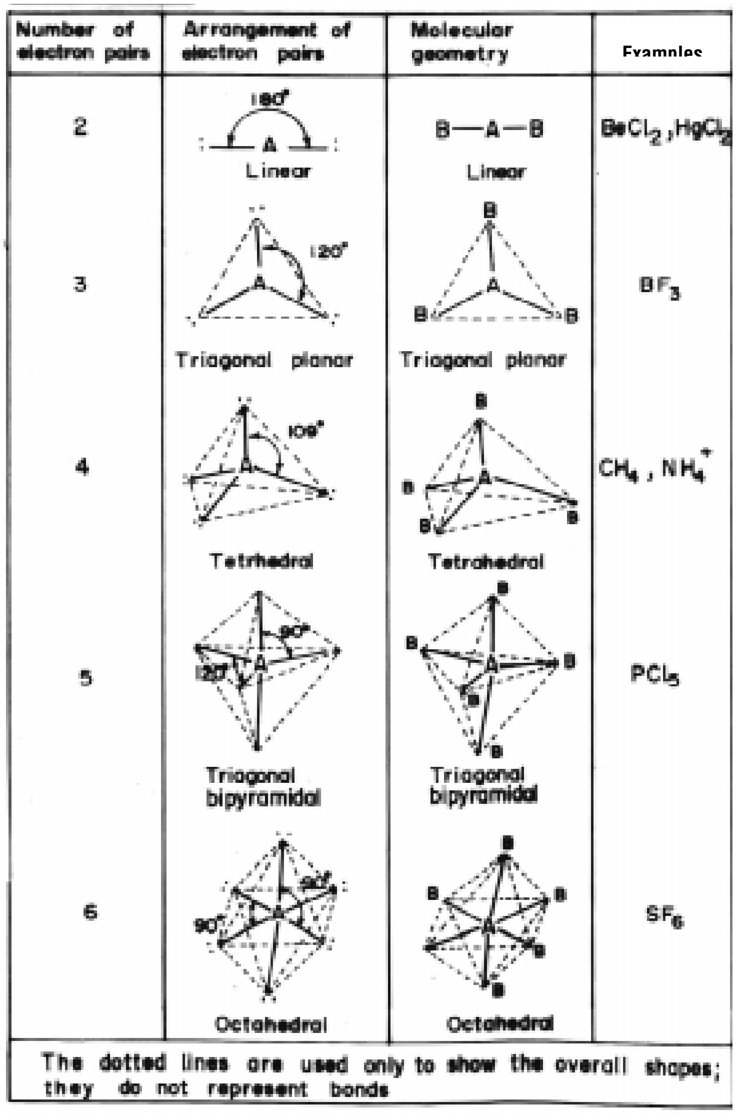
(d) PCl_5

Fig. 10.6 Geometrical structures of some molecules (a) $BeCl_2$ (b) BF_3 (c) CH_4 and (d) PCl_5

www.tntextbooks.in

Table 10.1

Geometry of molecules in which the central atom has no lone pair of electrons



Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	180° A Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	120° A Triagonal planar	B A B B Triagonal planar	BF_3
4	109° A Tetrhedral	B A B B B Tetrahedral	CH_4, NH_4^+
5	90° 120° A Triagonal bipyramidal	B B A B B B Triagonal bipyramidal	PCl_5
6	90° 90° A Octahedral	B B B A B B B Octahedral	SF_6
The dotted lines are used only to show the overall shapes; they do not represent bonds			

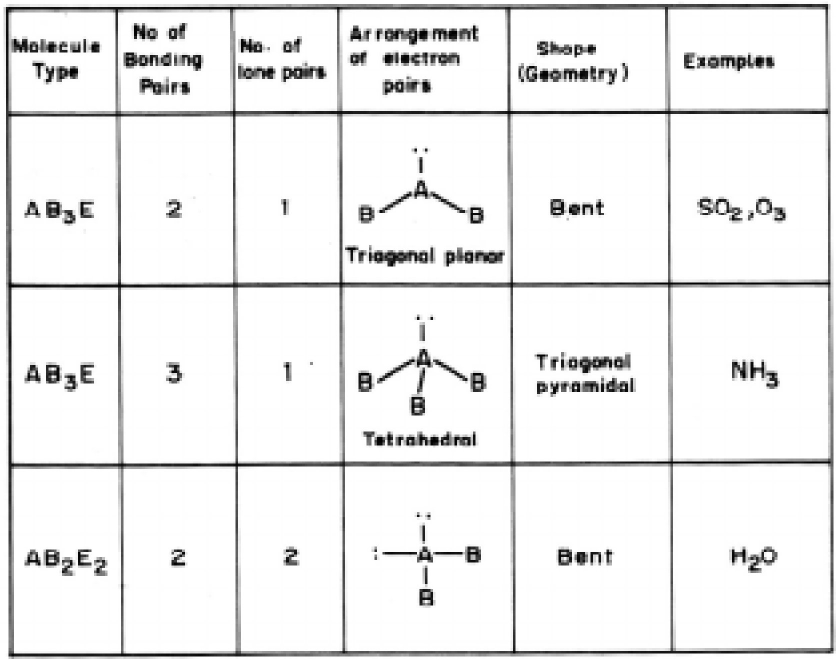
In case of molecules with the central atom having one or more lone pairs VSEPR treatment is as follows: In these type of molecules, both lone pairs and bond pairs of electrons are present. The lone pairs are localised on the central atom, and bonded pairs are shared between two atoms. Consequently, the lone pair electrons in a molecule occupy more space as compared to the bonding pair electrons. This causes greater repulsions between lone pairs of electrons as compared to the lone pairs of electrons to the lone pair (lp) - bonding pair and bonding pair - bonding pair repulsions (bp).

The descending order of repulsion interaction is

$$\boxed{\text{lp - lp > lp - bp > bp – bp}}$$

These repulsion effects cause deviations from idealised shapes and alterations in the predicted bond angles in molecules.

Table 10.2

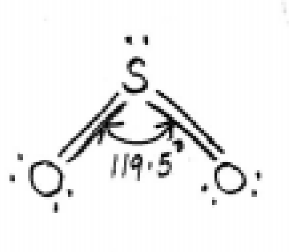


Molecule Type	No of Bonding Pairs	No. of lone pairs	Arrangement of electron pairs	Shape (Geometry)	Examples
AB_3E	2	1	Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	Tetrahedral	Triagonal pyramidal	NH_3
AB_2E_2	2	2		Bent	H_2O

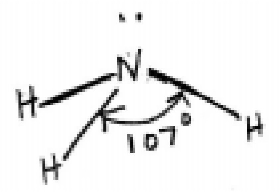
Examples : In sulphur dioxide molecule there are three electron pairs on the S atom. The overall arrangement is trigonal planar. However, because one of the three electron pairs is a lone pair, the SO_2 molecule has a `bent' shape and due to the lp - lp repulsive interactions the bond angle is reduced

www.tntextbooks.in

to 119.5° from the value of 120°.



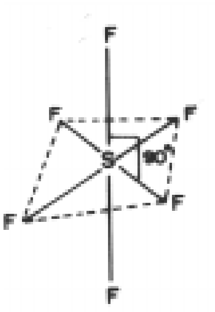
In the ammonia (NH_3) molecule, there are three bonding pairs and one lone pair of electrons. The overall arrangement of four electron pairs is tetrahedral. In NH_3, one of the electron pairs, on nitrogen atom is a lone pair, so the geometry of NH_3 is pyramidal (with the N atom at the apex of the pyramid). The three N-H bonding pairs are pushed closer because of the lp-bp repulsion and the HNH angle gets reduced from 109°28' (which is the tetrahedral angle) to 107°.



The water H_2O molecule, oxygen atom contains two bonding pairs and two lone pairs of electrons. The overall arrangement for four electron pairs is tetrahedral, but the lp - lp repulsions being greater than lp-bp repulsions in H_2O. The HOH angle is reduced to 104.5° than 109°28'. The molecule has a bent shape.

104.5°

The molecule SF_6 belongs to AB_6 type consisting of 6 bp of electrons around the central sulphur atom. The geometrical arrangement will be a regular octahedral.



SF$_6$ molecule

10.6 Directional Properties of Covalent Bonds

When the overlapping of orbitals occur along the internuclear axis (Line joining the two nuclei) then the electron orbitals merge to form cylindrically symmetrical region and the bond is called as `σ' bond. In a σ bond, maximum extent overlap of orbitals are possible and the bond formed is also stronger.

For e.g : H-H bond is a σ bond.

Consider the valence bond description of O_2 molecule : the valence shell electron configuration of each O atom is $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. It is conventional to take z axis as the inter nuclear axis or molecular axis. Along the molecular axis, overlap of $2P_z$ orbital of two O atoms occur with cylindrical symmetry thus forming a **σ bond.**

The remaining two $2p_y$ orbitals of two O atoms cannot overlap to the full extent like a σ bond as they do not have cylindrical symmetry around the internuclear axis. Instead, $2p_y$, orbitals overlap laterally (sideways) above and below the axis and share the pair of electrons. The bond formed by lateral overlap of p orbitals above and below the axis together is called a **π (Pi) bond**. Since $2p_y$ orbitals are perpendicular to $2p_z$ orbitals, π bond formed is perpendicular to the σ bond. Thus bonding in oxygen molecule is represented as in fig. 10.8(a).

There are two bonds in O_2 molecule. One of which is a σ bond and another is π bond.

Similarly, in N_2 molecule, 3 bonds are present between 2N atoms. The nature of orbital overlaps in the 3 bonds can be considered as in fig. 10.8(b).

www.tntextbooks.in

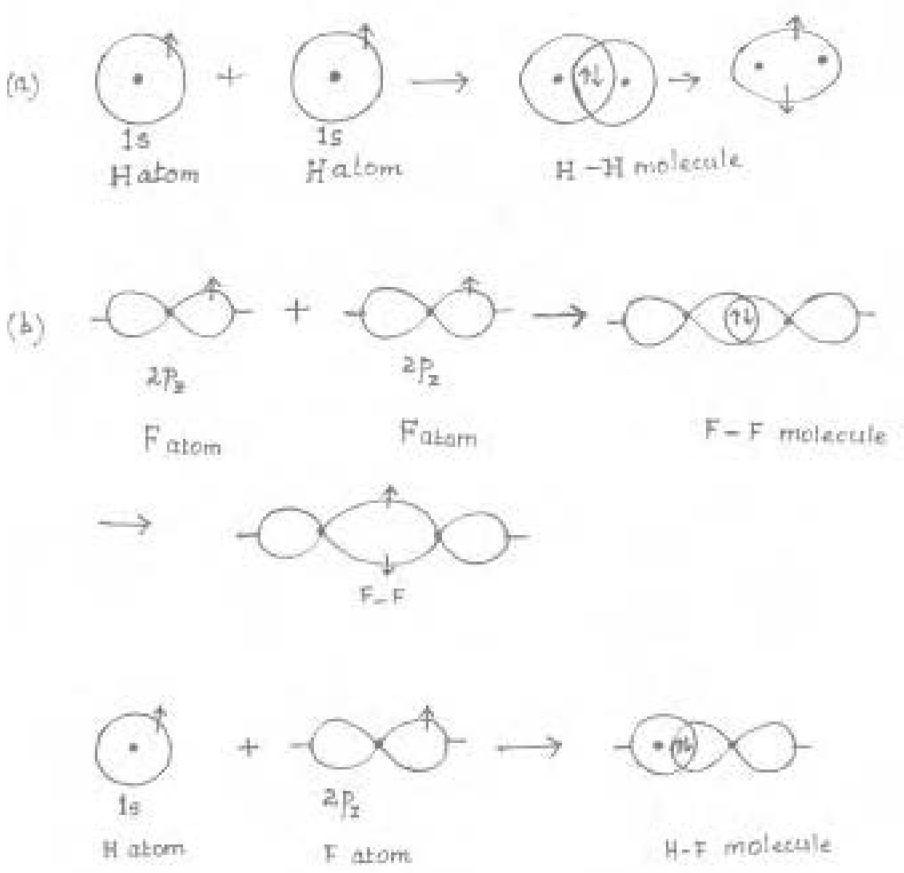


Fig.10.7

www.tntextbooks.in

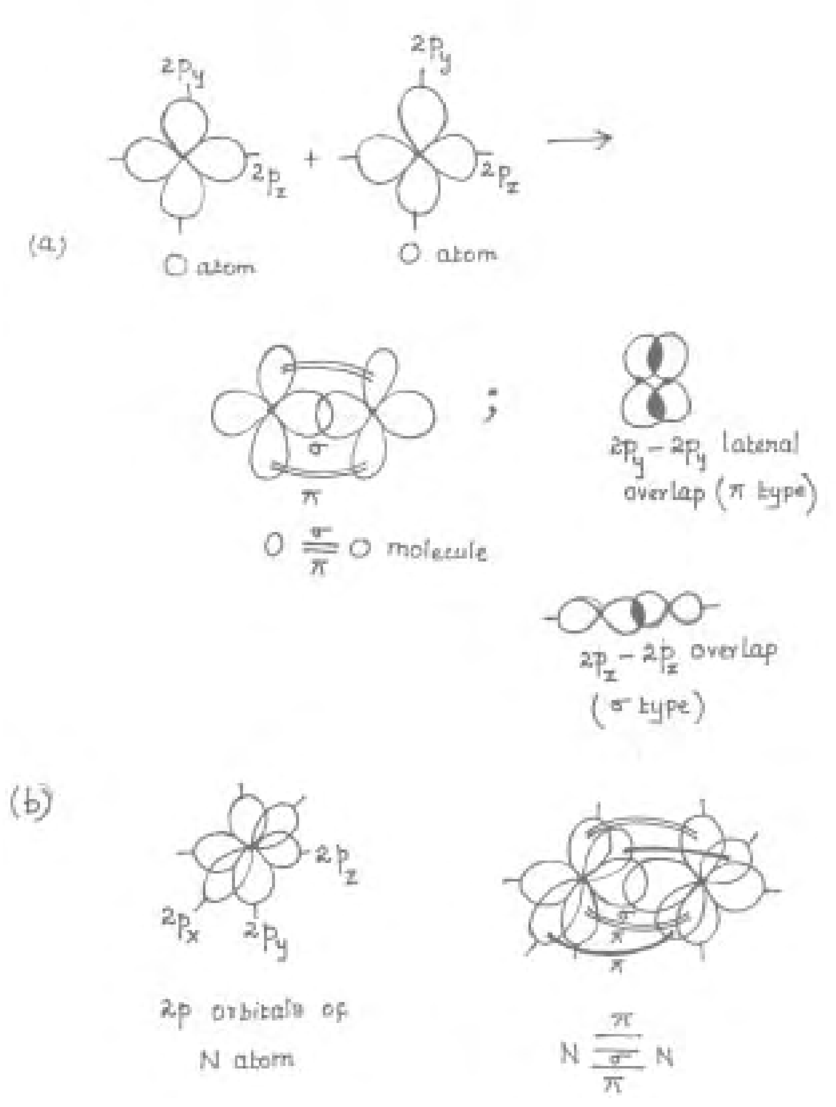


Fig.10.8

to the σ bond. Thus bonding in oxygen molecule is represented as in Fig. 10.8(a).

There are two bonds in O_2 molecule. One of which is a σ bond and another is π bond.

Similarly, in N_2 molecule, 3 bonds are present between 2N atoms. The nature of orbital overlaps in the 3 bonds can be considered as in Fig. 10.10.

The valence electronic configuration of nitrogen atom is $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$.

Cylindrically symmetrical overlap of two $2p_z$ orbitals give a σ bond and lateral overlap of two $2p_y$ orbitals give a π bond perpendicular to σ bond. Similarly, two $2p_z$ orbitals laterally overlap to give another π bond which is perpendicular to both σ, π bonds.

Based on the valence bond orbital overlap theory, the H_2O molecule is viewed to be formed by the overlap 1s orbital of a H atom with $2p_y$ orbital of O atom containing one electron each forming a σ bond. Another σ bond is also formed by the overlap of 1s orbital of another H atom with $2p_x$ orbital of O atom each containing an unpaired electron. The bond angle is therefore 90° (i.e : HOH bond angle is 90°), since $2p_x$ and $2p_y$ orbitals are mutually perpendicular to each other. However the actual bond angle value is found to be 104°. Therefore based on VB theory, pure orbital overlaps does not explain the geometry in H_2O molecule.

Similarly, in NH_3, according to VB theory each of N-H bonds are formed by the overlap of a 2p orbital of N and 1s orbital of H atoms respectively. Here again the bond angle of HNH bond is predicted as 90°. Since $2p_x$, $2p_y$ and $2p_z$ orbitals of N are mutually perpendicular. However the experimental bond angle of HNH bond value is found to be 107°.

10.6.1 Theory of Hybridisation

The failures of VB theory based on pure orbital overlaps are explained agreeably based on the concept of hybridisation of orbitals or mixing up of orbitals. There are three major processes that are considered to occur in hybridisation of orbitals. These are:

i) Promotion of electrons to higher or similar energy levels

ii) Mixing up of various s,p,d,f orbitals to form the same number of new orbitals and

www.tntextbooks.in

iii) Stabilisation of the molecule through bond formations involving hybrid orbitals by release of certain amount of energy which compensates the energy requirement in the electron promotion process.

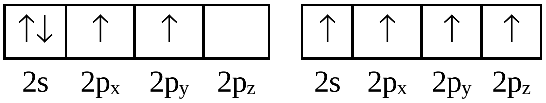
i) Promotion (Excitation) of Electrons

Atoms of elements like Beryllium, Boron and Carbon have electronic configuration as,

Be (At. no : 4) : $1s^2 2s^2$
B (At. no : 5) : $1s^2 2s^2 2px^1$
C (At. no : 6) : $1s^2 2s^2 2px^1 2py^1$

According to VB theory, Beryllium is expected to behave like a noble gas due to its filled shells, which in practice forms a number of compounds like BeF_2 and BeH_2 proving its bivalency. In case of Boron VB theory predicts univalency due to the presence of one unpaired electron but in practice Boron is trivalent since compounds as BCl_3, BH_3 etc. are found.

The stable state (Ground State) electronic configuration of C is ($2s^2 2p_x^1 2p_y^1$). Electronic configuration of C suggests only bivalency. But carbon forms over a million compounds in all of which carbon is tetravalent. This suggests only tetravalency. This deficiency is overcome by allowing for **promotion** (or) **the excitation** of an electron to an orbital of higher energy. Although for electron promotion energy is needed, if that energy is recovered back during a covalent bond formation, or by a bond with a greater strength or by many number of bonds formation, then the electron promotion becomes energetically allowed and assumed to take place initially. In carbon, promotion of an electron to an orbital which is close to itself with an empty orbital of only slightly higher energy which is the $2p_z$ orbital can take place. Then the electron pair is unpaired itself by absorbing the required energy available by the atom from its surrounding and one of the electrons in the original orbital 2s or 2p shifts to the empty higher energy orbital.



Ground state electronic configuration of C

Excited state configuration of C.

Thus promotion of an electron leads to four unpaired electron in the excited state electronic configuration of carbon atom. Each electron can now be utilised to form a covalent bond by sharing an electron coming from the combining atom. Thus four σ covalent bonds are possible, each with equivalent strength and overlapping tendency. Further, chemical and physical evidences reveal the four bonds of carbon to be equivalent and that they are tetrahedrally oriented. The promotion of an electron from 2s to 2p orbital leads to four half filled orbitals which can form four bonds leading to greater energy lowering. This energy is more than the initial energy required for the promotion of 2s electron to 2p orbital.

Hybridisation (mixing of orbitals)

After an electron promotion the 4 electrons are not equivalent, since one of them involves with an s orbital while the other three involve with p orbitals. To explain the equivalence of the four bonds, the concept of hybridisation is introduced.

Dissimilar orbitals like s,p,d with one or many numbers, with nearly the same energy on the same atom may combine or mix completely to form an equal number of equivalent energy new orbitals with properties of their own. This is called **as hybridisation** of orbitals. The new orbitals formed are known as hybrid orbitals and these orbitals possess the properties of the pure orbitals that are mixed to form them. The hybrid orbitals of an atom are symmetrically distributed around it in space. Essentially, mixing up of orbitals to form new orbitals explains the different geometries of many compounds like CH_4, SF_6 etc.

10.7 Concept of Resonance

According to the concept of resonance whenever a single Lewis structure cannot describe a molecular structure accurately, a number of structures with similar energy, positions of nuclei, bonding and non bonding pairs of electrons are considered to represent the structure. Each such structure is called as canonical structure. A resonance hybrid consists of many canonical structures. All the canonical structures are equally possible to represent the structure of the molecule.

For example, in ozone (O_3) molecule, the two canonical structures as shown below and their hybrid represents the structure of O_3 more

www.tntextbooks.in

accurately. Resonance is represented by a double headed arrow placed between the canonical structures. There are two canonical forms of O_3.

The resonance structures are possible for molecular ions also. For example, consider resonance in CO_3^{2-} ion:-

The single Lewis structure based on the presence of two single bonds and one double bond between each carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to experimental findings all carbon to oxygen bonds in CO_3^{2-} are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms as shown in Fig. 10.9 b.

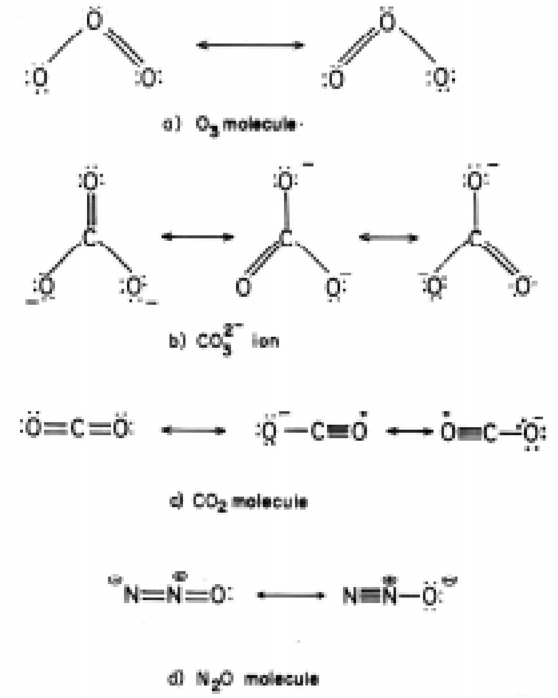


Fig. 10.9 Resonance structures of (a) Ozone (b) Carbonate ion (c) Carbon dioxide (d) Nitrousoxide

There are three canonical forms of CO_3^{2-}.

Structure of CO_2 molecule is also an example of resonance, the experimental C-O bond length is found to be shorter than C-O single bond length and longer than C=O bond length and lies intermediate in value between a pure single and a pure double bond lengths. Also the two C=O bond length in the CO_2 molecule are equivalent and the properties of the two bonds are also the same. Therefore, a single lewis structure cannot depict the structure of CO_2 as a whole and it is best described as a resonance hybrid of the canonical forms given in Fig. 10.9c.

In N_2O molecule which is a linear molecule, structures with charges on atoms can be written similar to CO_2.

- Here also the experimental bond length of N-N-bond lies between a double and triple bond and that of N-O bond length lies between a single and a double bond. Therefore N_2O exists as a hybrid structure of the two canonical forms with a linear geometry.

10.8 Co-ordinate-covalent bonding or Dative bonding

The electron contributions of combining atoms in a covalent bond are generally equal. In each shared pair of electrons one electron is contributed from each atom of the bond. However in some bond formation, the whole of the shared pair of electrons comes from only one of the combining atoms of the bond, which is to referred as the donor atom. The other atom which does not contribute the electron to the shared pair but tries to pull the pair of electron towards itself is called as the acceptor atom. The bond thus formed is between the donor and acceptor atoms is called as the **co-ordinate or co-ordinate - covalent or dative bond.**

A coordinate bond is showed as an arrow which points from the donor to the acceptor atom. In some cases, the donated pair of electron comes from a molecule as a whole which is already formed to an already formed acceptor molecule as a whole.

For Example, coordination bond between $H_3N:$ and BF_3 molecules. The molecule, ammonia (donor) which gives a pair of electron (lone pair) to BF_3 molecule which is electron deficient (acceptor) which has an empty orbital to accommodate the pair of electrons. Thus a dative bond is formed and the molecule as a whole is represented as $H_3N \rightarrow BF_3$ (Fig. 10.10a).

When Proton is added to ammonia, a pair of electron is donated by nitrogen to proton and then proton shares the electron pair to form coordinate covalent bond.

www.tntextbooks.in

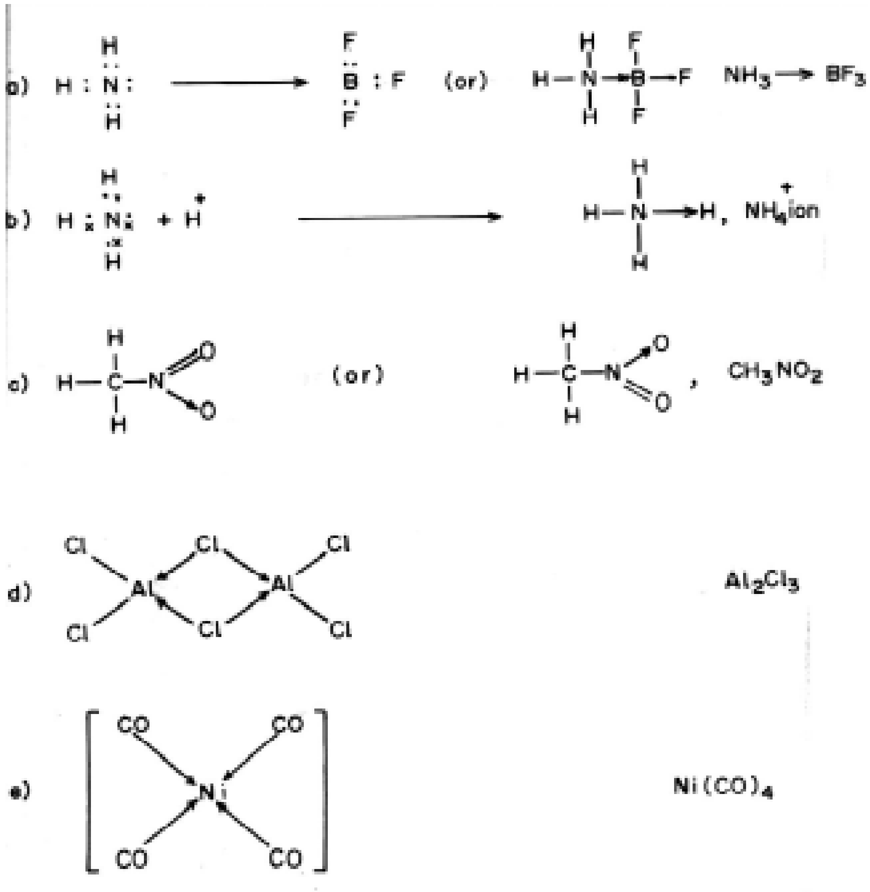


Fig. 10.10 Coordinate bonding in
(a) ammonia-borontrifluoride (b) ammonium ion
(c) nitromethane
(d) Aluminium chloride and
(e) Nickel tetracarbonyl

Similarly in (NH_4Cl) ammonium chloride, covalent - coordinate bond exists in NH_4^+ ion only and Cl^- ion exists as it is.

Few examples of covalent - coordinate bond :

In nitro methane (CH_3 - NO_2), one of the N-O-bond exists in a covalent coordinate type.

www.tntextbooks.in

Aluminum chloride Al_2Cl_6 (dimeric form)

Lone pairs of electron from chlorine are donated to electron deficient aluminium atoms in such a way that dimers of $AlCl_3$ are formed easily (Fig. 10.10d). The two chlorine atoms act as bridge to link the two Aluminium atoms.

In some complex ion formations, if the central transition metal-ion has empty `d' orbitals then lone pair of electrons from neutral molecules or anions are donated resulting in the formation of coordination bonds. Example : In Nickel tetracarbonyl, the four bonds between central Ni atom and the carbonyl ligands are mainly covalent -coordinate type. This complex exists in square planar geometry.

Questions

A. Choose the correct answer

1. The crystal lattice of electrovalent compounds is composed of
   (a) Atoms (b) Molecules
   (c) Oppositely charged ions (d) Both molecules and ions
2. The compound which contains both ionic and covalent is
   (a) CH_4 (b) H_2 (c) KCN (d) KCl

B. Fill in the blanks

3. In NaCl, Na^+ ion has _______________ and Cl^- ion has _________ electron configurations.
4. Linear overlap of two atomic p-orbitals leads to ____________.
5. Born-Haber cycle is related with ________.
6. Two atoms of similar electronegativity are expected to form ____ compounds.
7. Repulsion between bond pair-bond pair is than in between lonepair-lone pair.

C. Match the following

1. Electrovalent bonding	a. Benzene
2. Covalent bonding	b. Heitler and London
3. Valence Bond theory	c. Electron transfer
4. Polarised Bond	d. Electron sharing
5. Resonance	e. Fajan's theory
	f. Aluminium chloride

D. Write in one or two sentence

1. Arrange NaCl, $MgCl_2$ and $AlCl_3$ in the increasing order of covalent character.
2. Find σ and π bonds in the following :

   CH_3-CH_3, CH_2=CH_2, CH≡CH
3. Among Na^+, Ca^{+2}, Mg^{+2}, Al^{+3} which has high polarising power ?
4. What is the structure of $BeCl_2$?
5. Write the differences between electrovalent and covalent bonds.
6. Give reason : CCl_4 is insoluble in H_2O while NaCl is soluble.
7. sp^3 hybridisation is involved in CH_4, H_2O and NH_3. Why are the bond angles different in three cases?
8. Explain the co-ordinate bond formation between BF_3 & NH_3.
9. What is octet rule? Explain with an example.
10. What are the different types of bonds?
11. What is meant by electrovalent bond. Explain the bond formation in $AlBr_3$ and CaO.
12. Give the electron dot representation for PH_3 and ethane.
13. Write the Lewis dot structures for the following. S, S^{2-}, P, P^{3-}, Na, Na^+, Al and Al^{3+}.
14. What are the important features of valence bond theory?
15. What is meant by hybridisation?
16. Define resonance. Give the various resonance structures of CO_2 and CO_3^{2-} ion.

E. Explain briefly on the following

1. Discuss the important properties of electrovalent compounds.
2. Calculate the lattice energy of NaCl using Born-Haber cycle.
3. Explain the important properties of covalent compounds.
4. Discuss the partial covalent character in ionic compounds using Fajan's rule.
5. Explain the polarity of covalent bonds in H_2O and HCl.
6. Discuss the shapes of following molecules : NH_3, H_2O, CH_4, PCl_5 and SO_2.

7. Discuss VSEPR model applied for linear, trigonal planar, tetrahedral and octahedral geometries of molecules.
8. Explain the formation and difference between a sigma bond and a pi-bond. Which has more bond strength?
9. Calculate the lattice enthalpy of $CaCl_2$ given that the enthalpy of :

i) Sublimation of Ca in 121 kJ mol^{-1}

ii) Dissociation of Cl_2 to 2Cl is 242.8 kJ mol^{-1}

iii) Ionisation of Ca to Ca^{2+} is 2422 kJ mol^{-1}

iv) Electron gain for Cl to Cl^- is -355 kJ mol^{-1}

v) $\Delta H_f^{(o)}$ overall is -795 kJ mol^{-1}

(Ans : 2870.8 kJ mol^{-1})

SUMMARY

- Chemical bonding is defined and Kossel-Lewis approach to understand chemical bonding by using the octet rule is studied. Except helium, atoms share or transfer valence electrons to attain the stable octet shell as the electronic configuration.
- Ionic bonding results due to complete electron transfer from electropositive elements to electronegative elements forming cation and anion. Electrostatic force of attraction between ions describe the ionic bonding. Mutual sharing of electrons between the two atoms result in covalent bonding. The directional character, partial ionic character by the pure orbital overlaps are also studied with suitable examples.
- The geometry of simple molecules are predicted using the postulates of VSEPR model $BeCl_2$: linear; CH_4 : Tetrahedral; BCl_3 : trigonal; PCl_5 : trigonal bipyramidal; SF_6 : Octahedral.
- The concept of hybridisation of C, N, O are learnt. σ and π bonds are studied and differentiated. Resonance in benzene, carbonate ion, molecules are understood.
- Formation of coordinate covalent (dative) bonding between Lewis acids and electron donors are studied. $Al_2 Cl_6$ is covalent but in water, it is ionic. Coordinate-covalent bonding in $Ni(CO)_4$ is also understood.

11. COLLIGATIVE PROPERTIES

OBJECTIVES

- *To know about colligative properties and the scopes to determine molar mass of the non-volatile solute.*
- *To define Raoult's law and relate the relative lowering of vapour pressure to the molar mass of the solute in the solution.*
- *To determine experimentally the depression in freezing point by Beckmann method and use it to find the molar mass of a non-volatile solute.*
- *To know cottrell's method of elevation of boiling point and use it know the molar mass of a nonvolatile solute.*
- *To understand the concept of osmosis and to find the molar mass of a solute using osmotic pressure.*
- *To explain abnormal colligative properties as due to association and dissociation of solute molecules.*

11.1 Colligative Properties and its Scope

A solution may be considered as a homogeneous (single phase) mixture of two or more substances. It is said to be `binary' if two substances are present and `ternary' if three substances are present and `quaternary' if four substances are being present etc. In a binary solution, the component present in larger amount is called as solvent and the component in smaller amounts is called as solute. Solvent and solute together make a solution. In dilute solutions, very small amount of the solute is present.

A colligative property of a solution depends purely on the number of particles dissolved in it, rather than on the chemical nature of the particles. The colligative properties can be regarded as the properties of the solvent in a given solution. Generally, the solute is considered as non-volatile. The various colligative properties are as below :

i. Lowering of vapour pressure of the solvent (Δp)

www.tntextbooks.in

ii. Elevation of boiling point of the solvent (ΔT_b)
iii. Depression of freezing point of the solvent (ΔT_f)
iv. Osmotic pressure (π).

The important scope of the measurement of colligative properties lies on its use to determine the molar mass of the non-volatile solute dissolved in the dilute solution.

11.2 Lowering of Vapour Pressure (Δp)

If we take a pure liquid in a closed container, we find that a part of the liquid evaporates and fills the available space with its vapour. The vapour exerts a pressure on the walls of the container and exists in equilibrium with the liquid. This pressure is referred as the vapour pressure of the liquid.

When a non-volatile solute is dissolved in the solvent so that a dilute and homogeneous solution results, then again the vapour pressure of the solution will be made up of entirely from the solvent since the solute does not evaporate. This vapour pressure of the dilute solution is found to be lower than the vapour pressure of the pure solvent.

From Fig.11.1 it may be seen the surface of a dilute solution is partly occupied by solute molecules, thereby the number of solvent molecules at the surface being reduced. Consequently the vapour pressure of the solvent molecules gets lowered on the surface of the solution.

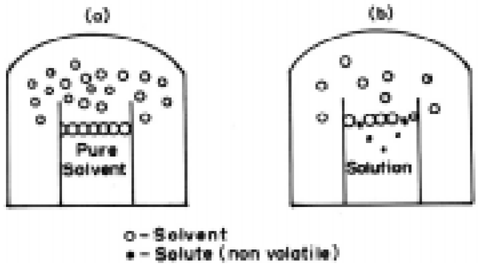


Fig. 11.1 Effect of solute in the solution on the vapour pressure

11.3 Raoult's Law

The relationship between the vapour pressure of the solution and its concentration is given by a French chemist named Francois Marie Raoult (1886). According to Raoult's law, at constant temperature the vapour pressure of the solution (p) is directly proportional to the molefraction of the solvent (X_1) present in the solution. That is, $p \propto X_1$ (or) $p = kX_1$ where k is the proportionality constant. The value of k is known as follows: For a pure solvent, $X_1 = 1.0$ and p becomes p° corresponding to the vapour pressure of the pure solvent. Thus, $p^\circ = k\,(1.0)$. Substituting the value of k,

$$\boxed{p = p^\circ X_1} \qquad \ldots\ 11.1$$

Equation 11.1 is generally known as Raoult's law.

When n_1 and n_2 are the number of moles of solvent and solute present in the solution, the molefraction of the solvent $X_1 = n_1/(n_1 + n_2)$ and the mole fraction of solute $X_2 = n_2/(n_1+n_2)$. Also, $X_1 + X_2 = 1.0$

If W_1 and W_2 are the weights of solvent and solute present, then $n_1 = W_1/M_1$ and $n_2 = W_2/M_2$. M_1 and M_2 are the molar masses of solvent and solute respectively.

It is generally observed that p is lower than P°. The lowering of vapour pressure of the solvent in the solution equals to $(p^\circ - p) = \Delta p$.

The relative lowering of the vapour pressure, is defined as the ratio of the lowering of vapour pressure to the vapour pressure of the pure solvent. Thus relative lowering of vapour pressure is given by

$$\frac{p^\circ - p}{P^\circ} = \frac{\Delta p}{P^\circ}$$

$$\frac{p^\circ - p}{p^\circ} = \frac{p^\circ - p^\circ X_1}{p^\circ} \qquad \text{since } p = p^\circ X_1$$

$$\frac{P^\circ(1-X_1)}{P^\circ} = 1-X_1 = X_2 \ldots \text{ since } \{X_1+X_2 = 1\}$$

$$\boxed{\therefore \frac{p^\circ - p}{p^\circ} = X_2} \qquad \ldots\ 11.2$$

Equation 11.2 represents the mathematical from of Raoults law. Thus, the statement of Raoult's law for dilute solutions containing non-volatile non-electrolyte solute is: Relative lowering of vapour pressure is equal to the mole fraction of the solute. Since mole fraction of the solute (X_2) is given by $n_2/(n_1+n_2)$, the quantity $(p^\circ-p)/p^\circ$ depends upon the number of moles or molecules of the solute in solution and not on its chemical nature. Thus, relative lowering of vapour pressure is a colligative property.

11.3.1 Determination of molecular weights from relative lowering of vapour pressure

In dilute solutions, the number of moles of solvent (n_1) is large compared to the number of moles of solute (n_2) and thus ($n_1 + n_2$) can be approximated to n_1 and x_2 becomes equal to n_2/n_1.

$$\text{Thus} \quad \frac{\Delta p}{p^\circ} = \frac{n_2}{n_1} = \frac{W_2.M_1}{M_2.W_1} \qquad \text{... 11.3}$$

Substituting for n_1 and n_2 as W_1/M_1 and W_2/M_2 we get $\Delta p/p^\circ = M_1.W_2/W_1.M_2$. Knowing M_1,W_1 and W_2 and from the measurement of lowering of vapour pressure, M_2 the molar mass of the solute can be determined using equation 11.3.

Problem 1

The vapour pressure of CCl_4 at 30°C is 143 mm of Hg.0.5 gm of a non-volatile non electrolyte substance with molar mass 65 is dissolved in 100 ml of CCl_4. What will be the vapour pressure of the solution. Density of CCl_4 at 30°C = 1.58 gm per cc.

Solution

Vapour pressure of pure solvent, P°=143mm of Hg.

Vapour pressure of solution, p = ?

Weight of solute, $W_2 = 0.5$ gm

Mol. wt of solute, $M_2 = 65$

Mol. wt of solvent (CCl_4), $M_1 = 154$

Weight of solvent, $W_1 = 100\text{x}1.58 = 158$ gm

(mass = density x volume)

$$\frac{p^\circ - p}{P^\circ} = \frac{W_2}{M_2} \cdot \frac{M_1}{W_1} \text{ (By Raoult's law)}$$

$$\therefore \frac{143 - P}{143} = \frac{0.5}{65} \times \frac{154}{158}$$

$$\therefore p = 141.93 \text{ mm of Hg.}$$

11.3.2 Experimental determination of relative lowering of vapour pressure

Dynamic method (or) Ostwald - Walker method

This method is based on the principle that when dry air is successively passed through a series of containers possessing solution and pure solvent respectively, the air becomes saturated with the solvent vapours and an equal amount of weight loss in solution and solvent containers takes place.

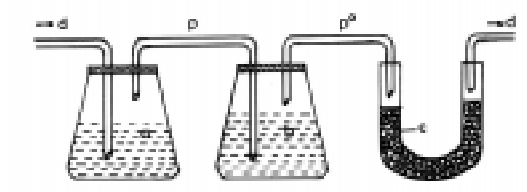


Fig. 11.2 Ostwald - walker apparatus

In Fig. 11.2 the first chamber (a) contains a weighed amount of the solution under examination and the next chamber (b) contains a weighed amount of the pure solvent. A weighed amount of anhydrous and dry calcium chloride is taken in the U-tube (c) connected at the end. The chambers and the U-tube are connected by a series of delivery tubes (d) through which air is passed. The dry air is first allowed to pass through the solution chamber until the air is saturated with the solvent vapour to maintain the vapour pressure of the solution `p'. Consequently, a loss in weight of the solution results in the solution chamber since some amount solvent molecules have evaporated. When this air is allowed to pass through the pure solvent chamber some more solvent vapour gets in stream with air, until the vapour pressure of pure solvent p°, is maintained. This

www.tntextbooks.in

happens so because p° is greater than p. Consequently, the weight loss registered in the solvent chamber is proportional to the (p°-p) quantity.

The weight loss in solution chamber α p
The weight loss in solvent chamber α p°-p
Sum of the loss in weights of solution
and solvent chamber α (p+p°-p) α p°

When the air saturated with solvent vapours is passed through $CaCl_2$ U-tube, the solvent vapours are absorbed and the dry air gets out. The gain in weight of the $CaCl_2$ U-tube should be equal to the total loss in weight of solution and solvent chambers, which is inturn proportional to p°.

$$\frac{\text{Loss in weight of the solvent chamber}}{\text{Gain in weight of } CaCl_2 \text{ tube}} = \frac{p^\circ - p}{p^\circ}$$

= relative lowering of the vapour pressure

Thus, using the experimental (p°-p)/p° values and applying Raoult's law, the molecular weight of the solute can be determined.

Problem 2

Dry air was passed successively through a solution of 5 gm of solute dissolved in 80.0 gm of water and through pure water. The loss in weight of the solution was 2.5 gm and that of the pure solvent was 0.04 gm. What is the molecular weight of the solute?

$p \;\alpha\; 2.5$ gm; $(p^\circ - p) \;\alpha\; 0.04$ gm

$\therefore p^\circ \;\alpha\; 2.54$ gm.

$$\left.\begin{array}{l}\text{The relative lowering of}\\ \text{vapour pressure}\end{array}\right\} = \frac{p^\circ - p}{p^\circ}$$

$$= \frac{W_2}{M_2} \cdot \frac{M_1}{W_1}$$

$$\therefore \frac{0.04}{2.54} = \frac{5 \times 18}{M_2 \times 80} \quad (\therefore M_2 = 71.43)$$

www.tntextbooks.in

M_2 = mol.wt of solute = 71.43

Problem 3

Calculate the vapour pressure of the solution. The molefraction of the solute is 0.25. The vapour pressure of the pure solvent is 0.8atm.

$$\frac{p^\circ - p}{p^\circ} = X_2$$

$$\frac{0.8 - p}{0.8} = 0.25$$

$$p = 0.6 \text{ atm}$$

Vapour pressure of the solution = 0.6 atm

11.4 Depression of freezing point of dilute solution

Freezing point is the temperature at which solid and liquid states of a substance have the same vapour pressure. According to Raoult's law, addition of a non-volatile solute to solvent lowers the vapour pressure of the solvent and hence, the vapour pressure of pure solvent is greater than the vapour pressure of solution. Thus the temperature at which the solution and its solid form existing in equilibrium and possessing the equal vapour pressures, is lowered. That is, the freezing point of solution is lowered. The lowering of the freezing point of the solution from that of the freezing point of the pure solvent is known as depression in freezing point of the solution.

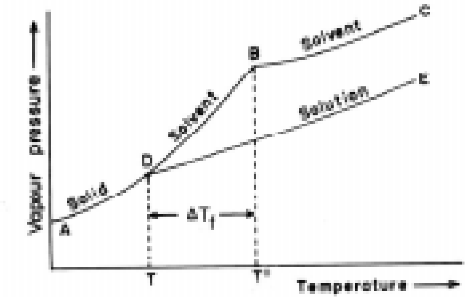


Fig. 11.3 Vapour pressure - temperature curves for depression in freezing point

Consider the vapour pressure curves shown in Fig.11.3. Generally when

www.tntextbooks.in

the temperature of a solid substance that is used as the solvent is raised, the vapour pressure also raises. AB curve depicts this. Similarly curve BC represents the increase in vapour pressure of the liquid solvent with increase in temperature. Curves AB and BC meet at B corresponding to T^o temperature which is the freezing point of the pure solvent. At T^o, the vapour pressure of the liquid and solid states of the solvent are equal at B. Since the vapour pressure of the solution is always lower than that of its pure solvent, the vapour pressure curve of the solution DE always lie below that of the pure solvent.

D is the point of intersection of the vapour pressure curves of solution and pure solvent. The temperature at D is the freezing point of the solution and is seen to be lower than T^o. The depression in freezing point is $\Delta T_f = T^o - T$. The measured depression in freezing point (ΔT_f) is found to be directly proportional to the molality (m) of the solute in solution. That is, $\Delta T_f \; \alpha \; m$ (or) $\Delta T_f = K_f \, m$, where K_f is called as the **cryoscopic constant (or) molal freezing point depression constant.** `K_f' is defined as the depression in freezing point produced when one mole of solute is dissolved in 1 kg solvent. It is also the depression in freezing point of one molal solution. Freezing point depression of a dilute solution is found to be directly proportional to the number of moles (and hence the no.of molecules) of the solute dissolved in a given amount of the solvent. Also ΔT_f is independent of the nature of the solute as long as it is non-volatile. Hence depression in freezing point is considered as a colligative property.

Determination of molecular weight from depression in freezing point

$$\Delta T_f = K_f . m$$

where m = molality

$$m = \frac{n_2}{W_1} \quad \text{and} \quad n_2 = \frac{W_2}{M_2}$$

W_1 = Weight of the solvent in Kg;
M_2 = Molecular weight of solute

$$\therefore m = \frac{W_2}{M_2 W_1}$$

$$\therefore \Delta T_f = K_f \frac{W_2}{M_2.W_1}$$

$$\therefore M_2 = \frac{K_f.W_2}{\Delta T_f.W_1} \quad \frac{K.kg\ mol^{-1}g}{K.kg}$$

$$M_2 = \frac{K_f}{\Delta T_f}.\ \frac{W_2}{W_1}\ g\ mol^{-1}$$

Thus the molecular weight of the solute can be calculated.

Problem 4

1.00 g of a non-electrolyte dissolved in 50.5g of benzene lowered its freezing point by 0.40K. The freezing point depression constant of benzene is 5.12K.kg mol^{-1}. Find the molecular mass of the solute.

Solution

ΔT_f = 0.40K

K_f = 5.12K.kg mol^{-1}

W_2 = 1g

$$W_1 = 50.5\ gm = \frac{50.5}{1000}\ kg$$

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

$$\therefore M_2 = \frac{5.12}{0.40} \times \frac{1}{50.5} \times 1000$$

$$= 256\ g\ mol^{-1}$$

Thus, the molecule mass of the solute = 256 g mol^{-1}.

Problem 5

What is the freezing point of solution containing 3g of a non-volatile solute in 20g of water. Freezing point of pure water is 273K, K_f of water = 1.86 Kkg/mol. Molar mass of solute is 300 g/mol.

$$\boxed{T^\circ - T = K_f\, m}$$

$$m = \frac{W_2}{M_2 W_1}$$

$$= \frac{3}{300 \times 20} \times 1000$$

$$T^\circ - T = \frac{1.86 \times 3 \times 1000}{300 \times 20} = 0.93\ K$$

$$T = 273\ K - 0.93\ K = 272.07\ K$$

$\therefore$ Freezing point of the solution = 272.07 K

11.4.1 Beckmann Method

Beckmann thermometer is used to measure small temperature changes in the freezing point of pure solvent and solution. Beckmann thermometer is not used in determining the absolute value of freezing temperature of the solvent or that of the solution. It is therefore called a differential thermometer. Temperature differences of even 0.01K can easily be measured.

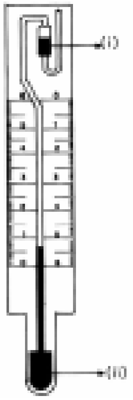


Fig. 11.4 Beckmann thermometer

Beckmann thermometer (Fig.11.4) consists of a large thermometer bulb at the bottom of a free capillary tube (ii) which is connected to a reservoir of mercury (i) placed at the top. As the capillary has fine bore, a small change of temperature causes a considerable change in the height of mercury column (level) in the capillary. The whole scale of a Beckmann thermometer covers only about 6K. Initially the level of mercury in the capillary should be on the scale. This is achieved by transferring mercury from the lower bulb to the reservoir and viceversa. When the Beckmann thermometer is used at high temperatures, some of the mercury from the thermometer bulb is transferred into the upper reservoir. At lower temperature mercury from the reservoir falls down in to the thermometer bulb.

Measurement of freezing point depression by Beckmann method

A simple Beckmann apparatus is shown in Fig.11.5. It consists of a freezing tube (a) with a side arm (c) through which a known amount of a solute can be introduced. A stopper carrying a Beckmann thermometer (b) and a stirrer (d) is fitted in to the freezing tube. To prevent rapid cooling of the contents of the freezing tube, A, a guard tube (e) surrounds the tube so that there is an air space between a and e. This assembly, as a whole, is placed in a wide vessel V which contains a freezing mixture (f) maintaining a low temperature around 5°C below the freezing point of the pure solvent.

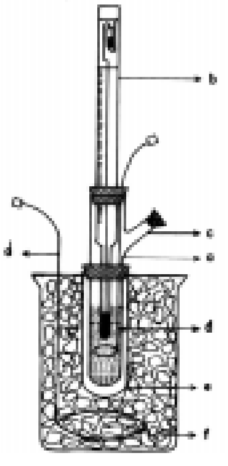


Fig. 11.5 Apparatus for Beckmann method

A known weight of the pure solvent is placed in the tube (a). It is cooled with gentle and continuous stirring. As a result of super cooling, the temperature of the solvent will fall by about 0.5°C below its freezing point. Vigorous stirring is then set in when solid starts separating and the temperature rises to the exact freezing point. This temperature remains constant, for some time, until all the liquid solvent gets solidified and is noted as T^o.

The tube (a) is taken out, warmed to melt the solid and a known weight of the solute is added through the side arm (c). When the solute is dissolved in to the solvent forming a solution, the tube (a) is put back in to the original position and the freezing point of the solution (T) is redetermined in the same manner as before. The difference between the two readings gives the freezing point depression (ΔT_f).

Depression in freezing point $\Delta T_f = T^o - T$. From this value, the molecular mass of the non-volatile solute can be determined using the expression and known K_f value.

$$\boxed{M_2 = \frac{K_f}{\Delta T_f} \cdot \frac{W_2}{W_1}} \quad \ldots 11.4$$

Table 11.1 Molal Depression (cryoscopic) constants, K_f (One mole of solute per 1000 grams of solvent)

Solvent	F. Pt. K	K_f (K.kg.mole^{-1})
Acetic acid	289.60	3.90
Bromoform	281.30	14.30
Benzene	278.53	5.10
Cyclohexane	279.55	20.20
Camphor	451.40	37.70
Naphthalene	353.25	7.00
Nitrobenzene	278.70	6.90
Phenol	314.10	7.27
Water	273.00	1.86

11.5 Elevation of boiling point of dilute solutions

The boiling point of a pure liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. Since the vapour pressure of a solution is always lower than that of the pure solvent, it follows that the boiling point of a solution will always be higher than of the pure solvent.

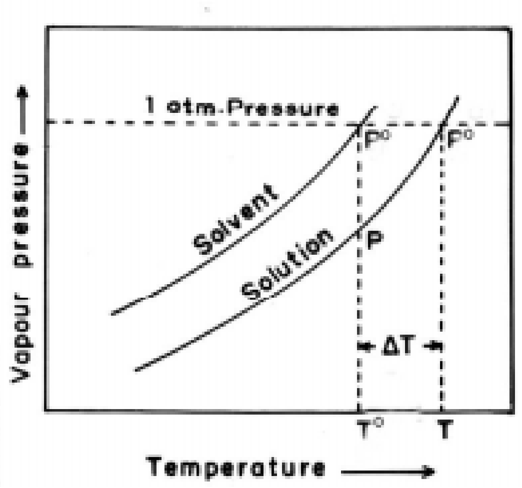


Fig. 11.6

In the Fig.11.6, the upper curve represents the vapour pressure - temperature dependance of the pure solvent. The lower curve represents the vapour pressure - temperature dependance of a dilute solution with known concentration. It is evident that the vapour pressure of the solution is lower than that of the pure solvent at every temperature. The temperature T^o gives the boiling point of the pure solvent and T the boiling point of the pure solution. This is because at these temperatures (T^o, T) the vapour pressures of pure solvent and solution becomes equal to the atmospheric pressure.

The elevation of boiling point = $\Delta T_b = T - T^o$.

Elevation of boiling point is found directly proportional to the molality of the solution (or) inturn the number of molecules of solute. Also it is independent of the nature of the solute for a non-volatile solute. Hence, boiling point elevation is a colligative property.

Thus it may be written as

$$\boxed{\Delta T_b \ \alpha \ m} \qquad \dots 11.5$$

Determination of molecular weight from boiling point elevation

By measuring the boiling point elevation of a solution of a known concentration, it is possible to calculate molecular weight of a non-volatile non-electrolyte solute.

$$\Delta T_b \ \alpha \ m$$

$$\therefore \Delta T_b = K_b \, m \qquad \dots 11.6$$

The proportionality constant K_b is characteristic of the solvent and it is called the **molal boiling point elevation constant** or **ebullioscopic constant**. It is defined as the elevation of boiling point of one molal solution.

When n_2 moles of the solute is dissolved in W_1 kg of the solvent, the molality is given by n_2/W_1.

$$\Delta T_b = K_b \frac{n_2}{W_1} \qquad \text{since} \quad n_2 = \frac{W_2}{M_2}$$

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

Since W_2, is the weight of the solute, we can calculate the molecular weight of the solution using the following expression.

$$\boxed{\therefore M_2 = \frac{K_b \, . \, W_2}{\Delta T_b \, . \, W_1}}$$

Table 11.2 Molal Elevation (Ebullioscopic) constants (One mole of solute per 1000 grams of solvent)

Solvent	B. Pt K	K_b (K.kg.mole^{-1})
Water	373.00	0.52
Benzene	353.10	2.57
Methanol	337.51	0.81
Ethanol	351.33	1.20
Carbon tetra chloride	349.72	5.01
Chloroform	334.20	3.88
Acetic acid	391.50	3.07
Acetone	329.15	1.72
Carbon disulphide	319.25	2.41
Phenol	455.10	3.56

Problem 5

A solution containing 2.5 g of a non-volatile solute in 100 gm of benzene boiled at a temperature 0.42K higher than at the pure solvent boiled. What is the molecular weight of the solute? The molal elevation constant of benzene is 2.67 K kg mol^{-1}.

K_b = 2.67 K kg mol^{-1}

ΔT_b = 0.42 K

$$W_1 = 100 \text{ g} = \frac{100}{1000} \text{ kg} = 0.1 \text{ Kg}$$

$$W_2 = \frac{K_b}{\Delta T_b} . \frac{W_2}{W_1}$$

www.tntextbooks.in

$$M_2 = \frac{2.67}{0.42} \times \frac{2.5}{0.1}$$

$$M_2 = 158.98 \text{ g mol}^{-1}$$

11.5.1 Determination of elevation of boiling point by Cottrell's Method

The apparatus (Fig.11.7) consists of a boiling tube (a) which is graduated and contains weighed amount of the liquid under examination. An inverted funnel tube (b) placed in the boiling tube collects the bubbles rising from a few fragments of a porous pot placed inside the liquid. When the liquid starts boiling, it pumps a stream of a liquid and vapour over the bulb of the Beckmann thermometer (f) held a little above the liquid surface. In this way, the bulb is covered with a thin layer of boiling liquid which is in equilibrium with the vapour. This ensures that the temperature reading is exactly that of the boiling liquid and that superheating is minimum. After determining the boiling point of the pure solvent, a weighed amount of the solute is added and procedure is repeated for another reading. The vapours of the boiling liquid is cooled in a condenser (C) which has circulation of water through (d) and (e). The cooled liquid drops into the liquid in (a).

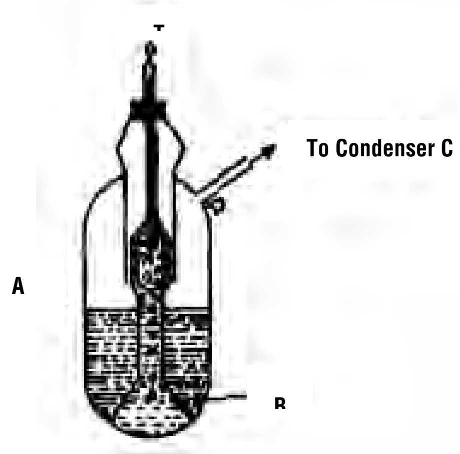


Fig. 11.7

Problem 7

0.900g of a solute was dissolved in 100 ml of benzene at 25°C when its density is 0.879 g/ml. This solution boiled 0.250°C higher than the boiling

www.tntextbooks.in

point of benzene. Molal elevation constant for benzene is 2.52 $K.Kg.mol^{-1}$. Calculate the molecular weight of the solute.

Solution

Weight of benzene = 100 x 0.879 = 87.9g

$$\text{Molality of solution, } m = \frac{0.900/M_2}{87.9} \times 1000$$

$$= \frac{900}{87.9\ M_2}$$

$$\Delta T_b = K_b\ m \text{ (or) } 0.250 = 2.52 \times \frac{900}{87.9\ M_2}$$

$$\therefore\ M_2 = \frac{900 \times 2.52}{87.9 \times 0.250}$$

$$M_2 = 103.2 \text{ g/mole}$$

$$\therefore \left.\begin{array}{l}\text{Molecular weight}\\ \text{of the solute}\end{array}\right\} = 103.2 \text{ g/mole}$$

11.6 Osmosis in solution

Spontaneous movement of solvent particles from a dilute solution or from a pure solvent towards the concentrated solution through a semipermeable membrane is known as **osmosis** (Greek word : 'Osmos' = to push).

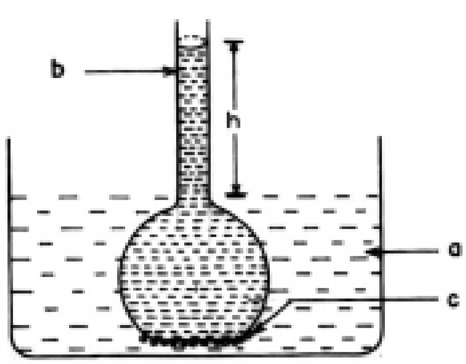


Fig. 11.8 Osmosis apparatus

www.tntextbooks.in

Fig. 11.8 depicts Osmosis in a simple way. The flow of the solvent from its side (a) to solution side (b) separated by semipermeable membrane (c) can be stopped if some definite extra pressure is applied on the solution risen to height (h). This pressure that just stops the flow of solvent is called **osmotic pressure** of the solution. This pressure (π) has been found to depend on the concentration of the solution.

Osmosis is a process of prime importance in living organisms. The salt concentration in blood plasma due to different species is equivalent to 0.9% of aqueous sodium chloride. If blood cells are placed in pure water, water molecules rapidly move into the cell. The movement of water molecules into the cell dilutes the salt content. As a result of this transfer of water molecules the blood cells swell and burst. Hence, care is always taken to ensure that solutions that flow into the blood stream have the same osmotic pressure as that of the blood.

Sodium ion (Na^+) and potassium ions (K^+), are responsible for maintaining proper osmotic pressure balance inside and outside of the cells of organism. Osmosis is also critically involved in the functioning of kidneys.

Characteristics of Osmotic Pressure (π)

- It is the minimum external pressure which must be applied on solution side in order to prevent osmosis if separated by a solvent through a semi permeable membrane.
- A solution having lower or higher osmotic pressure than the other is said to be hypotonic or hypertonic respectively in respect to other solution.
- Two solutions of different substances having same osmotic pressure at same temperature are said to be isotonic to each other. They are known as isotonic solutions.

11.6.1 Osmotic pressure and concerned laws

Vant Hoff noted the striking resemblance between the behaviour of dilute solutions and gases. He concluded that, a substance in solution behaves exactly like gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it is a gas at the same temperature occupying the same volume as the solution. Thus it is proposed that solutions also obey laws similar to gas laws.

1. Boyle's - Vant Hoff law

The osmotic pressure (π) of the solution at constant temperature is directly proportional to the concentration (C) of the solution.

$\therefore \pi \propto C$ at constant T.

C = Molar concentration

2. Charle's - Vant Hoff law

At constant concentration the osmotic pressure (π) of the solution is directly proportional to the temperature (T).

$\pi \propto T$ at constant C. Combining these two laws,

$$\pi \propto CT$$

$$\text{(or)} \quad \boxed{\pi = CRT} \qquad 11.7$$

where R is the gas constant.

Determination of molecular weight by osmotic pressure measurement

The osmotic pressure is a colligative property as it depends, on the number of solute molecules and not on their identity.

Solution of known concentration is prepared by dissolving a known weight (W_2) of solute, in a known volume (V dm^3) of the solvent and its osmotic pressure (π) is measured at room temperature (T)

Since $\pi = CRT$

$$C = \frac{n_2}{V} = \frac{\text{number of moles of solute}}{\text{Volume of the solution in dm}^3}$$

$$C = \frac{W_2}{M_2V}$$

Substituting in the equation 11.8,

$$\text{We get } \pi = \frac{W_2}{M_2V}RT$$

www.tntextbooks.in

$$\text{(or)} \quad \boxed{M_2 = \frac{W_2 RT}{\pi V}} \qquad 11.8$$

Thus M_2, molecular weight of the solute can be calculated by measuring osmotic pressure value.

11.6.2 Determination of osmotic pressure by Berkley-Hartley method

The osmotic pressure of a solution can be conveniently measured by Berkley - Hartley method. The apparatus (Fig. 11.9) consists of two concentric tubes. The inner tube (a) is made of semipermeable membrane (c) with two side tubes. The outer tube (b) is made of gun metal which contains the solution. The solvent is taken in the inner tube. As a result of osmosis, there is fall of level in the capillary indicator (d) attached to the inner tube. The external pressure is applied by means of a piston (e) attached to the outer tube so that the level in the capillary indicator remains stationary at (d). This pressure is equal to the osmotic pressure (π) and the solvent flow from inner to outer tube is also stopped.

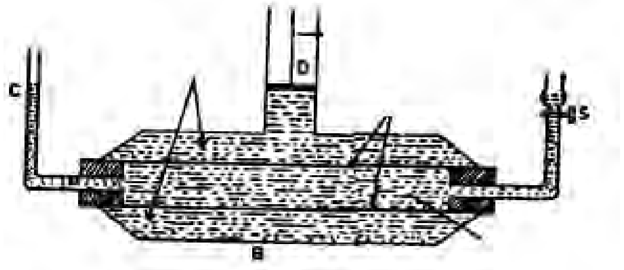


Fig. 11.9 Berkley - Hartley apparatus

Advantages of this Method

1. The osmotic pressure is recorded directly and the method is quick.
2. There is no change in the concentration of the solution during the measurement of osmotic pressure.
3. The osmotic pressure is balanced by the external pressure and there is minimum strain on the semipermeable membrane.

Problem 8

10g of an organic substance when dissolved in two litres of water gave an osmotic pressure of 0.59 atm, at 7°C. Calculate the molecular weight of the substance.

Solution

$$\pi = \frac{\text{Moles of solute}}{\text{Litres of solution}} \text{ x RT}$$

$$0.59 = \frac{10 \text{ x } 0.082 \text{ x } 280}{\text{M x 2}}$$

$$\text{M} = \frac{10 \text{ x } 0.082 \text{ x } 280}{2 \text{ x } 0.59} = 194.6 \text{ g/mol}$$

Molecular weight = 194.6 g/mole

11.7 Abnormal Colligative Properties

The experimental values of colligative properties in most of the cases resemble closely to those obtained theoretically by their formula. However, in some cases experimental values of colligative properties differ widely from those obtained theoretically. Such experimental values are referred to as abnormal colligative properties.

The abnormal behaviour of colligative properties has been explained in terms of dissociation and association of solute molecules.

a. Dissociation of solute molecules

Such solutes which dissociate in solvent (water) i.e. electrolytes, show an increase in number of particles present in solution. This effect results in an increase in colligative properties obtained experimentally.

The Van't Hoff factor (i)

$$\text{i} = \frac{\text{Experimental colligative property}}{\text{Normal colligative property}}$$

i > 1 for dissociation. We can calculate the degree of dissociation (α) using the equation.

$$\alpha_{\text{dissociation}} = \frac{i - 1}{n - 1} \qquad \dots 11.9$$

where `n' is the total number of particles furnished by one molecule of the solute.

For example, sodium chloride in aqueous solution exists almost entirely as Na^+ and Cl^- ions. In such case, the number of effective particles increases and therefore observed colligative property is greater than normal colligative property.

Problem 9

A 0.5 percent aqueous solution of KCl was found to freeze at 272.76K. Calculate the Van't Hoff factor and degree of dissociation of the solute at this concentration (K_f for water = 1.86 k.kg.mol^{-1}). Normal molar mass of KCl = 74.5.

T_f° of water = 273 K

T_f of the solution = 272.76 K

$\therefore \Delta T_f = T_f^\circ - T_f$ = + 0.24 K

$$M_2 = \frac{K_f . W_2}{\Delta T_f . W_1}$$

Observed molecular mass

$$M_2 = \frac{1.86 \times 0.5 \times 1000}{100 \times 0.24} = 38.75 \text{ g.mol}^{-1}$$

The colligative property is inversely related to the molar mass.

$\therefore$ Van't Hoff factor

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$= \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}}$$

$$\text{Vant Hoff factor (i)} = \frac{74.5}{38.75} = 1.92$$

$$\text{Degree of dissociation } \alpha = \frac{i-1}{n-1}$$

n = 2 for KCl

$$\therefore \alpha = \frac{1.92-1}{2-1}$$

$$= 0.92$$

$\therefore$ Degree of dissociation = 0.92

b. Association of the solute molecules

Such solute which associate in a solvent show a decrease in number of particles present in solution. This effect results in a decrease in colligative properties obtained experimentally.

Here,

Experimental Colligative Property < Normal Colligative Property

$\therefore$ Vant Hoff factor

$$i = \frac{\text{Experimental Colligative Property}}{\text{Normal colligative property}}$$

i < 1 for association

Using this, the degree of association `α' can be calculated from

$$\boxed{\alpha_{\text{association}} = \frac{(1-i)n}{(n-1)}} \quad \ldots 11.10$$

where `n' is the number of small molecules that associate into a single larger new molecule.

www.tntextbooks.in

For example, molecules of acetic acid dimerise in benzene due to intermolecular hydrogen bonding. In this case, the number of particles is reduced to half its original value due to dimerisation. In such case, the experimental colligative property is less than normal colligative property.

$$2\,(CH_3COOH) \rightleftharpoons (CH_3COOH)_2$$

Problem

The depression in the freezing point of a benzene solution containing 0.784g of Acetic acid dissolved in 100ml of benzene is 0.35k. Calculate the van't Hoff factor and the degree of association of the solute at this concentration

(k_f for benzene = 5.10 k.kg.mol^{-1}, molar mass of acetic acid is 60.01).

$$\Delta T_f = 0.35k$$

$$M_2 = \frac{k_f.W_2}{\Delta T_f.W_1}$$

$$= \frac{5.10 \times 0.784 \times 1000}{100 \times 0.35} = 114.24$$

The colligative property is inversely related to molar mass.

∴ Van't Hoff factor

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$= \frac{\text{Theoretical molar mass}}{\text{Observed molar mass}}$$

$$\text{Van't Hoff factor } i = \frac{60}{114.24}$$

$$= 0.525$$

$$\text{Degree of association } \alpha = \frac{n\,(1-i)}{n-1}$$

n = 2 for dimerisation

Acetic acid exist as dimers in benzene

$$\alpha = 2\,\frac{(1-0.525)}{2-1} = 0.95$$

∴ Degree of association = 0.95

Summary

Relationship between colligative properties and molecular mass of the non-volatile solute

1.	Relative lowering of vapour pressure $\frac{p^\circ-p}{p^\circ}$	The ratio of lowering of vapour pressure of the pure solvent	$\frac{P^\circ-P}{P^\circ} = \frac{W_2}{M_2} \cdot \frac{M_1}{W_1}$
2.	Elevation of boiling point (ΔT_b)	Boiling point of the solution is greater than the solvent	$T-T^o = \Delta T_b$ $\Delta T_b = \frac{W_2}{M_2 W_1} \cdot K_b$
3.	Depression in freezing point (ΔT_f)	Freezing point of the solution is lower than solvent.	$T^o-T = \Delta T_f$ $\Delta T_f = \frac{W_2\,K_f}{M_2\,W_1}$
4.	Osmotic pressure (π)	Excess pressure applied on the concentrated solution side to stop the osmosis.	$\pi = CRT$
5.	Abnormal colligative property (i)	Due to dissociation and association of molecules, there is a change in the experimental colligative property value	Van't Hoff factor $i = \frac{\text{Observed colligative property}}{\text{Theoretical colligative property}}$

www.tntextbooks.in

Questions

A. Choose the correct answer

1. Properties which depend only on number of particles present in solution are called
   (a) Additive (b) Constitutive (c) Colligative (d) None
2. Which solution would possess the lowest boiling point
   (a) 1% NaCl solution (b) 1% Urea solution
   (c) 1% glucose solution (d) 1% sucrose solution
3. In cold countries, ethylene glycol is added to water in the radiators of cars during winters. It results in :
   (a) Lowering boiling point (b) Reducing viscosity
   (c) Reducing specific heat (d) Lowering freezing point
4. Which of the following 0.1M aqueous solutions will have the lowest freezing point?
   (a) Potassium sulphate (b) Sodium chloride
   (c) Urea (d) Glucose
5. The Van't Hoff factor of 0.005M aqueous solution of KCl is 1.95. The degree of ionisation of KCl is
   (a) 0.94 (b) 0.95 (c)0.96 (d) 0.59

B. Fill in the blanks

6. Relative lowering of vapour pressure is equal to ___________ in solution.
7. A liquid having high vapour pressure has __________ boiling point.
8. The least count of Beckmann's thermometer is ____________ .
9. Molal elevation constant is a characteristic constant for a given __________.
10. Semipermeable membrane allows the passage of ____________through it.
11. For a deliquescence to occur, the vapour pressure of water in the air must be_____than that of the saturated solution.
12. Depression in freezing point is______ pronounced if camphor is used as a solvent in place of water for same amount of solute and solvent.
13. Every solution behaves as ideal solution _______ .
14. The osmotic pressures of 0.1M glucose and 0.1M NaCl solutions are __________.
15. Solutions that have same osmotic pressure are called solutions.

C. Answer the following in one (or) two sentences

16. What are colligative properties?
17. Define relative lowering of vapour pressure.

18. What do you understand by molal elevation of boiling point? What are abnormal solutes?
19. Addition of non-volatile solute always increases the boiling point of the solution. Why?
20. Volatile hydrocarbons are not used in the brakes of automobile as lubricant, but non-volatile hydrocarbon are used as lubricants. Why?
21. Prove that the depression in freezing point is a colligative property.
22. Explain the terms osmosis and osmotic pressure.
23. What are isotonic solutions?
24. What are the advantages of Berkley-Hartley method?
25. Explain how the degree of dissociation of an electrolyte may be determined from the measurement of a colligative property.

Problems

26. The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A non-volatile non-electrolyte solid weighing 2.175 g is added to 39 g of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance? [69.6]
27. Calculate the freezing point of an aqueous solution of a non-electrolyte having an osmotic pressure 2.0 atm at 300 K. K_f = 1.86 k.kg.mol^{-1}. R = 0.0821 lit.atm.k^{-1} mol^{-1}

    [-0.151°C]
28. What weight of non-volatile solute (urea) NH_2 CO NH_2 needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%. What will be the molality of solution? [13.88 m]
29. 20 g of sucrose solution in one litre is isotonic with a solution of boric acid containing 1.63 g of boric acid in 450 ml. Find the molecular weight of boric acid. [61.94]
30. A solution containing 6 gm of a solute dissolved in 250 ml of water gave an osmotic pressure of 4.5 atmosphere at 27°C. Calculate the boiling point of the solution. The molal elevation constant for water is 0.52 [373.095]

D. Explain briefly on the following

31. Explain the determination of relative lowering of vapour pressure by Ostwald- Walker method?
32. Describe about Beckmann thermometer.
33. Explain the determination of depression in freezing point by Beckmann method.

34. What is elevation of boiling point? Explain its determination by Cottrell's method.
35. Explain the laws of osmotic pressure?

    Explain its determination by Berkley-Hartley method.
36. What are abnormal colligative properties?

    Explain with example and write its determination using Van't Hoff factor.

REFERENCES

1. Physical Chemistry by Lewis and Glasstone.
2. Physical Chemsitry by Maron and Prutton.
3. Physical Chemistry by P.L.Soni.

12. THERMODYNAMICS - I

OBJECTIVES

- *To predict the possibility of a process.*
- *To differentiate system and surroundings from universe.*
- *To define various processes, properties; state and path functions; spontaneous and non-spontaneous; exo- and endo-thermic processes.*
- *To learn to interrelate work, heat and energy.*
- *To define Zeroth and first laws of thermodynamics.*
- *To measure changes in internal energy and enthalpy.*
- *To relate E and H.*
- *To determine enthalpy changes of various physical processes.*
- *To determine enthalpy changes in formation, combustion, neutralisation.*
- *To understand non-conventional energy resources and to identify different renewable energy resources.*

12.1 Introduction

The term **thermodynamics** is derived from Greek word, **`Thermos'** meaning heat and **`dynamics'** meaning flow. Thermodynamics deals with the inter-relationship between heat and work. It is concerned with the interconversions of one kind of energy into another without actually creating or destroying the energy. **Energy** is understood to be the capacity to do work. It can exist in many forms like electrical, chemical, thermal, mechanical, gravitational etc. Transformations from one to another energy form and prediction of the feasibility (possibility) of the processes are the important aspects of thermodynamics.

As an illustration, from our common experience steam engines are seen to transform heat energy to mechanical energy, by burning of coal which is a fossil fuel. Actually, the engines use the energy stored in the fuel to perform mechanical work. In chemistry, many reactions are encountered that can be utilised to provide heat and work along with the required products. At present thermodynamics is widely used in physical, chemical

www.tntextbooks.in

and biological sciences focussing mainly on the aspect of predicting the possibility of the processes connected with each sciences. On the other hand, it fails to provide insight into two aspects: Firstly, the factor of time involved during the initial to final energy transformations and secondly, on the quantitative microscopic properties of matter like atoms and molecules.

12.2 Terminology used in Thermodynamics

It is useful to understand few terms that are used to define and explain the basic concepts and laws of thermodynamics.

System

Thermodynamically a system is defined as any portion of matter under consideration which is separated from the rest of the universe by real or imaginary boundaries.

Surroundings

Everything in the universe that is not the part of system and can interact with it is called as surroundings.

Boundary

Anything (fixed or moving) which separates the system from its surroundings is called **boundary**.

For example, if the reaction between A and B substances are studied, the mixture A and B, forms the system. All the rest, that includes beaker, its walls, air, room etc. form the surroundings. The boundaries may be considered as part of the system or surroundings depending upon convenience. The surroundings can affect the system by the exchange of matter or energy across the boundaries.

Types of systems

In thermodynamics different types of systems are considered, which depends on the different kinds of interactions between the system and surroundings.

Isolated system

A system which can exchange neither energy nor matter with its surroundings is called an isolated system. For example, a sample in a sealed thermos flask with walls made of insulating materials represents an isolated

www.tntextbooks.in

system (Fig.12.1).

Closed system

A system which permits the exchange of energy but not mass, across the boundary with its surroundings is called a closed system.

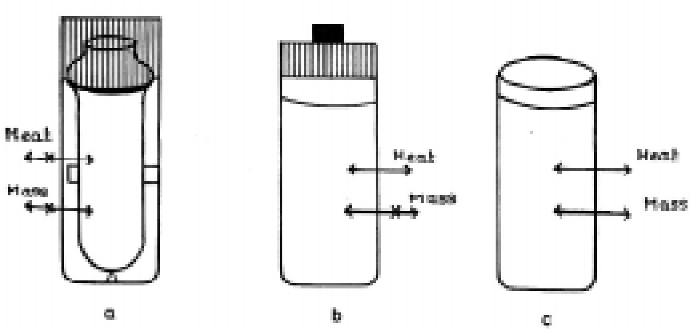
For example: A liquid in equilibrium with its vapours in a sealed tube represents a closed system since the sealed container may be heated or cooled to add or remove energy from its contents while no matter (liquid or vapour) can be added or removed.

Open system

A system is said to be open if it can exchange both energy and matter with its surroundings.

For eg. a open beaker containing an aqueous salt solution represents open system. Here, matter and heat can be added or removed simultaneously or separately from the system to its surroundings.

All living things (or systems) are open systems because they continuously exchange matter and energy with the surroundings.



↮ exchange impossible ↔ exchange possible

Fig. 12.1 Examples of
(a) isolated (thermos flask)
(b) closed (closed beaker)
(c) open (open beaker) systems

www.tntextbooks.in

Homogeneous and Heterogeneous systems

A system is said to be **homogeneous** if the physical states of all its matter are uniform. For eg. mixture of gases, completely miscible mixture of liquids etc.

A system is said to be **heterogeneous**, if its contents does not possess the same physical state. For eg: immiscible liquids, solid in contact with an immiscible liquid, solid in contact with a gas, etc.

Macroscopic properties of system

The properties which are associated with bulk or macroscopic state of the system such as pressure, volume, temperature, concentration, density, viscosity, surface tension, refractive index, colour, etc. are called as macroscopic properties.

Types of macroscopic properties of system

Measurable properties of a system can be divided into two types.

Extensive properties

The properties that depend on the **mass** or **size** of the system are called as extensive properties. Examples: volume, number of moles, mass, energy, internal energy etc. The value of the extensive property is equal to the sum of extensive properties of smaller parts into which the system is divided. Suppose x_1 ml, x_2 ml,x_3 ml of 1,2,3 gases are mixed in a system, the total volume of the system equals to $(x_1 + x_2 + x_3)$ ml. Thus volume is an extensive property.

Intensive properties

The properties that are independent of the mass or size of the system are known as intensive properties. For eg. refractive index, surface tension, density, temperature, boiling point, freezing point, etc., of the system. These properties do not depend on the number of moles of the substance in the system.

If any extensive property is expressed per mole or per gram or per ml, it becomes an intensive property. For eg: mass, volume, heat capacity are extensive properties while density, specific volume, specific heat are intensive properties.

www.tntextbooks.in

12.2.1 State functions

State of a system

A system is said to be in a particular physical state when specific values of the macroscopic properties of the system are known. For eg. The gaseous state of matter can be described by parameters like Pressure (P), Volume (V), Temperature (T) etc. The values of these parameters change when the matter is in liquid state. Thus, the **state of a system** is defined by specific measurable macroscopic properties of the system.

The **initial state** of system refers to the starting state of the system before any kind of interaction with its surroundings.

The **final state** of system refers to the state after the interaction of system with its surroundings. A system can interact with its surroundings by means of exchange of matter or heat or energy or all.

The variables like P,V,T, composition (no. of moles) `n' that are used to describe the state of a system are called as **state variables or state functions**. When the state of the system changes, the values of the state variables of the system also change. Thus, state functions depend only on the initial and final states of system and not on how the changes occur. Also, if the values of state functions of a system are known, all other properties like mass, viscosity, density etc. of the system become specified.

For specifying a state of the system, it is not necessary to know all the state variables, since they are interdependent and only a few of them (state variables) are sufficient. A system which satisfies the conditions of thermal, mechanical and chemical equilibria and contains the macroscopic properties which are independent of time is said to be in **thermodynamic equilibrium**.

Thermodynamic equilibrium sets the condition that there should be no flow of heat from one portion or part of the system to another portion or part of the same system. ie. temperature of the system remaining constant at every point of the system.

Mechanical equilibrium implies that there is no work done by one portion or part of the system over another portion or part of the same system. ie. Pressure of the system being constant at all its points.

Chemical equilibrium demands that the composition of one or more phases of chemicals present in the system should remain constant.

12.2.2 Thermodyanamic processes

A thermodynamic (physical or chemical) process may be defined as the pathway of series of intermediate changes that occur when a system is changed from initial to final state. Processes starting with the same initial state and ending at different final states correspond to different thermodynamic processes.

Different types of processes are commonly used in the study of thermodynamics.

Isothermal process is defined as one in which the temperature of the system remains constant during the change from its initial to final states. During the isothermal process, the system exchanges heat with its surroundings and the temperature of system remains constant.

Adiabatic process is defined as that one which does not exchange heat with its surroundings during the change from initial to final states of the system.

A thermally and completely insulated system with its surroundings can have changes in temperature during transformation from initial to final states in an adiabatic process. This is because, the system cannot exchange heat with its surroundings.

Isobaric process is that process in which the pressure of the system remains constant during its change from the initial to final state.

Isochoric process shows no change in volume of system during its change from initial to final state of the process.

Cyclic process: The process which brings back the system to its original or initial state after a series of changes is called as cyclic process.

Spontaneous process are those that occur on their own accord. For example heat flowing from a hotter end of a metal rod to a colder end. In these processes, the transformation of the system from initial, to final state is favourable in a particular direction only. Many of the spontaneous processes are natural processes and are also, irreversible processes.

www.tntextbooks.in

Non-spontaneous process are those that does not occur on their own accord. For example, although carbon burns in air evolving heat to form carbon dioxide, on its own carbon does not catch fire and an initial heat supply is required. Since many of the non-spontaneous processes are slow processes, they also exist as equilibrium processes.

Reversible process. In a reversible process the series of changes carried out on the system during its transformation from initial to final state may be possibly reversed in an exact manner.

This is possible when the changes are carried out very slowly in many smaller steps on the system during its change from initial to final state. By doing so, each of its intermediate state will be in equilibrium with its surroundings. Under such conditions the initial and final states of the system become reversible completely.

For example, when ice melts a certain amount of heat is absorbed. The water formed can be converted back to ice if the same amount of heat is removed from it. This indicates that many reversible processes are non-spontaneous processes also.

Irreversible Process

An irreversible process is one which cannot be retraced to the initial state without making a permanent change in the surroundings. Many of the spontaneous processes are irreversible in nature.

For eg. Biological ageing is an irreversible process. Water flowing down a hill on its own accord is an irreversible process.

Some of the characteristics of thermodynamically reversible and irreversible processes are compared as below:

Reversible process	Irreversible process
It is a slow process going through a series of smaller stages with each stage maintaining equilibrium between the system and surroundings.	In this process the system attains final state from the initial state with a measurable speed. During the transformation, there is no equilibrium maintained between the system and surroundings.
A reversible process can be made to proceed in forward or backward direction.	Irreversible process can take place in one direction only.

The driving force for the reversible process is small since the process proceeds in smaller steps.	There is a definite driving force required for the progress of the irreversible process.
Work done in a reversible process is greater than the corresponding work done in irreversible process.	Work done in a irreversible process is always lower than the same kind of work done in a reversible process.
A reversible process can be brought back to the initial state without making an change in the adjacent surroundings.	An irreversible process cannot be brought back to its initial state without making a change in the surroundings.

Exothermic and endothermic processes

When the thermodynamic process is a chemical reaction or a physical transformation, process is classified as either exothermic or endothermic depending on the nature of heat involved in the over all process. These two processes are differentiated as follows:

Endothermic process	**Exothermic process**
A process when transformed from initial to final states by absorption of heat is called as an endothermic process.	A process when transformed from initial to final states by evolution of heat is called as exothermic process.
The final state of the system possesses higher energy than the initial state. The excess energy needed is absorbed as heat by the system from the surroundings.	The final state of the system possesses lower energy than the initial state. The excess energy is evolved as heat. Example: All combustion processes are exothermic.
Generally in a physical transformation which is endothermic heat is supplied to bring about the initial to final state. Example: melting of a solid by supplying heat is an endothermic process.	If the physical transformation is exothermic heat is removed to bring about the initial to final state. Example: Freezing of a liquid at its freezing point is an exothermic process.

12.3 Nature of thermodynamic functions

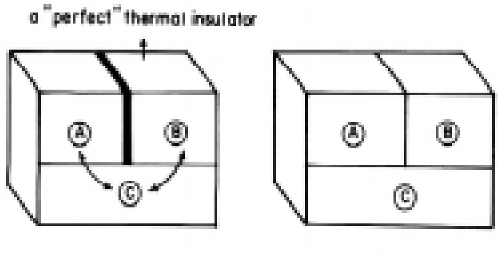
The properties of a thermodynamic system depend on variables which are measurable and change in values when the state of the system changes. These variables are classified as state variables or state functions and path variables (or) path functions.

The **state functions** considered in a gaseous system like, P, V and T are called as state variables. A **state function** is a thermodynamic property of a system which has a specific value for each state of the system and does not depend on the path (or manner) in which a particular state is reached. Other than P,V,T there are other important thermodynamic properties existing as state functions like internal energy (U), enthalpy (H), free energy (G) etc. (The properties of U,H and G are to be studied later).

A **path function** is a thermodynamic property of the system whose value depends on the path or manner by which the system goes from its initial to final states. It also depends on the previous history of the system. For example, work (w) and heat (q) are some of the thermodynamic properties of the system that are path functions. Their values change when there is a change in manner in which the system goes from initial to final states.

12.4 Zeroth law of thermodynamics

Consider any two objects each maintained at different temperature, when brought in thermal contact with each other such that heat is exchanged until a thermal equilibrium is reached, then the two objects are considered to have equal temperatures. For example, if a beaker containing water and a thermometer are the two objects, while reading the temperature of the water in the beaker using the thermometer, a thermal equilibrium is reached between the two objects having a contact with each other. Also, when the temperatures of the thermometer bulb and that of water in the beaker are same, thermal equilibrium has said to be occurred.



(i) (ii)

Fig. 12.2 i) A and B are in thermal equilibrium with C
ii)A,B and C are in thermal equilibrium with each other

Zeroth law of thermodynamics is also known as the law of thermal equilibrium. It provides a logical basis for the concept of temperature of a system. It can be stated as follows.

`If two systems at different temperatures are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves'.

Conversely, the Zeroth law can be stated in another manner as,

`When two objects are in thermal equilibrium with the third object, then there is thermal equilibrium between the two objects itself'.

12.5 Work, heat and energy

In order to formulate the laws of thermodynamics it becomes necessary to know the properties and nature of work (w) heat (q) and energy (u).

$$\boxed{1 \text{ Torr} = 1 \text{ mm of Hg}}$$

Work (w)

In thermodynamics work is generally defined as the force (F) multiplied by the distance of displacement(s). That is,

$$w = F.s.$$

Several aspects should be considered in the definition of work which are listed below:

(i) work appears only at the boundary of the system.

(ii) work appears during the change in the state of the system.

(iii) work brings in a permanent effect in the surroundings.

(iv) work is an algebraic quantity.

(v) work is a path function and it is not a state function.

Types of work

www.tntextbooks.in

Many types of work are known. Some of the types of work are as follows:

(i) Gravitational work

This work is said to be done when a body is raised to a certain height against the gravitational field. If a body of mass `m' is raised through a height `h' against acceleration due to gravity `g', then the gravitational work carried out is `mgh'. In this expression, force is `mg' and the distance is `h'.

(ii) Electrical work

This type of work is said to be done when a charged body moves from one potential region to another. The electrical work is Q .V. if V is the potential difference causing the quantity of electricity 'Q' during its movement

(iii) Mechanical work

This type of work is associated with changes in volume of a system when an external pressure is applied or lowered. This pressure-volume work is also referred to as the mechanical work.

Heat

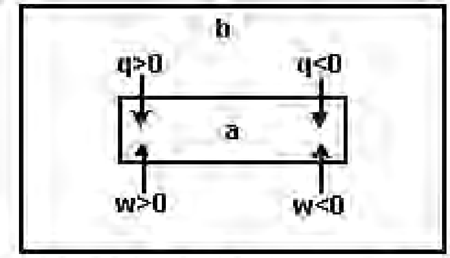
Like work, heat (q) is regarded in thermodynamics as energy in transit across the boundary separating a system from its surroundings. Heat changes result in temperature differences between system and surroundings. Heat cannot be converted into work completely without producing permanent change either in the system or in the surroundings. Some of the characteristics of heat (q) are:

(i) heat is an algebraic quantity.

(ii) heat is a path function and is not a state function.

(iii) heat changes are generally considered as temperature changes of the system.

Sign convention for heat (q) and work (w)



a = system; b = surroundings
q = heat; w = work

when,
- (i) heat is absorbed by the system (or) heat is lost by surroundings to the system: +q
- (ii) heat is evolved by the system (or) heat is gained by surroundings: -q.
- (iii) work is done by the system : -w
- (iv) work is done on the system : +w

If heat (q) is supplied to the system, the energy of the system increases and `q' is written as a positive quantity. If work is done on the system, the energy of the system increases and `w' is written as a positive quantity. When w or q is positive, it means that energy has been supplied to the system as work or as heat. In such cases internal energy (U) of the system increases. When w or q is negative, it means that energy is lost by the system as work or as heat. In such cases, the internal energy (U) of the system decreases.

Energy `U'

Energy is easily, defined as the capacity to do work. Whenever there is a change in the state of matter of a system, then there is a change in energy (ΔU) of the system. For example energy changes are involved in processes like melting, fusion, sublimation, vapourisation etc. of the matter in a system. Energy (U) exists in many forms. Kinetic energy (K.E.) arises due to motion of a body and potential energy (P.E.) arises due to its position in space.

In chemical systems, there are two types of energy available. The energies acquired by the system like electrical, magnetic, gravitational etc. and termed as external energies of the system. The internal energy is generally referred to as the energy (U) of a thermodynamic system which is considered to be made up of mainly by P.E. and K.E.

Characteristics of energy (U) are:

(i) U is a state function. Its value depend on the initial and final states of the system.

(ii) U is an extensive property. Its magnitude depend on the quantity of material in the system.

(iii) U is not a path function. Its value remains constant for fixed initial and final states and does not vary even though the initial and final states are connected by different paths.

In S.I. system the unit of energy is Joules `J' or kJ.

12.6 First law of thermodynamics

First law of thermodynamics is also known as the law of conservation of energy which may be stated as follows:

"Energy may be converted from one form to another, but cannot be created or be destroyed".

There are many ways of enunciating the first law of thermodynamics. Some of the selected statements are given below:

(i) "Energy of an isolated system must remain constant although it may be changed from one form to another".

(ii) "The change in the internal energy of a closed system is equal to the energy that passes through its boundary as heat or work".

(iii) "Heat and work are equivalent ways of changing a system's internal energy".

(iv) "Whenever other forms of energies are converted into heat or vice versa there is a fixed ratio between the quantities of energy and heat thus converted".

Significance of first law of thermodynamics is that, the law ascertains an exact relation between heat and work. It establishes that ascertain quantity of heat will produce a definite amount of work or vice versa. Also, when a system apparently shows no mechanical energy but still capable of

www.tntextbooks.in

doing work, it is said to possess internal energy or intrinsic energy.

12.7 Enthalpy

In chemistry most of the chemical reactions are carried out at constant pressure. To measure heat changes of system at constant pressure, it is useful to define a new thermodynamic state function called Enthalpy `H'.

H is defined as sum of the internal energy `U' of a system and the product of Pressure and Volume of the system.

That is,

$$\boxed{H = U + PV}$$

Characteristics of H

Enthalpy, H depends on three state functions U, P, V and hence it is also a state function. H is independent of the path by which it is reached. Enthalpy is also known by the term `heat content'.

12.7.1 Relation between enthalpy `H' and internal energy `U'

When the system at constant pressure undergoes changes from an initial state with H_1, U_1, V_1, P parameters to a final state with H_2, U_2, V_2, P parameters the change in enthalpy ΔH, is given by,

$$\Delta H = (H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$$

i.e. $\Delta H = \Delta U + P\Delta V$

Considering $\Delta U = q - w$ or $q - P\Delta V$ (assuming p - V work), $\Delta U + P\Delta V$ becomes equal to `$q_p$'. `q_p' is the heat absorbed by the system at constant pressure for increasing the volume from V_1 to V_2. This is so because, -w indicates that work is done by the system. Therefore volume increase against constant pressure is considered.

$$\therefore \text{ eqn. becomes } q_p = \Delta U + P\Delta V$$

$$= \Delta H.$$

$$\text{or} \quad \boxed{\Delta H = q_p.}$$

www.tntextbooks.in

`q_p' is the heat absorbed by the system at constant pressure and is considered as the heat content of the system.

Heat effects measured at constant pressure indicate changes in enthalpy of a system and not in changes of internal energy of the system. Using calorimeters operating at constant pressure, the enthalpy change of a process can be measured directly.

Considering a system of gases which are chemically reacting to produce product gases with V_r and V_p as the total volumes of the reactant and product gases respectively, and n_r and n_p as the number of moles of gaseous reactants and products, then using ideal gas law we can write that, at constant temperature and constant pressure,

$$PV_r = n_rRT \text{ and } PV_p = n_pRT.$$

Then considering reactants as initial state and products as final state of the system,

$$P(V_p - V_r) = RT\,(n_p - n_r)$$

$$\therefore P\Delta V = \Delta n_gRT \text{ where,}$$

Δn_g refers to the difference in the number of moles of product and reactant gases. But, we already know that, $\Delta H = \Delta U + P\Delta V$.

$$\therefore \boxed{\Delta H = \Delta U + \Delta n_gRT}$$

Incertain processes internal energy change $\Delta U = \Delta E$ also.

Example 1

From the following data at constant volume for combustion of benzene, calculate the heat of this reaction at constant pressure condition.

$$C_6H_{6(l)} + 7\tfrac{1}{2}O_{2(g)} \rightarrow 6CO_{2(g)} + 13H_2O_{(l)}$$

$\Delta E_{25^\circ C} = -781.1$ kcal

$\Delta H = \Delta E + \Delta ngRT$

$\Delta E = -781.1$ K.cal

www.tntextbooks.in

$\Delta n_g = 6 - 7\frac{1}{2} = -1.5$

$$\Delta H = -781.1 + \frac{(-1.5) \times 1.987 \times 298}{1000}$$

$= -781.1 - 0.888$

$\therefore \Delta H = -782$ k.cal

12.7.2 Standard enthalpy changes

The standard enthalpy of a reaction is the enthalpy change for a reaction when all the participating substances (elements and compounds) are present in their standard states.

The standard state of a substance at any specified temperature is its pure form at 1 atm pressure. For example standard state of solid iron at 500 K is pure iron at 500 K and 1 atm. Standard conditions are denoted by adding the superscript 0 to the symbol ΔH.

For a reaction, the standard enthalpy change is denoted by $\Delta_r H^0$. Similarly, the standard enthalpy changes for combustion, formation, etc. are denoted by $\Delta_c H^0$ and $\Delta_f H^0$ etc respectively. Generally the reactants are presented in their standard states during the enthalpy change.

12.8 Thermochemical equations

A balanced chemical equation together with standard conventions adopted and including the value of ΔH of the reaction is called a thermochemical equation.

The following conventions are necessarily adopted in a thermochemical equation :

(i) The coefficients in a balanced thermochemical equation refers to number of moles of reactants and products involved in the reaction.

(ii) The enthalpy change of the reaction $\Delta_r H$ has unit KJ mol^{-1} and will remain as it is, even if more than one mole of the reactant or product are involved but with only the magnitude changing.

(iii) When a chemical equation is reversed the value of ΔH is reversed in sign with the magnitude remaining the same.

(iv) Physical states of all species is important and must be specified in a thermochemical equation since ΔH depends on the phases of reactants and products.

(v) If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also be multiplied by the same number value.

(vi) The negative sign of $\Delta_r H^0$ indicates the reaction to be an exothermic reaction and positive sign of $\Delta_r H^0$ indicates an endothermic type of reaction.

For example, consider the following reaction,

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \quad \Delta_r H^0 = -483.7 \text{ KJ.mol}^{-1}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \quad \Delta_r H^0 = -571.1 \text{ KJ.mol}^{-1}$$

The above thermochemical equations can be interpreted in several ways.

483.7 KJ given off per mole of the reaction ≡

483.7 KJ given off per 2 moles of $H_{2(g)}$ consumed ≡

483.7KJ given off per mole of $O_{2(g)}$ consumed ≡

483.7 KJ given off per 2 moles of water vapour formed

The above equation describes the combustion of H_2 gas to water in a general sense. The first reaction can be considered as the formation reaction of water vapour and the second reaction as the formation of liquid water. Both the reaction refer to constant temperature and pressure.

The negative sign of ΔH indicates that it is an exothermic reaction. The reaction which is exothermic in the forward direction is endothermic in the revere direction and vice-versa. This rule applies to both physical and chemical processes.

eg. $2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \qquad \Delta_r H^0 = +571.1 \text{ KJ.mol}^{-1}$

$2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)} \qquad \Delta H_r^0 = +483.7 \text{ KJ.mol}^{-1}$

www.tntextbooks.in

12.9 Enthalpy of combustion

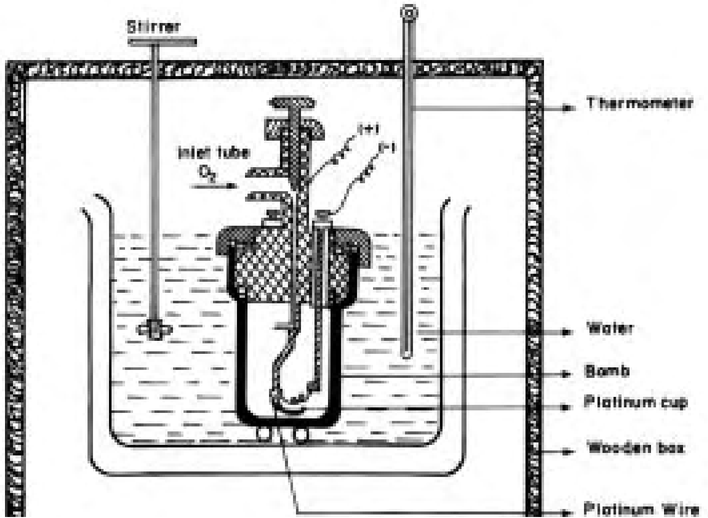
Generally combustion reactions occur in oxygen atmosphere (excess oxygen) with evolution of heat. These reactions are exothermic in nature. Enthalpy changes of combustion reactions are used in industrial heating and in rocket fuels and in domestic fuels.

Enthalpy change of combustion $\Delta_c H$, of a substance at a given temperature is defined as the enthalpy change of the reaction accompanying the complete combustion of one mole of the substance in presence of excess oxygen at that temperature. The enthalpy change of combustion of substances in their standard states are known as standard enthalpy change of combustion ($\Delta_c H^\circ$). These values are useful to experimentally determine the standard enthalpy change of formation of organic compounds.

12.9.1 Bomb calorimeter

Enthalpy changes of combustion of chemical substances are experimentally determined using a bomb calorimeter.

The bomb calorimeter apparatus is shown in Fig.12.3. The inner vessel or the bomb and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws. A weighed amount of the substance is taken in a platinum cup or boat connected with electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurised with excess oxygen. The bomb is lowered in water which is placed inside the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred, uniformly. The reaction is started in the bomb by heating the substance through electrical heating. During burning, the exothermic heat generated inside the bomb raises the temperature of the surrounding water bath. The enthalpy measurements in this case corresponds to the heat of reaction at constant volume. Although the temperature rise is small (only by few degrees), the temperature change can be measured accurately using Beckmann thermometer.



www.tntextbooks.in

Fig. 12.3 Bombcalorimeter

In a typical bomb calorimeter experiment, a weighed sample of benzoic acid (w) is placed in the bomb which is then filled with excess oxygen and sealed. Ignition is brought about electrically. The rise in temperature (ΔT) is noted. Water equivalent (ω_c) of the calorimeter is known from the standard value of enthalpy of combustion of benzoic acid.

$\Delta H_c^o C_6H_5COOH_{(s)} = -3227 \text{ kJ mol}^{-1}$

$$\therefore \quad \Delta H_c^o C_6H_5COOH \times \frac{w}{M_2} = w_c.\Delta T$$

(where M_2 = mol.wt benzoic acid).

Knowing ω_c value, the enthalpy of combustion of any other substance is determined adopting the similar procedure and using the substance in place of benzoic acid. By this experiment, the enthalpy of combustion at constant volume (ΔH_{cVol}) is known

$$\Delta H_c^o{}_{(Vol)} = w_c.\Delta T.$$

Enthalpy of combustion at constant pressure of the substance is calculated from the equation,

$$\Delta H_c^o{}_{(Pr)} = \Delta H_c^o{}_{(Vol)} + \Delta n_{(g)}RT$$

www.tntextbooks.in

and $\Delta n_{(g)}$ is known from the difference in the number of moles of the products and reactants in the completely balanced equation of combustion of the substance with excess oxygen.

Example 2

Calculate the enthalpy of combustion of ethylene at 300K at constant pressure if its enthalpy of combustion at constant volume is -1406 kJ mol^{-1}.

Solution

The complete ethylene combustion reaction can be written as,

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_{2(g)} + 2H_2O_{(l)}$
$\Delta H = \Delta E + RT\,\Delta n_{(g)}$,
where $\Delta n_{(g)} = n_{p(g)} - n_{r(g)}$.
$\therefore\ \Delta_{n(g)} = 2 - (3+1) = -2$.

Enthalpy of combustion at constant volume = ΔE = -1406 kJ mol^{-1}

$\therefore$ Overall enthalpy of combustion
$= \Delta H_c = -1406 + (-2 \times 8.314 \times 10^{-3} \times 300)$
$= -1406 - 4.9884$
$\Delta H_c = -1410.9$ kJ mol^{-1}.

12.10 Enthalpy of neutralisation

The **enthalpy change of neutralisation** is defined as the enthalpy change accompanied by the complete neutralisation of one gram – equivalent amount of a strong acid by a gram-equivalent amount of strong base under fully ionised state in dilute conditions. It is found that the enthalpy of neutralisation of a strong acid and a strong base is a constant value equal to -57.32 kJ. This value is independent of the nature of the strong acid and strong base. Strong acids and strong bases exist in the fully ionised form in aqueous solutions as below:

$H_3O^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + 2H_2O$
(or)
$H_3O^+_{(aq)} + OH^-_{(aq)} \rightarrow 2H_2O_{(l)}\ \Delta_{neu}H^o = -57.32$ KJ.

The H^+ ions produced in water by the acid molecules exist as H_3O^+. During the neutralisation reaction, water and salt (existing as ions) are produced in solution. Thus, enthalpy change of neutralisation is essentially due to enthalpy change per mole of water formed from H_3O^+ and OH^- ions. Therefore, irrespective of the chemical nature, the enthalpy of neutralisation of strong acid by strong base is a constant value. At infinite dilutions, complete ionisation of acids and bases are ensured and also the inter ionic interactions exist in the lowest extents.

In case of neutralisation of a weak acid like acetic acid (CH_3COOH) by a strong base (NaOH) or neutralisation of weak base (NH_4OH) by a strong acid, two steps are involved. The first step is the ionisation of weak acid or weak base since these molecules are only partially ionised. The second step being the neutralisation step of H_3O^+ and OH^- ions. Since ionisation of weak acids and weak bases in water are endothermic and some energy will be used up in dissociating weak acid and weak base molecules.

Thus, acetic acid with NaOH and ammonium hydroxide with HCl neutralisation reactions can be written as,

$$CH_3COOH_{aq} + H_2O_2 \rightarrow CH_3COO^-_{aq} + H_3O^+_{aq}$$
$$Na^+_{aq} + H_3O^+_{aq} + OH^-_{aq} \rightarrow 2H_2O_{(l)} + Na^+_{aq}$$

and

$$NH_4OH \rightarrow NH_4^+ + OH^-$$
$$H_3O^+ + Cl^- + OH^- \rightarrow 2H_2O + Cl^-.$$

Enthalpy of neutralisation of a weak acid or a weak base is equal to -57.32 kJ + enthalpy of ionisation of weak acid (or) base. Since enthalpy of ionisation of weak acid or base is endothermic it is a positive value, hence enthalpy of neutralisation of a weak acid or base will be lower than the neutralisation of strong acid and strong base.

Example 3

(a) The measured heats of neutralization of acetic acid, formic acid, hydrocyanic acid, and hydrogen sulphide are 13.20, 13.40, 2.90 and 3.80 KCal per g.equiv. respectively. Arrange these acids in a decreasing order of strength.

(b) Heat of neutralization of formic acid by NH_4OH is 11.9 KCal per g.equiv. What is the heat of ionization of NH_4OH?

Solution

(a) $\Delta H_{(neutralization)} = \Delta H_{(ionization)} + \Delta H_{(H^+ + OH^-)}$

$\therefore\ \Delta H_{(ionization)} = \Delta H_{(neutralization)} - \Delta H_{(H^+ + OH^-)}$

57.32KJ = 13.2 Kcal.

$\Delta H_{(neutralization)}$ for all acids have a -ve sign.

ΔH for ionisation of acetic acid.

$= -13.20 - (-13.70)$

$= +0.50$ Cal/g.equiv

ΔH for ionisation of formic acid

$= -13.40 + 13.70$

$= +0.30$ Cal/g.equiv.

ΔH for ionization of hydrocyanic acid

$= -2.90 + 13.70$

$= +10.80$kCal/g. equiv.

ΔH for ionisation of hydrogen sulphide

$= -3.80 + 13.70$

$= + 9.90$ KCal/g.equiv.

The acid with the lowest positive value of heat of ionization will be the strongest acid. Thus formic acid is the strongest and hydrocyanic acid the weakest acid. The trend in decreasing strength of acids is:

Formic acid > acetic acid > hydrocyanic acid > hydrogen sulphide.

(b) The thermochemical equations are:

(1) $HCOOH + NH_4OH \rightarrow HCOONH_4 + H_2O$ $\qquad \Delta H_1 = -11.9$ KCal

(2) $HCOOH \rightarrow HCOO^- + H^+$ $\qquad \Delta H_2 = + 0.30$ KCal.

(3) $NH_4OH \rightarrow NH_4^+ + OH^-$. $\qquad \Delta H_3 = x$. KCal.

(4) $H^+ + OH^- \rightarrow H_2O_{(l)}$; $\qquad \Delta H_4 = -13.70$ KCal.

The sum of reactions (2), (3) and (4) should equal reaction (1).

$\therefore\ \Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$

$-11.90 = 0.30 + x - 13.70$

$x = -11.90 - 0.30 + 13.70$

$= + 1.50$ KCal.g.equiv^{-1}

ΔH for ionization of

$NH_4OH = +1.50$ kCal/g.equiv.

Questions

A. Choose the correct answer :

1. Which of the following is not a state functions?

   (a) q (b) q + w (c) ΔH (d) V +PV

2. Which of the following is an extensive property?

   (a) volume (b) density (c) refractive index (d) molar volume

3. Which of the following is an exothermic reaction?

   (a) melting of ice (b) combustion reactions
   (c) hydrolysis (d) boiling of water

4. Which of the following is reversible process?

   (a) Diffusion (b) melting (c) neutralization (d) combustion

5. In which process, work is maximum?

   (a) reversible (b) irreversible (c) exothermic (d) cyclic

B. Fill in the blanks

1. Translational energy of molecules is a part of _______ energy of the system.
2. Specific heat of a liquid system is________ property.
3. Work done in the reversible expansion is
4. Combustion is an _______ process.
5. Heat of neutralisation of a strong acid is ____ than that of a weak acid.

C. Write in one or two sentence:

1. Name the equipment using which heat of combustion of compounds are determined?
2. Energy can be created and be destroyed. State whether this is true or false.
3. Define zeroth law of thermodynamics.
4. Give the relation between ΔU and ΔH.
5. Define an adiabatic process.
6. Write the differences between an exothermic and an endothermic process.
7. What are intensive and extensive properties?.
8. Define first law of thermodynamics.
9. Explain thermal and mechanical equilibrium processes.

D. Explain briefly on the following

10. Describe a bomb calorimeter and explain how heat of formation of an organic compound is determined.

www.tntextbooks.in

11. Compare the enthalpy changes that occur between the neutralisation of a strong acid and a weak acid by sodium hydroxide. Explain the differences seen.

Miscellaneous

1. Calculate the enthalpy of combustion of acetic acid (l) when burnt in excess of O_2 in a bomb calorimeter. Given that $\Delta H_f°$, $H_2O_{(l)}$ = -285.84 KJ mol^{-1} and $\Delta_f H°$, $CO_2(g)$ = -393.52 KJ mol^{-1}; $\Delta_f H°$ $CH_3COOH_{(l)}$ = -463 KJ mol^{-1}. (Ans : $\Delta_c H°$ = -895.72 KJ.mol^{-1})
2. Heat of neutralisation of a weak acid HA by NaOH is -12.13 kJ mol^{-1}. Calculate the enthalpy of ionization of HA. (Ans : $\Delta H^{\sigma}_{ionisation}$ = +43.77 kJ mol^{-1})
3. ΔH for the reaction at 298 K $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_{2(g)}$ is 282.85 KJ mol^{-1}. Calculate ΔU of the reaction. (Ans : ΔU = 283.85 KJ mol^{-1})

SUMMARY

In this chapter the importance of thermodynamics with a lot of experiments and problems are discussed. The definitions like system, surroundings, intensive and extensive properties, thermodynamic properties are given with brief explanations. The laws of thermodynamics are explained with simple examples. To understand thermodynamics, several problems are given both worked out and practice.

REFERENCES

1. Thermodynamics by Samuel Glasstone.
2. Physical Chemistry by Lewis and Glasstone.
3. Physical Chemistry by Castllan.
4. Physical Chemistry by P.L.Soni.
5. Atkins' Physical Chemistry seventh edition 2002.
Oxford University Press
Page 57

IUPAC recommendation

In common usage , the transition subscript is often attached to ΔH, as in

Transition - Δ_{trs} H
Fusion - Δ_{fus} H
Vaporisation - Δ_{vap} H

www.tntextbooks.in

13. CHEMICAL EQUILIBRIUM - I

OBJECTIVES

- *to understand the scopes of chemical equilibrium and to know the extent of completeness of chemical reactions.*
- *to compare and learn about the reversible and irreversible reactions.*
- *to study the dynamic nature of the chemical equilibrium.*
- *to explain the equilibrium existing in physical and chemical changes.*
- *to define law of chemical equilibrium and the equilibrium constant. To express equilibrium constant in terms of concentration and partial pressures and inter relate them.*
- *to deduce expressions for equilibrium constants of homogeneous and heterogeneous chemical equilibria and study suitable examples in each.*

Equilibrium in Chemical Reactions

Consider a chemical reaction between A and B to form products C and D. After allowing sufficient period of time for the reaction, upon analyses, when A and B are absent in the reaction mixture, then the reaction is understood to be complete and only the presence of C and D will be detected. For example, when sodium reacts with water, sodium hydroxide and hydrogen gas are produced, and the reverse reaction to form back the reactants never occurs even when the reaction vessel is a closed one. Reactions when go to completion and never proceed in the reverse direction are called as **irreversible reactions**. The chemical equations of such reactions are represented with a single arrow as $A + B \rightarrow C + D$.

For Example. $2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$

However, even after allowing sufficient period of time for reaction, when the presence of A and B are always detected along with C and D, then such reactions are understood to be never complete.

For example, when H_2 and I_2 are reacted, 2 HI is formed. Initially the reaction proceeds to form HI until a certain period of time and with further increase in the reaction time, HI molecules dissociate to produce back H_2 and I_2 in such a way that, the reaction mixture always contain H_2, I_2 and HI for any length of time until external factors like temperature, pressure, catalyst etc. are applied. Reactions which never proceed to completion in both forward and backward direction are called as **Equilibrium reactions**.

The chemical equation of such reactions are represented as,

$$A + B \rightleftharpoons C + D$$

Example $H_2 + I_2 \rightleftharpoons 2\,HI$

when both forward and reverse reaction rates are equal, the concentration of reactants and products do not change with any length of reaction time. Physical transformations of matter like change of solid to liquid states or liquid to vapour states also take place under equilibrium conditions with both the states of matter being present together. For example, at 0°C, melting ice and freezing water are both present.

13.1 Scope of Chemical Equilibrium

Study of chemical equilibria possesses many scopes. The knowledge on whether the equilibrium lies in favour of reactants or products under certain experimental conditions is useful to increase yields in industrial processes, to establish the exact proton transfer equilibria in aqueous protein solutions. Since small changes in equilibrium concentration of hydrogen ion may result in protein denaturing and cell damage etc. This study is also useful or certain acids, bases and salts in water exist in ionic equilibria which control their use as buffers, colour indicators etc.

13.2 Reversible and Irreversible Reactions

A reaction which can go in the forward and backward direction simultaneously under the same conditions, is called a **reversible reaction**.

If the forward reaction is written as

$$A + B \xrightarrow{k_f} C + D$$

then, the reverse reaction is written as

$$C + D \xrightarrow{k_r} A + B.$$

The reversible reaction is represented as

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D$$

Some examples of reversible reactions are :

$$2\,NO_{2(g)} \rightleftharpoons N_2\,O_{4(g)}$$

$$PCl_{5(s)} \rightleftharpoons PCl_{3(s)} + Cl_{2\,(g)}$$
$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}.$$

In a reaction when the product molecules never react to produce back the reactants, then such a reaction is called as **irreversible reaction**. For example,

$$NaCl_{(aq)} + AgNO_{3(aq)} \longrightarrow NaNO_{3(aq)} + AgCl \downarrow$$

In irreversible reactions only forward reaction takes place and the reaction goes to completion. After the completion, only products exist.

13.3 Nature of Chemical Equilibrium

The occurrence of chemical equilibrium is seen in reversible reactions only. Chemical equilibrium may be defined as the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentration of reactants and products do not change with time. The true equilibrium of a reaction can be attained from both sides.

For X $\longrightarrow$ Y reaction, $a = \frac{-d[x]}{dt}$; $b = \frac{d[Y]}{dt}$

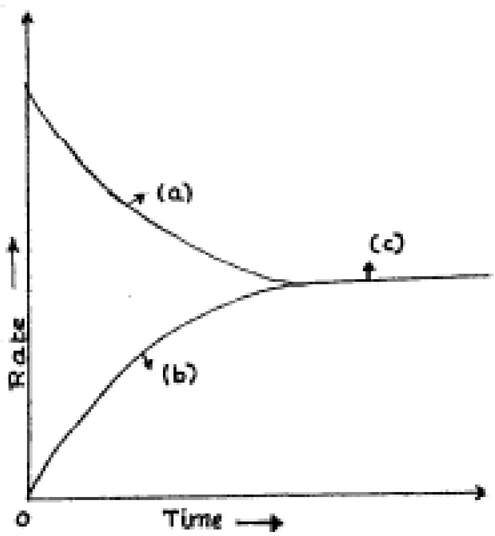


Fig. 13.1. (a) Forward rate (b) reverse rate (c) Equilibrium condition.

The equilibrium concentrations of reactants and products do not change

www.tntextbooks.in

with time. This is because, since the forward reaction rate equals with backward reaction rate as and when the products are formed, they react back to form the reactants in equal capacity. The equilibrium concentrations of reactants are different from their initial concentrations.

The equilibrium concentrations are represented by square brackets with subscript \`eq' or as $[\ ]_{eq}$. Thus $[A]_{eq}$ denotes the equilibrium concentration of A in moles per litre. In modern practice, the subscript \`eq' is not used.

13.3.1 Dynamic Equilibrium

When a reversible reaction attains equilibrium it appears that the concentrations of individual reactants and that of the products remain constant with time. Apparently, the equilibrium appears as dead (or) as not proceeding. Actually, the reactant molecules are always reacting to form the product molecules. When the product molecules are able to react with themselves under the same experimental condition to form the same amount of reactants simultaneously (at the same time) in an equal rate of the forward reaction, then the process is a ceaseless phenomenon. Thus chemical equilibrium is **dynamic** when the forward and reverse reactions take place **endlessly and simultaneously with equal rates**. Therefore chemical equilibrium is called as dynamic equilibrium.

13.3.2 Characteristics of Chemical Equilibrium

(i) Constancy of concentrations

When a chemical equilibrium is established in a closed vessel at constant temperature, the concentrations of various species like reactants and products remain unchanged.

The reaction mixture consisting of reactants and products at equilibrium is called as equilibrium mixture.

The concentrations of reactants and products at equilibrium are called as equilibrium concentrations.

(ii) **Equilibrium can be initiated from either side.** The state of equilibrium of a reversible reaction can be arrived at whether we start from reactants or products.

For example, this equilibrium $H_{2(g)} + I_{2(g)}$ _ $2HI_{(g)}$ can be achieved whether we start with H_2 and I_2 or with HI.

(iii) Equilibrium cannot be attained in an open vessel

www.tntextbooks.in

Only in a closed vessel, a reaction can be considered to attain equilibrium since no part of reactants or products should escape out. In an open vessel, gaseous reactants or products may escape so that no possibility of attaining equilibrium exists. Equilibrium can be attained when all the reactants and products are in contact with each other.

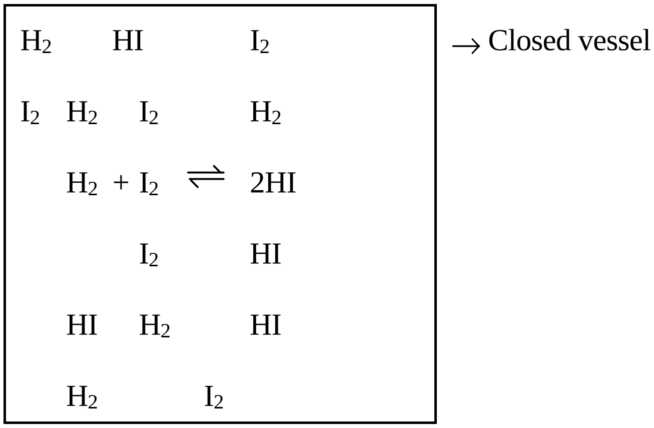


Fig. 13.2 A chemical equilibrium between $H_2 + I_2$ and 2HI

(iv) Catalyst does not alter the equilibrium

When a catalyst is added to the equilibrium system, it speeds up the rates of both forward and reverse reactions to an equal extent. Therefore the equilibrium is not changed but the state of equilibrium is attained earlier.

(v) The value of equilibrium constant does not depend upon the initial concentration of reactants.

(vi) At equilibrium, the free energy change is minimum or zero.

(vii) When temperature is changed, the forward and backward reaction rates are changed and the equilibrium concentrations of reactants and products are changed.

13.3.3 Equilibrium in physical processes

When there is a change in the state of occurrence of matter, then a physical transformation is said to have occurred. The equilibrium concepts are also applicable to physical state transformations of matter.

(i) Solid-liquid equilibria

Here, the solid and the liquid forms of a substance co exist at characteristic temperature and pressure. At 1 atm and at the melting point of a substance, there is a solid-liquid equilibrium existing. For example, the solid-liquid equilibrium of water at 0°C,

$$\text{water}_{(l)} \rightleftharpoons \text{ice}_{(s)}$$

occurs at 1 atm pressure. Here, both the liquid and ice exist together. Also, at melting point of ice or freezing point of water, the rate of melting of ice equals with rate of freezing of water. With change in pressure the temperature at which this equilibrium onsets changes.

(ii) Liquid-vapour equilibrium

Here the vapour and the liquid forms of a substance exist simultaneously at a characteristic temperature called as boiling point and at 1 atm pressure. For example at 100°C which is the boiling point of water, and 1 atm pressure,

$$\text{Water}_{(l)} \rightleftharpoons \text{Steam}_{(g)}$$

both liquid water and water vapour (steam) exist simultaneously, provided the vapour does not escape.

(iii) Solid-solid equilibrium

When a substance existing in a particular crystalline solid transforms to another crystalline form retaining its solid nature at a characteristic temperature called the transition temperature with both the solid forms coexisting, at 1 atm pressure then it is said to be in solid-solid equilibrium. For example, solid sulphur exhibits equilibrium with rhombic to monoclinic forms at its transition temperature.

$$S_{(\text{rhombic})} \rightleftharpoons S_{(\text{monoclinic})}$$

13.3.4 Equilibrium in chemical processes

Chemical equilibrium exists in two types such as homogeneous and heterogeneous equilibria. In a chemical reaction existing in equilibrium, if all the reactants and products are present in the same phase, then a homogeneous equilibria is said to have occurred.

For example,

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$.

Here all the reactants and products exist in gaseous state. This is an example of gas-phase equilibrium.

The chemical equilibrium in which all the reactants and products are in the liquid phase are referred to as liquid equilibria. For example,

$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$

Both gas phase and liquid phase equilibria are collectively called as homogeneous equilibria.

Heterogeneous equilibrium

In a chemical equilibrium, if the reactants and products are in different phases then heterogeneous equilibrium is said to have occurred.

Examples :

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

Here, only when the reaction is carried out in closed vessel, the equilibrium state is established.

13.4 Law of chemical equilibrium and equilibrium constant

Law of Mass action

Two Norwegian Chemists, Guldberg and Waage, studied experimentally a large number of equilibrium reactions. In 1864, they postulated a generalisation called the **Law of Mass action**. It states that:

"the rate of a chemical reaction is proportional to the active masses of the reactants". By the term `active mass', it is meant the molar concentration i.e., number of moles per litre.

Law of Mass Action based on the Molecular Collision theory

www.tntextbooks.in

We assume that a chemical reaction occurs as the result of the collisions between the reacting molecules. Although some of these collisions are ineffective, the chemical change produced is proportional to the number of collisions actually taking place. Thus at a fixed temperature the rate of a reaction is determined by the number of collisions between the reactant molecules present in unit volume and hence its concentration, which is generally referred as the active mass.

13.4.1 Equilibrium constant and equilibrium law

Let us consider a general reaction

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D$$

and let [A], [B], [C] and [D] represent the molar concentrations of A,B,C and D at the equilibrium point. According to the Law of Mass action,

Rate of forward reaction $\alpha[A]\,[B] = k_f\,[A]\,[B]$

Rate of reverse reaction $\alpha[C]\,[D] = k_r\,[C]\,[D]$

where k_f and k_r are rate constants for the forward and reverse reactions.

At equilibrium, rate of forward reaction = rate of reverse reaction.

Therefore,

$$k_f[A]\,[B] = k_r\,[C]\,[D]$$

or $$\frac{k_f}{k_r} = \frac{[C]\,[D]}{[A]\,[B]} \qquad \text{... (1)}$$

At any specific temperature k_f/k_r is a constant since both k_f and k_r are constants. The ratio k_f/k_r is called **equilibrium constant** and is represented by the symbol K_c. The subscript `c' indicates that the value is in terms of concentration of reactants and products. The equation (1) may be written as

www.tntextbooks.in

$$\underset{\uparrow}{K_f} = \frac{[C]\,[D] \leftarrow \text{Products concentration}}{[A]\,[B] \leftarrow \text{Reactants concentrations}} \qquad \ldots (2)$$

Equilibrium constant

This equation is known as the equilibrium constant expression or equilibrium law. Hence [C], [D] [A] and [B] values are the equilibrium concentrations and are equal to equilibrium concentrations.

13.4.2 Equilibrium Constant Expression for a Reaction in General Terms

The general reaction may be written as

$$aA + bB \rightleftharpoons cC + dD.$$

where a,b,c and d are numerical quotients of the substance A,B,C and D respectively. The equilibrium constant expression is

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad \ldots(3)$$

where K_c is the Equilibrium constant. The general definition of the equilibrium constant may thus be stated as :

The product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.

For Example

(a) Consider the equilibrium constant expression for the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3\,(g)$

(1) The equation is already balanced. The numerical quotient of H_2 is 3 and NH_3 is 2.

(2) The concentration of the `product' NH_3 is $[NH_3]^2$.

(3) The product of concentrations of the reactants is $[N_2]\,[H_2]^3$.

(4) Therefore, the equilibrium constant expression is

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

(b) Consider the equilibrium constant expression for the reaction

$N_2O_5\,(g) \rightleftharpoons NO_{2(g)} + O_2\,(g)$

(1) The equation as written is not balanced. Balancing yields

$2N_2O_5 \rightleftharpoons 4NO_2 + O_2$.

(2) The coefficient of the product NO_2 is 4 and of the reactant N_2O_5 is 2.

(3) The product of the concentrations of products is $[NO_2]^4\,[O_2]$.

(4) The concentration of the reactant is $[N_2O_5]^2$

(5) The equilibrium constant expression can be written as

$$K_c = \frac{[NO_2]^4\,[O_2]}{[N_2O_5]^2}$$

(c) Consider the equilibrium constant expression of the reaction.

$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$

(i) Write the product of concentrations of `products' divided by the product (multiplication) of concentrations of `reactants'.

(ii) The concentration of H_2 is to be raised by its coefficient in the balanced equation. Thus, the equilibrium constant expression is :

$$K_c = \frac{[CO]\,[H_2]^3}{[CH_4]\,[H_2O]}$$

13.4.3 Equilibrium Constant Expression for Gaseous Equilibrium

www.tntextbooks.in

When all the reactants and products are gases, we can formulate the equilibrium constant expression in terms of partial pressures exactly similar to equation (1).

The partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature.

Considering equation (1) : $K_p = \dfrac{p_C^c p_D^d}{p_A^j p_B^k}$

The gaseous equilibrium reaction of SO_2 can be written as follows

$$2S0_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3\,(g)}$$

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2 .\, p_{O_2}} \text{ atm}^{-1}$$

As an example, K_p value can be calculated from the following data:

The total pressure in the reaction flask is 1 atm and the partial pressures of oxygen, SO_2 and SO_3 at equilibrium are 0.1 atm, 0.57 atm, 0.33 atm respectively.

$$\therefore K_p = \frac{(0.33)^2}{(0.57)^2 \text{ x } 0.1} \text{ atm}^{-1}$$

$$= \frac{(0.33)^2}{0.03249} \text{ atm}^{-1}$$

$$K_p = 3.3518 \text{ atm}^{-1}.$$

In the ammonia formation reaction, the gaseous chemical equilibrium exists as:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

where p = partial pressure

Similarly for HI formation in the gaseous state from H_2 and I_2 gases, the equilibrium constant (K_p) can be written as

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

$$K_p = \frac{p_{HI}^2}{p_{H_{2(g)}} p_{I_{2(g)}}}$$

here K_P has no units.

Problem 1

Equivalent amounts of hydrogen and iodine are allowed to reach equilibrium at a given temperature. $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$. If 80% of the hydrogen can be converted to hydrogen iodide, what is the value of K_c and K_p at this temperature.

	H_2	I_2	HI
Initial concentration mol dm^{-3}	1	1	0
Equilibrium concentration	1-0.8	1-0.8	1.6
	= 0.2	= 0.2	1.6

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{1.6 \text{ x } 1.6}{0.2 \text{ x } 0.2} = 64.$$

$K_p = K_c(RT)^{\Delta n}$

In this reaction $\Delta n = 0$

$\therefore\ K_p = K_c$

$K_c = 64$

13.4.4 Degree of dissociation (x)

In the study of dissociation equilibrium, it is easier to derive the equilibrium constant expression in terms of **degree of dissociation (x)**. It is considered as the fraction of total molecules that actually, dissociate into the simpler molecules x has no units. If x is the degree of dissociation then for completely dissociating molecules x = 1.0. For all dissociations involving equilibrium state, x is a fractional value. If x is known, K_c or K_p can be calculated and vice-versa.

Equilibrium constants in terms of degree of dissociation

(i) Formation of HI from H_2 and I_2

The formation of HI from H_2 and I_2 is an example of gaseous homogeneous equilibrium reaction. It can be represented as

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad \Delta H = -10.4\ \text{kJ}$$

This equilibrium is an exothermic one.

Let us consider that one mole of H_2 and one mole of I_2 are present initially in a vessel of volume V dm^3. At equilibrium let us assume that x mole of H_2 combines with x mole of I_2 to give 2x moles of HI. The concentrations of H_2, I_2 and HI remaining at equilibrium can be calculated as follows :

	$H_{2(g)}$	$I_{2(g)}$	$HI_{(g)}$
Initial number of moles	I	I	0
Number of moles reacted	x	x	-
Number of moles remaining at equilibrium	1-x	1-x	2x
Equilibrium concentration	$\left(\frac{1\text{-x}}{V}\right)$	$\left(\frac{1\text{-x}}{V}\right)$	$\left(\frac{2x}{V}\right)$

According to the law of mass action,

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]}$$

Substituting the values of equilibrium concentrations in the above equation, we get

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{4x^2}{V^2} \text{ x } \frac{V^2}{(1-x)^2}$$

$$\therefore \quad \boxed{4x^2}$$

$$\boxed{K_c = \frac{\quad}{(1\text{-}x)^2}}$$

If the initial concentration of H_2 and I_2 are equal to a and b moles dm^{-3} respectively, then it can be shown that

$$K_c = \frac{4x^2}{(a\text{-}x)(b\text{-}x)}$$

Derivation of K_p in terms of x

Let us consider one mole of H_2 and one mole of I_2 are present initially. At equilibrium, let us assume that x mole of H_2 combines with x mole of I_2 to give 2x moles of HI. Let the total pressure at equilibrium be P atmosphere. The number of moles of H_2, I_2 and HI present at equilibrium can be calculated as follows :

	$H_{2(g)}$	$I_{2(g)}$	$HI_{(g)}$
Initial number of moles	I	I	O
Number of moles reacted	x	x	-
Number of moles remaining at equilibrium	I-x	I-x	2x
$\therefore$ The total number of moles at equilibrium	= 1 - x + 1 - x + 2x = 2		

We know that partial pressure is the product of mole fraction and the total pressure. Mole fraction is the number of moles of that individual component divided by the total number of moles in the mixture. Therefore,

$$p_{H_2} = \frac{1-x}{2}P, p_{I_2} = \frac{1-x}{2}P, p_{HI} = \frac{2x}{2}P$$

$$\text{We know that } K_p = \frac{p^2_{HI}}{p_{H_2} \cdot p_{I_2}}$$

Substituting the values of partial pressures in the above equation, we get

$$K_p = \frac{\left(\frac{2x}{2}p\right)^2}{\left(\frac{1-x}{2}\right)p\left(\frac{1-x}{2}\right)p} = \frac{4x^2P^2}{4} x \frac{4}{(1-x)^2 p^2}$$

$$\therefore \quad \boxed{K_p = \frac{4x^2}{(1-x)^2}}$$

we see that K_p and K_e are equal in terms of x values. The influence of various factors on the chemical equilibrium can be explained as below:

(i) Influence of pressure : The expressions for the equilibrium constants K_c and K_p involve neither the pressure nor volume term. So the equilibrium constants are independent of pressure and volume. Pressure has therefore no effect on the equilibrium.

(ii) Influence of concentration : The addition of either H_2 or I_2 to the equilibrium mixture well increase the value of the denominator in the equation $K_e = [HI]^2/[H_2][I_2]$ and hence tends to decrease the value of K_e. In order to maintain the constancy of K_c, the increase in the denominator value will be compensated by the corresponding increase in the numerator value. In other words, the forward reaction will be favoured and there will be corresponding increase in the concentration of HI.

(iii) Influence of catalyst : A catalyst affects both the forward and reverse reactions to the same extent. So it does not change the relative amounts of reactants and products at equilibrium. The values of K_e and K_p are not affected. However the equilibrium is attained quickly in the presence of a catalyst.

(ii) Dissociation of PCl_5

Phosphorus pentachloride dissociates in gas phase to give PCl_3 and Cl_2. This is an example of gaseous homogeneous equilibrium. It can be represented as

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

www.tntextbooks.in

For this reaction $\Delta n = 1$ $\therefore K_p = K_c (RT)$

Let us consider that one mole of PCl_5 is present initially in a vessel of volume V dm^3. At equilibrium let x mole dissociates to give x mole of PCl_3 and x mole of Cl_2. The equilibrium concentrations of the components can be given as follows :

	$PCl_{5(g)}$	$PCl_{3(g)}$	$Cl_{2(g)}$
Initial number of moles	I	0	0
Number of moles reacted	x	-	-
Number of moles at equilibrium	1-x	x	x
Equilibrium concentration	$\left(\frac{1-x}{V}\right)$	$\left(\frac{x}{V}\right)$	$\left(\frac{x}{V}\right)$

According to law of mass action,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5}$$

Substituting the values of equilibrium concentrations in the above equation we get,

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)} = \frac{x^2}{V^2} \frac{V}{1-x}$$

$$\boxed{K_C = \frac{x^2}{(1-x)V}}$$

Derivation of K_p in terms of x

Let us consider that one mole of PCl_5 is present initially. At equilibrium, let us assume that x mole of PCl_5 dissociates to give x mole of

www.tntextbooks.in

PCl_3 and x mole of Cl_2. Let the total pressure at equilibrium be P atmosphere. The number of moles of PCl_5, PCl_3 and Cl_2 present at equilibrium can be given as follows :

	$PCl_{5(g)}$	$PCl_{3(g)}$	$Cl_{2(g)}$
Initial number of moles	1	0	0
Number of moles reacted	x	-	-
Number of moles at equilibrium	1-x	x	x

$\therefore$ Total number of moles at equilibrium $= 1 - x + x + x$

$= 1 + x$

We know that partial pressure is the product of mole fraction and the total pressure. Mole fraction is the number of moles of that component divided by the total number of moles in the mixture. Therefore

$$p_{PCl_5} = \frac{1-x}{1+x} P; \quad p_{PCl_3} = \frac{x}{1+x} P; \; p_{Cl_2} = \frac{x}{1+x} . P$$

we know that $K_p = \dfrac{p_{PCl_3} \, . \, p_{Cl_2}}{p_{PCl_5}}$

substituting the values of partial pressures in this expression

$$K_p = \frac{\left(\frac{x}{(1+x)} P\right)\left(\frac{x}{(1+x)} P\right)}{\left(\frac{1-x}{1+x} P\right)}$$

$$= \frac{x^2.P^2}{(1+x)^2} \quad \frac{(1+x)}{(1-x)} \quad \frac{1}{P}$$

$$K_p = \frac{x^2P}{1-x^2}$$

When $x << 1$, x^2 value can be neglected when compared to one.

$$\therefore K_p \simeq x^2P$$

This equation can be used to predict the influence of pressure on this equilibrium.

(i) Influence of pressure : The expression for K_c contains the volume term and the expression for K_p contains the pressure term. Therefore this equilibrium is affected by the total pressure. According to the above equation, increase in the value of P will tend to increase the value of K_p. But K_p is a constant at constant temperature. Therefore, in order to maintain the constancy of K_p the value of x should decrease. Thus, increase in total pressure favours the reverse reaction and decreases the value of x.

(ii) Influence of concentration : Increase in the concentration of PCl_5 favours the forward reaction, while increase in the concentration of either PCl_3 or Cl_2 favours the reverse reaction. Increase in the concentration of a substance in a reversible reaction will favour the reaction in that direction in which the substance is used up.

(iii) Influence of catalyst : A catalyst will affect the rates of the forward and reverse reactions to the same extent. It does not change either the amount of reactants and products present at equilibrium or the numerical value of K_p or K_p. However, the equilibrium is obtained quickly in the presence of a catalyst.

Problem 2

At 100°C and 1 atm pressure, the degree of dissociation of N_2O_4 is 0.9114. Calculate its equilibrium constant. What will be the degree of dissociation if temperature remains constant and pressure is doubled?

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

$$(1-x) \qquad 2x$$

x = degree of dissociation

1-x = fraction undissociated

P = total pressure

Total no. of molecules in equilibrium

= 1 – x + 2x = (1+x)

$$K_p = \frac{4x^2P}{1-x^2}$$

P = 1 atm and x = 0.9114 (given)

$$\therefore \; K_p = \frac{1 \text{ x } 4 \text{ x } 0.9114^2}{1 - 0.9114^2} = 19.63$$

Let y be the degree of dissociation at P = 2 atm

$$\text{Then } K_p = 19.63 = \frac{4y^2P}{1-y^2} = \frac{4y^2 \text{ x } 2}{1-y^2}$$

Solving for y, y = 0.8428

i.e., degree of dissociation at P = 2 atm is 0.8428.

In this case, increase in pressure lowers the degree of dissociation.

Problem 3

In the reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

at 298K, the partial pressures of $NO_{(g)}$, $O_{2(g)}$ $N_{2(g)}$ at equilibrium are 0.9, 0.3 and 0.01 atoms respectively. Calculate the value of K_p.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{(g)}$$

$$K_p = \frac{p^2_{NO}}{p_{N_2} \text{ x } p_{O_2}}$$

where p = partial pressure.

$$K_p = \frac{0.9 \times 0.9}{0.3 \times 0.01} = 270.0$$

13.4.5 Characteristics of Equilibrium constant

(i) The K_{eq} (K_c or K_p) values do not depend on the initial concentrations of reactants but depend only on the equilibrium concentration values.

(ii) When K_{eq} values are greater than unity, the equilibrium is favourable towards product formations and vice-versa.

(iii) K_{eq} values do not change in presence of catalyst catalyst only speeds up the forward and backward reactions.

(iv) Temperature changes on the chemical equilibrium changes the K_{eq} values. For exothermic equilibrium reactions increase in temperature, lowers the K_{eq} values and for endothermic equilibrium, increase in temperature increases the K_{eq} values. Generally, when T is raised, the equilibrium shifts in a direction in which heat is absorbed.

(v) Pressure changes on gaseous equilibrium alters the K_p values. For dissociation equilibrium, increase in pressure lowers the K_p values, while for association equilibrium (number of product molecules < number of reactant molecules) increase in pressure increases the K_p values. When the number of product and reactant molecules are equal, there is no pressure effect.

13.5 Heterogeneous equilibria

The chemical equilibrium in which the reactants and products are not in the same phases are called **heterogeneous equilibrium**. An example of heterogeneous equilibrium can be the decomposition of calcium carbonate which upon heating forms calcium oxide and carbondioxide under equilibrium conditions. When the reaction is carried out in a closed vessel, the following heterogeneous equilibrium is established.

$$CaCO_3 \rightleftharpoons CaO_{s)} + CO_2(g)$$

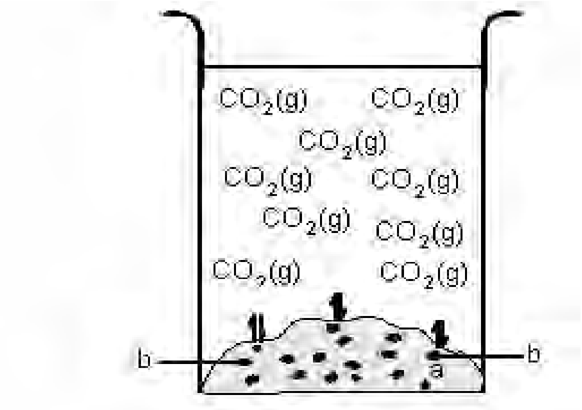


Fig. 13.3 Heterogeneous equilibrium

a = $CaCO_3$ Solid ; b = CaO Solid

The equilibrium constant expression for $CaCO_3$ dissociation can be written as

$$K = \frac{[CO_2]\,[CaO]}{[CaCO_3]}$$

But CaO and $CaCO_3$ are pure solids. The activity or concentration of pure solids is unity.

Thus $K_c = [CO_2]$

in terms of partial pressures,

$K_p = p_{co_2}$, where Pco_2 is the pressure of CO_2 alone in equilibrium.

There are many examples of heterogeneous chemical equilibria with K_p and K_c values different depending on the number of product and reactant molecules.

(i) The equilibrium constant expression for decomposition of liquid water would be

$$2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$$

$$K = \frac{[H_2]^2\,[O_2]}{[H_2O]^2}$$ but activity of liquid $H_2O = 1.0$

$\therefore\ K_c = [H_2]^2\,[O_2]$

www.tntextbooks.in

and $K_p = (p_{H_2})^2 \, (p_{O_2})$ p = partial pressure.

(ii) Consider the equilibrium reaction of decomposition of NH_4 Cl.

$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

$K_c = [NH_3]\,[HCl]$ because $[NH_4Cl_{(5)}] = 1.0$
$K_p = p_{NH_3} \;\; p_{HCl}$. p = partial pressure

(iii) Consider the hydrogen gas evolution equilibrium such as

$3Fe(s) + 4H_2O_{(g)} \rightleftharpoons Fe_3O_4 + 4H_2(g)$

$$K_c = \frac{[H_2]^4}{[H_2O]^4} \text{ and } k_p = \frac{(p_{H_2})^2}{(p_{H_2O})^4}$$

since activities of Fe(G) and $Fe_3O_4(s)$ are 1.0.

Problem 4

In the equilibrium reaction

$CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)}$ the partial pressure of CO2 and CO are 0.78 atm and 1.22 atm respectively at equilibrium. Calculate the equilibrium constant

(Ans. : Kp = 1.9 atm)

Questions

A. Choose the correct answer :

1. In which equilibrium pressure has no effect

   (a) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
   (b) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI(g)$
   (c) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
   (d) $NH_4Cl_{(g)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

2. For the equilibrium $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, the K_p and K_c values are related as

   (a) $K_p = K_c(RT)$ (b) $K_p = K_c\,(RT)^2$ (c) $K_p = K_c\,(RT)^{-1}$ (d) $K_p = K_c\,(RT)^{-2}$

3. For endothermic equilibrium, increase in temperature changes the K_{eq} value as

www.tntextbooks.in

(a) No change (b) Increases (c) Decreases

4. In the heterogenous equilibrium
$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ the K_{eq} value is given by
   (a) partial pressure of CO_2
   (b) activity CaO
   (c) activities of $CaCO_3$
   (d) $[CaO]/[CaCO_3]$
5. For the equilibrium reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
   (a) $K_p = K_c$ (b) $K_p > K_c$ (c) $K_p < K_c$ (d) $K_p = 1/K_c$

B. Fill in the blanks

6. In endothermic equilibrium reaction the increase in temperature__________the reaction.
7. When the reactant is a liquid which decomposes to gaseous products. Then the equilibrium is called as ______________
8. When reactants and products are in gaseous state, the equilibrium constant can be expressed in terms of
9. Value of the equilibrium constant is _______ of the initial concentration of reactants.
10. According to law of mass action, the rate of a chemical reaction is proportional to ________ of reactants.

C. Match the following

11. K_p	a. homogeneous equilibrium
12. $CaCO_3 \rightleftharpoons CaO_{(5)} + CO_{2(g)}$	b. active mass of reactants
13. Rate of reaction	c. irreversible reaction
14. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	d. Degree of dissociation
15. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$	e. $K_C(RT)^{\Delta n}$
	f. Heterogeneous equilibrium

D. Write in one or two sentence

16. Define law of mass action
17. Write the K_p expression for $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
18. Relate K_p and K_c when $\Delta n = 0$, $\Delta n = 1$; $\Delta n = 2.0$
19. Give an example of irreversible reaction
20. Reason out why equilibrium concentrations remain constant.

E. Explain briefly on the following

21. Differentiate irreversible and reversible reactions.
22. Explain the characteristics of a chemical equilibrium.
23. Write a note on heterogeneous equilibrium reaction.
24. Two moles of H_2 and three moles of I_2 are taken in 2 dm^3 vessel and

heated. If the equilibrium mixture contains 0.8 moles of HI, calculate K_p and K_c for the reaction

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ Ans : (0.036)

25. At 25°C, K_c for the reaction $3C_2H_{2(g)} \rightleftharpoons C_6H_{6(g)}$ is 4.0. If the equilibrium concentration of C_2H_2 is 0.5 mol. lit^{-1}. What is the concentration of C_6H_6?

    (Ans) $[C_6H_6] = 0.5$ mol.lit^{-1}

SUMMARY

- When the products of a chemical reaction do not react back to give the reactants, then the reaction is called as irreversible reaction.
- In reversible reactions in a closed system, when the rate of forward reaction equals the backward reaction, equilibrium state is reached. The equilibrium concentrations do not change with time.
- For a general equilibrium reaction,

  $$aA + bB \rightleftharpoons cC + dD,$$

  the equilibrium content, K_{eq} is given by $[C]^c [D]^d / [A]^a [B]^b$.
- For gaseous reaction K_{eq} can be expressed in partial pressures also which is `K_p' value.
- $K_p = K_c (RT)^{\Delta n}$ where Δn is the difference in the number of molecules of products and reactants in the equilibrium.
- K_{eq} value depend on Temperature, pressure, and equilibria concentrations and does not depend on catalyst and initial concentrations.
- Concepts of chemical equilibrium also applies to physical equilibria like solid to liquid, liquid to vapour and solid to solid physical state transformations which take place at constant temperature.
- When the places of the reactants and products in the equilibrium reaction are different like in solid (or) in liquid state then heterogeneous equilibrium is formed. In the equilibrium constant expression, the activities of pure solid and pure liquid form of reactants (or) products are taken as unity.

REFERENCES

1. Physical Chemistry by Maran and Prutton.
2. Physical Chemistry by Lewis and Glasstone.
3. Physical Chemistry by P.W. Atkins.

www.tntextbooks.in

14. CHEMICAL KINETICS - I

OBJECTIVES

- *To study the scope of chemical kinetics as to know the mechanism of reactions for maximum yield and rate in industrial processes.*
- *To define rate of chemical reactions and to deduce the rate constant of the overall process. Also, the factors affecting the rate and the rate constant are studied. To write the differential rate equations for simple reactions.*
- *To study the effects of nature of the reactant, temperature, concentration of the reactants, presence of catalyst surface area of reactants and irradiation on the overall rate of the processes are to be learnt.*
- *To write the rate law and to understand rate constant, order of the reaction. Different units of the rate constant for various orders of the reaction are to be deduced.*
- *Classification of rates of reactions based on order of the reaction is studied with suitable examples. Hence, zero, first, second, pseudo first order, fractional order, third order reactions are studied.*

14.1 Scope of chemical kinetics

Chemical kinetics is the study of the rates and the mechanism of chemical reactions. Commonly the measure of how fast the products are formed and the reactants consumed is given by the rate values.

The study of chemical kinetics has been highly useful in determining the factors that influence the rate, maximum yield and conversion in industrial processes. The mechanism or the sequence of steps by which the reaction occurs can be known. It is also useful in selecting the optimum conditions for maximum rate and yield of the chemical process.

14.1.1 Rate of chemical reactions

The rate of a reaction tells us how fast the reaction occurs. Let us consider a simple reaction.

$$A + B \rightarrow C + D$$

www.tntextbooks.in

As the reaction proceeds, the concentration of the reactant A and B decreases with time and the concentration of the products C + D increase with time simultaneously. The rate of the reaction is defined as the change in the concentration of any reactant or product in the reaction per unit time.

For the above reaction,

Rate of the reaction
= Rate of disappearance of A
= Rate of disappearance of B
= Rate of appearance of C
= Rate of appearance of D

During the reaction, changes in the concentration is infinitesimally small even for small changes in time when considered in seconds. Therefore differential form of rate expression is adopted. The negative sign shows the concentration decrease trend and the positive sign shows the concentration increase trend.

$$\therefore \text{Rate} = \frac{\text{concentration change}}{\text{time taken}} = \frac{-\Delta[A]}{\Delta t}$$

$$= \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{+d[C]}{dt} = \frac{+d[D]}{dt}$$

For a general balanced reaction, written with stoichiometries like x,y, for the reactant and l,m for the product, such as

$xA + yB \rightarrow lC + mD$.

The reaction rate is

$$\text{Rate} = \frac{-1}{x}\frac{d[A]}{dt} = \frac{-1}{y}\frac{d[B]}{dt} = \frac{+1d[C]}{l\,dt}$$

$$= +\frac{1}{m}\frac{d[D]}{dt}$$

For example : In the reaction,

$H_2 + Br_2 \rightarrow 2HBr$

The overall rate of the reaction is given by

www.tntextbooks.in

$$\text{Rate} = \frac{-d[H_2]}{dt} = \frac{-d[Br_2]}{dt} = \frac{1}{2}\frac{d[HBr]}{dt}$$

Consider the reaction, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

$$\text{Rate} = -\frac{1}{2}\frac{d[NO]}{dt} = \frac{-1}{2}\frac{d[H_2]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt}$$

Units of Rate

Reaction rate has units of concentration divided by time. Since concentration is expressed in mol lit^{-1} or mol dm^{-3} the unit of the reaction rate is mol lit^{-1} s^{-1} or mol dm^{-3} s^{-1}.

14.1.2 Factors influencing reaction rates

There are number of factors which influence the rate of the reaction. These are :

(i) Nature of the reactants and products
(ii) Concentration of the reacting species
(iii) Temperature of the system
(iv) Presence of catalyst
(v) Surface area of reactants
(vi) Exposure to radiation

(i) Effect of nature of the reactant and product

Each reactant reacts with its own rate. Changing the chemical nature of any reacting species will change the rate of the reaction. For example, in halogenation reactions, the reactions involving iodine is found to be slower than those involving chlorine.

In case of products, some of them are capable of reacting back to form reactants or some other kind of products. In such cases, the overall rate will be altered depending on the reactivity of the products.

(ii) Effect of reacting species

As the initial concentration of the reactants increase in the reaction mixture, the number of reacting molecules will increase. Since the chemical reaction occurs when the reacting species come close together and collide, the collisions are more frequent when the concentrations are higher. This effect increases the reaction rate.

(iii) Effect of temperature

Increase in temperature of the system increases the rate of the reaction. This is because, as the temperature increases the kinetic energy of the molecules increases, which increases the number of collisions between the molecules. Therefore the overall rate of the reaction increases. This condition is valid only for endothermic reaction. For exothermic reaction the overall rate decreases with increasing temperature.

(iv) Effect of presence of catalyst

A catalyst is a substance that alters the rate of a chemical reaction, while concentration of catalyst remaining the same before and after the reaction. The addition of catalyst generally increases the rate of the reaction at a given temperature. Also, catalyst is specific for a given reaction.

(v) Effect of surface area of reactants

In case of reactions involving solid reactants and in case of heterogeneous reactions, surface area of the reactant has an important role. As the particle size decreases surface area increases for the same mass. More number of molecules at the surface will be exposed to the reaction conditions such that the rate of the reaction increases. Thus the reactants in the powdered form (or) in smaller particles react rapidly than when present in larger particles.

(vi) Effect of radiation

Rates of certain reactions are increased by absorption of photons of energy. Such reactions are known as photochemical reactions. For example, H_2 and Cl_2 react only in the presence of light. With increase in the intensity of the light (or) radiation, the product yield increases. For photosynthesis light radiation is essential and the process does not proceed in the absence of light.

14.1.3 Rate law

According to concepts of chemical kinetics, the rate of the reaction is proportional to the product of the initial concentration of all the reactants with each reactant concentration raised to certain exponential powers.

Consider a general reaction

$$pA + qB \rightarrow cC + dD.$$

www.tntextbooks.in

The rate law is given by the expression,

$$\text{Rate} \propto [A]^p [B]^q$$

$$\therefore \text{Rate} = k[A]^p [B]^q$$

where k is proportionality constant also known as the rate constant or velocity constant of the reactions. p and q represent the order of the reaction with respect to A and B. The values of k, p and q are experimentally determined for a given reaction. Values of p and q need not be same as the stoichiometric coefficients of the reaction.

Rate constant

In the above general equation k represents the rate constant. Rate constant or velocity constant (or) specific reaction rate is defined as the rate of the reaction when the concentration of each of the reactants is unity in the reaction.

When concentration of A and B is unity then, the rate constant is equal to the rate of the reaction. When the temperature of the reaction mixture changes, the value of rate constant changes.

14.1.4 Order of the reaction

Order of a reaction is defined as the sum of the exponential powers to which each concentration is raised in the rate expression. For example, if the overall rate is given by the expression

$$\text{Rate} = k[A]^p [B]^q$$

Then, the overall order of the reaction is (p+q). The order with respect to A is p. The order with respect to B is q. If p=1; q=0 and vice versa, the order of the reaction is 1, and the reaction is called first order. If p=1, q=1, the order of the reaction is 2 and the reaction is called second order and so on.

A zero order reaction is one where the reaction rate does not depend upon the concentration of the reactant. In this type of reaction, the rate constant is equal to the rate of the reaction.

14.1.5 Unit of rate constant

In general, rate expression for the reaction,

$$pA + qB \longrightarrow cC + dD$$

Rate = $k\,[A]^p\,[B]^q$

$$k = \frac{\text{Rate}}{[A]^p\,[B]^q}$$

The unit for the rate constant `k' depends upon the rate of the reaction, the concentration of the reactants and the order of the reaction.

In the case of the first order reaction.

$$k = \frac{\text{Rate}}{[A]^1\,[B]^0}$$

$$k = \frac{\text{mol}\,\text{dm}^{-3}\,\text{sec}^{-1}}{\text{mol}\,\text{dm}^{-3}}$$

Unit of

$k = \text{sec}^{-1}$ for first order reaction.

Similarly unit of k = $\text{mol}^{-1}\,\text{dm}^{3}\,\text{sec}^{-1}$ for second order reaction
unit of k = $\text{mol}^{-(n-1)}\,\text{dm}^{3(n-1)}\,\text{sec}^{-1}$ for nth order reaction

Following are the important differences between rate and rate constant of a reaction

Rate of reaction	Rate constant of reaction
1. It represents the speed at which the reactants are converted into products at any instant.	1. It is the constant of proportionality in the rate law expression.
2. At any instant of time, the rate depends upon the concentration of reactants at that instant.	2. It refers to the rate of a reaction at the specific point when concentration of every reacting species is unity.
3. It decreases as the reaction proceeds.	3. It is constant and does not depend on the progress of the reaction.
4. Rate of rate determining step determines overall rate value.	4. It is an experimental value. It does not depend on the rate determining step.

14.2 Molecularity of the reaction

Molecularity is defined as the number of atoms or molecules taking part in an elementary step leading to a chemical reaction. The overall chemical reaction may consist of many elementary steps. Each elementary reaction has its own molecularity which is equal to number of atoms or molecules participating in it. If the reaction takes place in more than one step there is no molecularity for the overall reaction. However molecularity and order are identical for elementary reaction (one step).

There are many differences between the concepts of order and molecularity.

Order of a reaction	Molecularity of a reaction
1. It is the sum of powers raised on concentration terms in the rate expression.	1. It is the number of molecules of reactants taking part in elementary step of a reaction.
2. Order of a reaction is an experimental value, derived from rate expression.	2. It is a theoretical concept.
3. Order of a reaction can be zero, fractional or integer.	3. Molecularity can neither be zero nor fractional.
4. Order of a reaction may have negative value.	4. Molecularity can never be negative.
5. It is assigned for overall reaction.	5. It is assigned for each elementary step of mechanism.
6. It depends upon pressure, temperature and concentration (for pseudo order)	6. It is independent of pressure and temperature.

14.2.1 Rate determining step

Most of the chemical reactions occur by multistep reactions. In the sequence of steps it is found that one of the steps is considerably slower than the others. The overall rate of the reaction cannot be lower in value

www.tntextbooks.in

than the rate of the slowest step. Thus in a multistep reaction the experimentally determined rate corresponds to the rate of the slowest step. Thus the step which has the lowest rate value among the other steps of the reaction is called as the rate determining step (or) rate limiting step.

Consider the reaction,

$2A + B \rightarrow C + D$ going by two steps like,

$$A + B \xrightarrow{k_1} C + Z \quad - \quad \text{(1) step (slow)}$$

$$Z + A \xrightarrow{k_2} D \quad - \quad \text{(2) step (fast)}$$

$$\overline{\underline{2A + B \rightarrow C + D}}$$

Here, the overall rate of the reaction corresponds to the rate of the first step which is the slow step and thus, the first step is called as the rate determining step of the reaction. In the above reaction, the rate of the reaction depends upon the rate constant k_1 only. The rate of 2nd step doesn't contribute experimentally determined overall rate of the reaction.

Example

For a reaction $A + B \rightarrow$ Products, the following data has been provided to you for determining rate expression. Derive it and suggest order of reaction.

concentration in mole litre^{-1} & rate in mol litre^{-1} time^{-1}

[A]	[B]	rate
1	2	4
2	2	4
2	4	16

We can write

$$\begin{aligned} \text{rate} &= K[A]^m [B]^n \\ 4 &= K[1]^m [2]^n & \text{...(i)} \\ 4 &= K[2]^m [2]^n & \text{...(ii)} \\ 16 &= K[2]^m [4]^n & \text{...(iii)} \end{aligned}$$

By (i) & (ii) $m = 0$
By (i) & (iii) $n = 2$

$\therefore$ rate = $k[A]^0\,[B]^2$ & order of the reaction

$$= 0 + 2 = 2.$$

14.3 Classification of rates based on the order of the reaction

The rate law for a reaction must be determined by experiment. Usually the order of the reaction determined experimentally does not coincide with the stoichiometric coefficients of the reactants or products in the balanced chemical equation. Each reaction proceeds by a rate value determined by the rate constant and initial concentrations of the reacting species. Rate constant values differ for different `order' reactions even if concentrations are maintained the same. Therefore chemical reactions are classified according to its rate of chemical transformation which inturn depend on the order of the reaction. Let us consider a general rate equation such as

$$\text{rate} = k[A]^p\,[B]^q$$

Total order is p + q and order with respect to A is p and with respect to B in q respectively.

Zero order reaction

A reactant whose concentration does not affect the reaction rate is called as zero order reaction,

rate law is,

$$\text{rate} = k[A]^0 \qquad \text{(or)}$$

$$\frac{-d[A]}{dt} = k \qquad \text{or} \quad k = \frac{[A]_o - [A]t}{t}$$

Examples of zero order reaction is

$$H_2(g) + Cl_2(g) \overset{h\nu}{\rightleftharpoons} 2HCl(g)$$

The first order reaction

when aqueous solution of NH_4NO_2 is warmed it decomposes rapidly to H_2O and N_2.

$$NH_4NO_2 \rightarrow 2H_2O + N_2$$

This reaction goes by first order manner

rate constant k is given by

$$K = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t} \sec^{-1}$$

V_∞ and V_t are volume of N_2 collected at room temperature and 1 atm when a fixed amount of NH_4NO_2 decomposes at $t = \infty$ (after completion of reaction) and at any time `t'.

Second order reaction

A reaction is said to be second order if its reaction rate is determined by the variation of two concentration terms or square of a single concentration term.

Example

Saponification of an ester is second order

$NaOH + CH_3COOC_2H_5 \longrightarrow CH_3COONa + C_2H_5OH$

or if A = NaOH ; B = ester

then rate = $\frac{-d[A]}{dt} = \frac{-d[B]}{dt} = k.C_A C_B$

$$k = \frac{2.303}{t\{[A]o - [B]o\}} \log \frac{[A]_t\,[B]_o}{[A]_o\,[B]_t}$$

$[A]_0$; $[B]_0$ = initial concentrations of A and B at t = 0

$[A]_t$; $[B]_t$ = concentration of A and B at time = t

for $2A \longrightarrow$ products,

rate = $k[A]^2$

then

$$k = \frac{1}{t}\left[\frac{1}{[A]_t} - \frac{1}{[A]_o}\right] \quad \text{or} \quad k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] \text{lit mol}^{-1} \sec^{-1}$$

Third order reactions

A reaction is said to be third order if its rate is determined by the variation of three concentration terms.

Example

$2NO + Cl_2 \longrightarrow 2NOCl$

$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$.

$3A \rightarrow$ Products

Rate = $k[A]^3$ (or)

$$k = \frac{1}{2t}\left[\frac{1}{[A]_t^{\,2}} - \frac{1}{[A]_o^{\,2}}\right] \quad \text{(or)} \quad k = \frac{1}{2t}\left[\frac{x\,(2a-x)}{a^2\,(a-x)^2}\right] \text{lit}^2\,\text{mol}^{-2}\,\text{sec}^{-1}$$

A second (or) third (or) any other high order reaction can be experimentally followed in an easy way by reducing the overall order to first order type by adopting pseudo order conditions. In this method, excluding the concentration of one of reactants, concentrations of all other reactant are kept in excess (at least 10 times) of the concentration of one of the reactant whose concentrations are to be varied to study the changes in the rate.

Example : Thermal decomposition of acetaldehyde.

$$CH_3\,CHO \xrightarrow{450°C} CH_4 + CO$$

Order = 1.5. Here a chain mechanism has been proposed. Polymerisation reactions also show fractional orders.

Questions

A. Choose the correct answer

1. mol.dm^{-3} sec^{-1} is the unit of
   (i) rate (ii) rate constant (iii) order (iv) active mass
2. The elementary step with slow rate represents
   (i) rate determining step (ii) maximum rate step
   (iii) third order rate (iv) overall order
3. Molecularity is determined for
   (i) an elementary reaction (ii) an overall reaction
   (iii) an over all stoichiometric reaction (iv) a fractional order reaction

B. Fill up the blanks

4. Decomposition of aqueous NH_4NO_2 proceeds by _______ reaction.
5. Fractional orders are found in __________ reaction.
6. In a ________________ reaction rate does not depend on the reactant concentration.

C. Match the following

7. slow step	a. experimentally determined
8. order	b. zero order
9. molecularity	c. rate determining step

www.tntextbooks.in

10. unit of first order `k'	d. maximum rate
11. rate is independent of reactant	e. theoretical concept concentration
	f. sec^{-1}

D. Write very short answers

12. Define half life period.
13. Name the factors that affect the rate of reaction.
14. What is molecularity?
15. What is a rate determining step?
16. List the factors on which an order of the reaction depend.
17. Write the rate law of pA + qB $\longrightarrow$ lC + mD reaction.
18. Define the rate of a reaction.

E. Explain briefly on the following

19. Compare and contrast the terms, order and molecularity of a reaction.
20. Describe the factors on which the rate of a reaction depends.
21. What is a pseudo order reactions? How do you experimentally determine the pseudo first order rate constant of acid hydrolysis ester reaction?
22. Discuss the rate of the reaction

$$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$$

Problems

23. One ml of methyl acetate was added to 20 ml of 0.5 N sulphuric acid. 2 ml of the reaction mixture was with drawn at various time intervals and titrated against a solution of standard alkali. The titre values are tabulated. Show that the reaction is first order and calculate the rate constant and half life period of the reaction.

Time (s)	0	600	1200	2400	∞
Volume of alkali (ml)	19.3	19.9	20.5	21.7	41.9

[Ans : mean k=4.570x10^{-5} sec^{-1}; t_2=1.570x10^{4} sec]

24. In I order reaction the initial concentration of the reactant as 0.05 mole/litre and the rate constant 1.5x10^{-3} min^{-1}. What is the initial rate of the reaction. [Ans : 7.5 x 10^{-5} mol lit^{-1} min^{-1}]

25. If a reaction with $t_{1/2}$=69.3 second, has a rate constant value of 10^{-2} per second. Calculate the order of the reaction. [One]
26. The time for half life of a first order reaction is 1 hr. what is the time

taken for 87.5% completion of the reaction? [3 hrs]

27. The following results were obtained for the saponification of ethyl acetate using equal concentrations of ester and alkali.

Time	**0**	**4.89**	**10.07**	**23.66**	**∞**
Acid in ml	47.65	38.92	32.62	22.58	11.84

Show that the reaction is of the second order.

[Ans : Mean Value of k=9.68 x 10^{-4} lit mol^{-1} sec^{-1}].

SUMMARY

- Basic concepts of chemical kinetics used in writing the rate law of a general reaction along with order and rate constant units and various expressions are understood.
- Identification of rate determining step examples of reactions with measurable rates are studied. Decomposition of N_2O_5 reaction with various forms of rate expressions are studied.
- Order and molecularity are differentiated and various experimental methods of determination of order of the reaction was understood.
- Classification of rates based on the order of the reaction are understood with suitable examples each of the zero, first, second, pseudo first, third and fractional order reactions.

Order	**Unit of k**
Zero	mol $litre^{-1}$ $time^{-1}$
I	$time^{-1}$
II	litre mol^{-1} $time^{-1}$
III	$litre^{2}$ mol^{-2} $time^{-1}$
n^{th}	$litre^{(n-1)}$ $mol^{(1-n)}$ s^{-1}

REFERENCES

1. Physical Chemistry by Lewis and Glasstone.

www.tntextbooks.in

15. BASIC CONCEPTS OF ORGANIC CHEMISTRY

OBJECTIVES

This topic explains the nature of organic compounds and explores the possibilities of all basic concepts of organic chemistry.

- *Catenation and the reason for innumerable number of organic compounds.*
- *Classification of organic compounds based on functional groups.*
- *IUPAC method of naming all types of organic compounds.*
- *Details about isomerism.*
- *Fission of bonds and types of organic reactions.*
- *Nature of reagents, electrophiles and Nucleophiles.*
- *Knowledge about carboniumion and carbanion and free radicals.*
- *Different types of electron displacements in organic chemistry.*

Introduction

Initially (before 1828), the name organic chemistry was given for the chemistry of compounds obtained from plants and animals (i.e, from living organisms). The word organic signifies life. Lavoisier (who is considered as the father of chemistry) showed that the compounds obtained from plants are often made of C, H and O and the compounds obtained from animals contain C, H, O, N, S, P. ..... etc.

Berzelius proposed vital force theory (a theory of life process) to deal with organic compounds. The vital force theory suffered blow in 1828 when Wohler synthesized the first organic compound urea in the laboratory from an inorganic compound, i.e, from ammonium cyanate (NH_4 CNO).

$$2KCNO + (NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_4CNO + K_2SO_4$$

or $Pb(CNO)_2 + 2NH_4OH \xrightarrow{\Delta} 2NH_4CNO + Pb(OH)_2$

www.tntextbooks.in

$$NH_4CNO \xrightarrow[\text{Rearrangement}]{\Delta} NH_2CONH_2$$

Later on, a further blow to vital force theory was given by Kolbe (1845) who prepared acetic acid, the first organic compound, in laboratory from its elements.

Now a days organic chemistry is defined as **the chemistry of carbon compounds or the chemistry of hydrocarbons and their derivatives**. Organic compounds obey the same fundamental laws of chemistry as the inorganic compounds. However they are studied as a separate branch of chemistry because of two reasons:

i. The total number of organic compounds known so far exceeds several times the total number of inorganic compounds known.

ii. There are marked differences between the structure, composition and behaviour of organic and inorganic compounds. The phenomenon of **isomerism** and tendency of **catenation** are unique properties of organic compounds.

15.1Catenation

1. The tendency of atoms of an element to unite with each other forming a chain of covalent bond is known as **catenation.**
2. Catenation may give rise to open chain or closed chain compounds.
3. Carbon possesses maximum tendency for catenation i.e. **Bond energy (kcal mol^{-1}) for catenation of C is maximum.**

C-C,	Si-Si,	N-N,	P-P,	O-O,	S-S
85	54	39	50	35	54

4. Carbon also forms double as well as triple bonds.
5. A large number of compounds of carbon are known due to catenation.
6. The stability or strength of bond decreases as the bond energy decreases. Hence the catenation order among the following is $C > Si \approx S > P > N > O$.

15.2 Classification into open chain and cyclic compounds

The organic compounds are classified into two main types, namely.

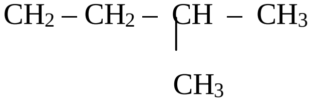
www.tntextbooks.in

(1) Open - chain or acyclic compounds or aliphatic compounds

The open chain or acyclic compounds are those in which carbon atoms are linked to each other either in linear or branched fashion such that the molecule is having open chain structure. These compounds are also called aliphatic compounds (Greek word : aliphar meaning fat).

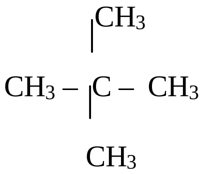
Examples

$CH_3 - CH_2 - CH_3$ propane



$$CH_2 - CH_2 - \underset{\overset{|}{CH_3}}{CH} - CH_3$$

2– methylbutane or isopentane



$$CH_3 - \overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}} - CH_3$$

neopentane

(2) Closed chain or cyclic compounds

Organic compounds with closed chain of atoms are called closed chain compounds or ring compounds.

These compounds are further classified into

(a) Homocyclic or carbocyclic compounds

(b) Heterocyclic compounds

(a) Homocyclic compounds : In these compounds the ring structure is made up of only carbon atoms.

These compounds are further classified into

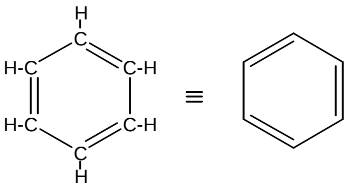
(i) Aromatic compounds and

(ii) Alicyclic compounds

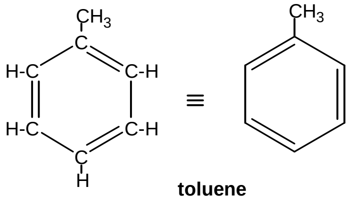
(i) Aromatic compounds (Benzenoid) : Compounds containing one or more benzene rings in their structure are classified as aromatic benzenoid compounds. Most of these compounds have pleasant odour (Greek : Aroma - sweet smell).

Examples

Monocyclic

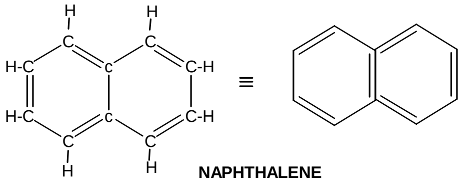


benzene

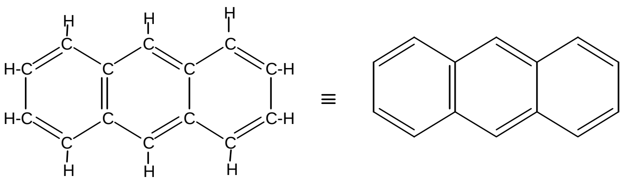


toluene

Polycyclic



NAPHTHALENE

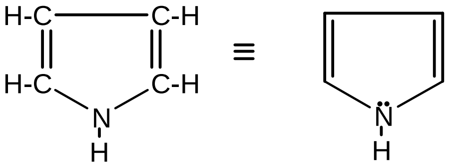


ANTHRACENE

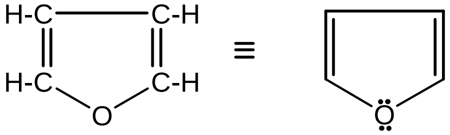
Heterocyclic compounds (Non - benzenoid aromatic) : Cyclic compounds in which the ring atoms are made up of hetero atoms like nitrogen, oxygen and sulphur in addition to carbon atoms are called heterocyclic compounds.

www.tntextbooks.in

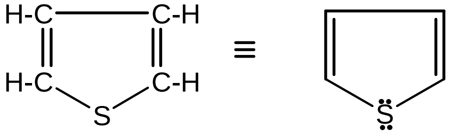
Examples



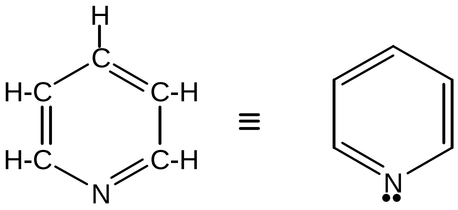
pyrrole



furan



thiophene



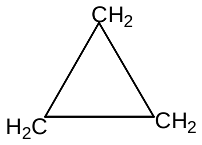
pyridine

The above compounds are aromatic non-benzenoid compounds.

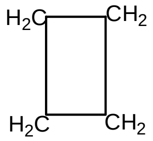
(ii) Alicyclic compounds : Cyclic compounds with ring structure containing only carbon atoms are called alicyclic or carbocyclic compounds. Though these compounds possess a ring structure, they behave more like aliphatic compounds.

www.tntextbooks.in

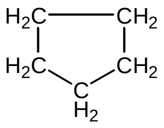
Examples



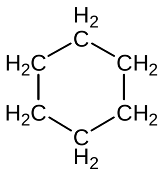
cyclopropane



cyclobutane

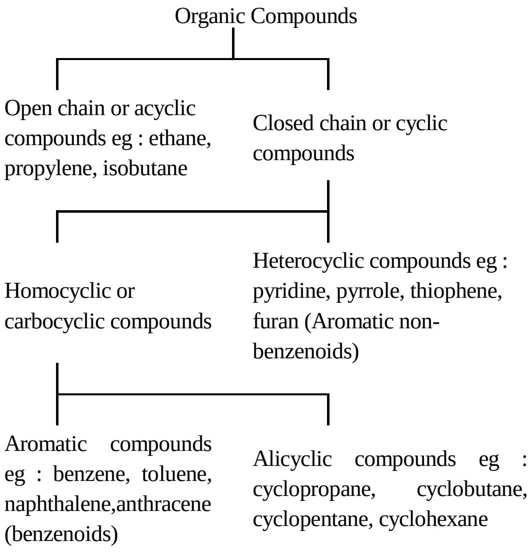


cyclopentane



cyclohexane

The above classification can be schematically represented as follows :



Characteristics of organic compounds

All organic compounds have the following characteristic properties

(1) Many organic compounds are inflammable

(2) They are mostly covalent compounds

(3) They are generally soluble in non - polar solvents like carbon tetrachloride, benzene etc.
(4) They have generally low boiling point and melting point.
(5) They exhibit isomerism

Homologous series

A group or class of organic compounds related to each other by a general molecular formula contributes homologous series.

Characteristics of homologous series

Homologous series have the following characteristics :

(1) All members of a series contain same elements and the same functional groups.

(2) All the members of a homologous series can be represented by a general formula

Examples

Alkanes	C_nH_{2n+2}
Alkenes	C_nH_{2n}
Alkynes	C_nH_{2n-2}

(3) All the members of a homologous series can be prepared by similar methods.

(4) All members of a homologous series usually undergo similar chemical reactions.

(5) Successive members in a series differ by a -CH_2 group

(6) The physical properties of the members of a homologous series vary in a regular way down the series. For example, boiling point, melting point and density of the alkane series vary in a regular way with increasing number of carbon atoms.

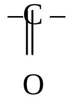
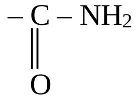
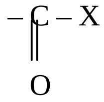
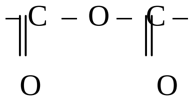
15.3 Functional groups

The chemical properties of all the members of a homologous series are characterised by a group called the functional group. It is characteristic of a particular series.

The following table gives a list of functional groups and names.

Halide	– X
Alcohol	– OH
Ether	– O –

www.tntextbooks.in

Aldehyde	– CHO
Ketone	 $-\underset{\underset{O}{\|}}{C}-$
Carboxylic acid	– COOH
Ester	– COOR
Amide	 $-\underset{\underset{O}{\|}}{C}-NH_2$
Acid halide	 $-\underset{\underset{O}{\|}}{C}-X$ (X = –Cl, –Br, –I)
Acid anhydride	 $-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-$
Amine	– NH_2
Nitro compounds	– NO_2

15.4 IUPAC system of nomenclature (1993)

The international union of pure and applied chemistry (abbreviated as IUPAC) has done a commendable job in framing set rules for naming organic compounds. Two commonly used systems of nomenclature are described below.

(1) Common or Trivial system (2) IUPAC system

IUPAC Nomenclature of Aliphatic Compounds

The IUPAC name of a compound essentially consists of three parts.

(a) Root word (b) Suffix (c) Prefix

Root words for alkanes

The root words for the first four members are taken from their trivial or common names.

e.g. Meth - for Methane
Eth - for Ethane
Prop - for Propane
But - for Butane

For the higher homologue, root words are derived from the Greek/Latin number indicating the total number of carbon atoms.

e.g. Pent - is derived from penta for five
Hex - is derived from hexa for six
Hept - is derived from hepta for seven
Oct - is derived from octa for eight

Suffix

There are two types of suffixes **Primary suffix** and secondary suffix.

Primary suffix

A primary suffix is added to the **Root word** to indicate whether the parent chain is saturated or unsaturated. Some primary suffixes are given below.

Sl. No.	Nature of carbon chain (parent chain)	Primary suffix
1.	Saturated	ane
2.	Unsaturated with One double bond Two double bond Three double bond	 ene diene triene
3.	Unsaturated with One triple bond Two triple bond	 yne diyne

Sl. No.	Structural formula	No. of C atoms	Root word	Primary suffix	IUPAC name
1.	CH_3-CH_2-CH_2-CH_3	4	But	ane	Butane
2.	CH_3-CH = CH_2	3	Prop	ene	Propene
3.	$CH \equiv CH$	2	Eth	yne	Ethyne
4.	CH_2=CH–CH = CH_2	4	Buta*	diene	Butadiene
5.	$HC \equiv C - C \equiv CH$	4	Buta*	diyne	Butadiyne

www.tntextbooks.in

[*] extra 'a' has been added to the root word since the primary suffix, ie diene or diyne begins with a consonant (d).

Secondary suffix

Secondary suffix is used to indicate the functional group in the organic compound secondary suffixes for various functional groups are given below.

Sl. No.	Class	Functional group	Secondary suffix	IUPAC name
1.	Alcohols (R-OH)	-OH	-ol	Alkanols
2.	Aldehyde (R-CHO)	-CHO	-al	Alkanals
3.	Ketones (RCOR')	>C=O	-one	Alkanones
4.	Carboxylic acids (R-COOH)	-COOH	-oic acid	Alkanoic acid
5.	Ester (RCOOR')	-COOR	-alkanoate	alkyl alkanoates

Secondary suffix is added to the primary suffix; ie written after the primary suffix. While adding the secondary suffix to the primary suffix following rules should be followed.

a) If the secondary suffix begins with a vowel, then the terminal **e** of the primary suffix is dropped before adding the secondary suffix.

b) If the secondary suffix begins with a consonant, then the last (terminal) **e** is retained and the secondary suffix is added after e.

c) If the secondary suffix has some **numerical prefix**, such as, **di, tri etc.**, before it then the terminal **e** of the primary suffix is retained.

The addition of the secondary suffix to the primary suffix is illustrated below

Sl. No.	Structu-ral formula	No. of C atoms	Root word	Primary suffix	Secondary suffix	IUPAC name	Remarks
1.	CH_3 | CH_2-OH	2	Eth	ane	ol	Ethanol	`e' of prim suffix dropped

www.tntextbooks.in

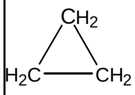
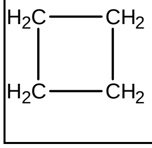
2.	CH_2-OH | CH_2-OH	2	Eth	ane	diol	Ethane diol	`e' of prim suffix not dropped
3.	CH_3 | CH_2 | CHO	3	Prop	ane	al	Propanal	`e' of the prim suffix dropped
4.	CH_3 | CH_2 | CH_2 | COOH	4	But	ane	oic acid	Butanoic acid	`e' of prim suffix dropped

Prefix

Prefix is a part of the name which appears before the root word. There are two types of prefixes - primary prefix and secondary prefix.

Primary prefix

A primary prefix is used to distinguish alicyclic (aliphatic cyclic compounds) from acyclic (open chain) compounds. If the given compound is an alicyclic compound, then a prefix cyclo is used just before the root word. For example.

Structural formula	No. of C atoms	Root word	Primary suffix	Primary prefix	IUPAC name
	3	Prop	ane	Cyclo	Cyclo propane
	4	But	ane	Cyclo	Cyclo butane

Secondary prefix

In the IUPAC system of nomenclature, certain characteristic groups are not considered as functional groups. Such characteristic groups are considered as the **substituents**. Each such group or substituent is denoted by a secondary prefix. Some typical secondary prefixes are listed below.

Substituent group	**Secondary prefix**
- F	Fluoro
- Cl	Chloro
- Br	Bromo
- I	Iodo
$- CH_3$	Methyl
$- C_2H_5$	Ethyl
$CH_3 - CH_2 - CH_2 -$	n-propyl
$(CH_3)_2 CH -$	Iso propyl
$(CH_3)_3 C -$	t - Butyl
$- NO_2$	Nitro
$- NH_2$	Amino
- NO	Nitroso
$N \equiv N$	Diazo
$- OCH_3$	Methoxy
$- OC_2H_5$	Ethoxy

In the case of open chain compounds, the secondary prefix is added just before the root word in the **alphabetical** order. This is illustrated below.

Sl. No.	**Structural formula**	**No. of C atoms**	**Root word**	**Suffix**		**Prefix**		**IUPAC Name**
				Primary	**Sec**	**Pri**	**Sec**	
1.	CH_3-CH_2-Cl	2	Eth	ane	-	-	Chloro	Chloro ethane
2.	CH_3-NO_2	1	Meth	ane	-	-	Nitro	Nitro methane

www.tntextbooks.in

Saturated Hydrocarbons : Alkanes

General formula : C_nH_{2n+2} **Suffix** : ane

Sl. No.	Structural formula	Common Name	IUPAC name
1.	CH_4	Methane	Methane
2.	$H_3C - CH_3$	Ethane	Ethane
3.	$H_3C - CH_2 - CH_3$	Propane	Propane
4.	$H_3C - CH_2 - CH_2 - CH_3$	n-butane	Butane

Alkyl groups

The univalent hydrocarbon unit derived from an alkane by the loss of one hydrogen atom is termed as alkyl group.

The alkyl groups are named after their parent alkanes by replacing the suffix-**ane** by- **yl**.

Continuous straight chain alkyl groups (or, normal alkyl (n-) groups)

Sl. No.	Alkane		Alkyl group	
	Formula	**Name**	**Formula**	**Name**
1.	CH_4	Methane	CH_3 -	Methyl
2.	$CH_3 - CH_3$	Ethane	$CH_3 - CH_2$ -	Ethyl
3.	CH_3-CH_2-CH_3	Propane	CH_3-CH_2-CH_2-	Propyl

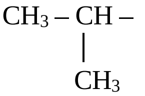
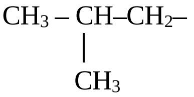
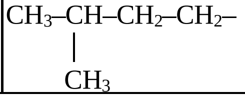
Branched chain alkyl groups

When a hydrogen atom from a secondary or tertiary carbon atom in any carbon chain is removed, a branched chain alkyl group is obtained. The common prefixes used are,

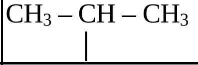
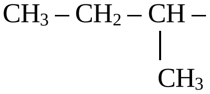
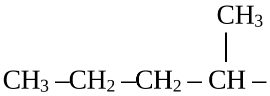
a) iso - b) sec - c) tert - d) neo –

a) **iso –** The alkyl group in which a - CH_3 branch is present at the end of the chain is designated as isoalkyl group. In other words, the alkyl group in which the second last carbon atom in the chain is branched to one - CH_3 group is called on isoalkyl group.

www.tntextbooks.in

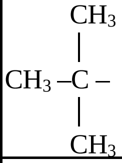
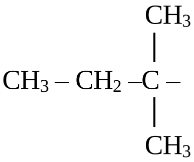
Sl.No.	Structure	IUPAC name
1.	 $CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-$	1-methyl ethyl (iso-propyl)
2.	 $CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-CH_2-$	2-methyl propyl (iso-butyl)
3.	 $CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-CH_2-CH_2-$	3-methyl butyl (iso-pentyl)

b) Sec - The prefix sec - before the name of the alkyl group indicates that the H-atom was removed from a secondary carbon atom.

Sl.No.	Structure	IUPAC name
1.	 $CH_3-\underset{\vert}{CH}-CH_3$	1 - Methyl ethyl (Sec - propyl)
2.	 $CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-$	1 - methyl propyl (Sec - butyl)
3.	 $CH_3-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{\vert}}{CH}-$	1 - methyl butyl (Sec - pentyl)

c) Tert - (or) t -

The prefix tert - before the name of the alkyl group indicates that the H - atom has been removed from a tertiary carbon atom.

Sl. No.	Structure	IUPAC name
1.	 $CH_3-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}-$	1,1 – dimethyl ethyl (tert - butyl)
2.	 $CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}-$	1,1 – dimethyl propyl (tert - pentyl)

Alkenes

General formula : C_nH_{2n} **Suffix : ene**

The common name of alkene is obtained by replacing the ending **- ane** from the name of its parent alkane with **- ylene**.

The IUPAC name of an alkene is obtained by replacing **- ane** of the alkane by **- ene**.

Structural formula	**Common Name**	**IUPAC name**
$CH_2 = CH_2$	Ethylene	Ethene
$CH_3 - CH = CH_2$	Propylene	Propene
CH_3-CH_2- CH= CH_2 (double bond starts at C_1)	1- Butylene	But-1-ene
CH_3-CH = CH-CH_3 (double bond starts at C_2)	2- Butylene	But-2-ene

Alkenyl group

The group obtained by removing a hydrogen atom from an alkene molecule, are called **alkenyl** group.

The IUPAC name of alkenyl group is obtained by replacing - **e** of the alkene by the suffix - **yl**.

Sl. No.	**Structure**	**Common name**	**IUPAC name**
1.	$CH_2 = CH_2$	vinyl	ethenyl
2.	CH_2=CH-CH_2-	allyl	Prop - 2 - enyl

Alkynes

General formula : C_nH_{2n-2} **Suffix** : - yne

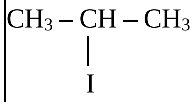
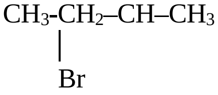
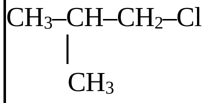
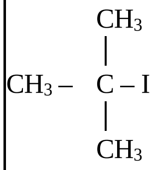
The IUPAC name of an alkyne is obtained by replacing the ending - **ane** from the name of the parent alkane with **- yne**.

www.tntextbooks.in

Sl. No.	Structural formula	Common Name	IUPAC name
1.	$HC \equiv CH$	Acetylene	Ethyne
2.	$CH_3 -C \equiv CH$	Methyl acetylene	Propyne
3.	$CH_3-C \equiv C - CH_3$	Dimethyl acetylene	But-2– yne

Alkyl halides

The general formula of alkyl halides is R-X where R stands for alkyl group and "X" stands for halogen (F, Cl, Br, I). They are named by introducing the prefix halo (chloro, bromo, iodo, fluoro) to the name of the parent alkane.

Formula	Common name	IUPAC name
CH_3-Cl	Methyl chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
$CH_3-CH_2-CH_2-Br$	n-propyl bromide	1-bromopropane
 $CH_3 - \underset{\underset{I}{\vert}}{CH} - CH_3$	Iso-propyl iodide	2-iodopropane
$CH_3-CH_2-CH_2-CH_2-Cl$	n-butyl chloride	1-chlorobutane
 $CH_3-CH_2-\underset{\underset{Br}{\vert}}{CH}-CH_3$	Sec-butyl bromide	2-bromobutane
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-Cl$	Isobutyl chloride	1-chloro-2-methyl propane
 $CH_3 - \overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}} - I$	ter-butyl iodide	2-iodo-2-methyl propane
$CH_2=CH-Cl$	Vinyl chloride	Chloroethene
$CH_2=CH-CH_2-Cl$	Allyl chloride	3-Chloro-1-propene

www.tntextbooks.in

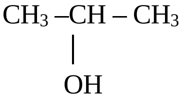
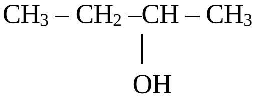
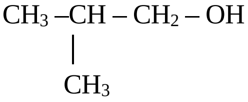
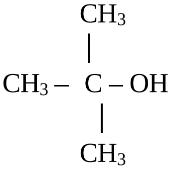
Alcohols

The term alcohol is applied to all organic compounds obtained by replacing one or more hydrogen atoms of an open-chain hydrocarbon by hydroxyl groups. The alcohols are further classified into **mono-**, **di-**, **tri-** hydric alcohols according to the number of hydroxyl groups which they may contain.

In IUPAC nomenclature, the terminal "**e**" of the alkane is replaced by "**ol**".

Monohydric alcohols

Alcohols which contain only one hydroxyl group per molecule are called monohydric alcohols.

Formula	Common name	IUPAC name
CH_3-OH	Methyl alcohol	methanol
CH_3-CH_2-OH	Ethyl alcohol	ethanol
CH_3-CH_2-CH_2-OH	n-propyl alcohol	1-propanol
 $CH_3-\underset{\underset{OH}{\vert}}{CH}-CH_3$	Isopropyl alcohol	2-propanol
CH_3-CH_2-CH_2-CH_2-OH	n-butyl alcohol	1-butanol
 $CH_3-CH_2-\underset{\underset{OH}{\vert}}{CH}-CH_3$	sec-butyl alcohol	2-butanol
 $CH_3-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-OH$	Isobutyl alcohol	2-methyl-1-propanol
 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-OH$	tert-butyl alcohol	2-methyl-2-propanol
CH_2=CH-CH_2-OH	Allyl alcohol	2-propene-1-ol

Dihydric alcohols

Alcohols which contain two -OH groups per molecule are called dihydric alcohols.

www.tntextbooks.in

Structural formula	Common name	IUPAC name
CH_2-OH $\vert$ CH_2-OH	Ethylene glycol	1,2-Ethanediol

Trihydric alcohols

Alcohols which contain three -OH groups per molecule are called trihydric alcohols.

Structural formula	Common name	IUPAC name
$CH_2 - OH$ $\vert$ $CH - OH$ $\vert$ $CH_2 - OH$	Glycerol	1,2,3-propanetriol

Ethers

An ether is a substance that has two organic groups bonded to the same oxygen atom, **R-O-R'**. The organic group may be alkyl or aryl. When the groups attached to the oxygen atom are the same, they are termed as simple ethers. When the groups attached to the oxygen atom are different, they are termed as mixed ethers.

In IUPAC system, ethers are considered to be alkoxy derivatives of hydrocarbons.

Structural formula	Common name	IUPAC name
Simple ethers		
CH_3-O-CH_3	Dimethyl ether	Methoxymethane
$CH_3-CH_2-O-CH_2-CH_3$	Diethyl ether	Ethoxyethane
Mixed ethers		
$CH_3-O-CH_2-CH_3$	Ethyl methyl ether	Methoxyethane
$CH_3-O-CH_2-CH_2-CH_3$	Methyl n-propyl ether	1-methoxypropane
$CH_3 - O - \underset{\underset{CH_3}{\vert}}{CH} - CH_3$	Isopropyl methyl ether	2-methoxypropane

Aldehydes

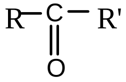
Aldehydes and ketones are two important classes of compounds containing the carbonyl group $-\underset{\substack{\| \\ O}}{C}-$. In aldehydes the $-\underset{\substack{\| \\ O}}{C}-$ group is linked to an alkyl group and a hydrogen or two hydrogens. Aldehydes are represented by the general formula R-CHO.

IUPAC names of aldehydes are obtained by replacing the terminal "**e**" of alkane with "**al**".

Structural formula	Common name	IUPAC name
H-CHO	Formaldehyde	Methanal
CH_3-CHO	Acetaldehyde	Ethanal
CH_3-CH_2-CHO	Propionaldehyde	Propanal
CH_3-CH_2-CH_2-CHO	Butyraldehyde	1-Butanal
$CH_3-\underset{\substack{\vert \\ CH_3}}{CH}-CHO$	Isobutyraldehyde	2-Methylpropanal

Ketones

In ketones $-\underset{\substack{\| \\ O}}{C}-$ group is united with 2 alkyl groups. These compounds are represented by the general formula.



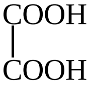
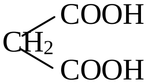
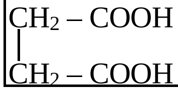
$$R-\underset{\substack{\| \\ O}}{C}-R'$$

Ketones are named by replacing the terminal "**e**" of the corresponding alkane name with "**one**".

Structural formula	Common name	IUPAC name
$CH_3-\underset{\substack{\| \\ O}}{C}-CH_3$	Acetone (Dimethyl ketone)	Propanone
$CH_3-CH_2-\underset{\substack{\| \\ O}}{C}-CH_3$	Ethylmethyl ketone	Butanone
$CH_3-CH_2-\underset{\substack{\| \\ O}}{C}-CH_2-CH_3$	Diethyl ketone	3-pentanone

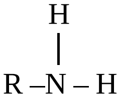
Carboxylic acids

These are represented by the general formula R-COOH. IUPAC name is derived by replacing the terminal "**e**" of the alkane name with "**oic acid**". These compounds are further classified into **mono-** and **di-**carboxylic acids.

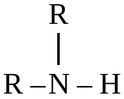
Structural formula	Common name	IUPAC name
Monocarboxylic acids		
H-COOH	Formic acid	Methanoic acid
CH_3-COOH	Acetic acid	Ethanoic acid
CH_3-CH_2-COOH	Propionic acid	Propanoic acid
CH_3-CH_2-CH_2-COOH	Butyric acid	Butanoic acid
Dicarboxylic acids		
 $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$	Oxalic acid	Ethanedioic acid
 $CH_2(COOH)_2$	Malonic acid	Propanedioic acid
 $\begin{array}{l}CH_2-COOH\\ \vert\\ CH_2-COOH\end{array}$	Succinic acid	Butanedioic acid

Amines

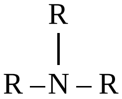
Amines are the derivatives of ammonia in which one or more H-atoms have been replaced by alkyl groups. They are designated as primary, secondary and tertiary amines according as one, two or three hydrogen atoms in ammonia molecule have been replaced by alkyl groups.



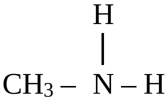
$R-\overset{\overset{\displaystyle H}{|}}{N}-H$



$R-\overset{\overset{\displaystyle R}{|}}{N}-H$

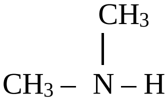


$R-\overset{\overset{\displaystyle R}{|}}{N}-R$



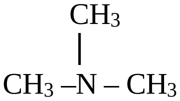
$CH_3-\overset{\overset{\displaystyle H}{|}}{N}-H$

Methylamine
(primary amine)



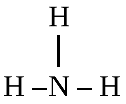
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{N}-H$

Dimethyl amine
(secondary amine)



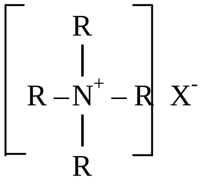
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{N}-CH_3$

Trimethyl amine
(teritary amine)



$H-\overset{H}{N}-H$

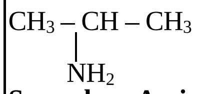
Ammonia

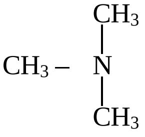
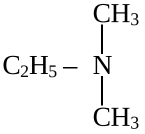


$\left[R-\underset{R}{\overset{R}{N^+}}-R\right]X^-$

(quarternary salt)

When one alkyl group is attached to N-atom, it is called primary amine, when two alkyl groups are attached to nitrogen atom, then it is called secondary amine. When three alkyl groups are attached to nitrogen atom it is called tertiary amine. When four alkyl groups are attached to nitrogen atom it is called quarternary salt.

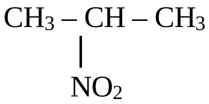
Structural formula	Common	IUPAC name
Primary Amines		
CH_3-NH_2	Methyl amine	aminomethane
$CH_3-CH_2-NH_2$	Ethyl amine	aminoethane
$CH_3-CH_2-CH_2-NH_2$	n-propyl amine	1-aminopropane
 $CH_3-\underset{NH_2}{CH}-CH_3$	Isopropyl amine	2-aminopropane
Secondary Amines		
$CH_3-NH-CH_3$	Dimethyl amine	(N-methylamino) methane
$CH_3-CH_2-NH-CH_2-CH_3$	Diethyl amine	(N-ethylamino) ethane
$CH_3-NH-CH_2-CH_3$	Ethylmethyl amine	(N-methylamino) ethane

Structural formula	Common name	IUPAC name
Tertiary Amines		
 $CH_3-\underset{CH_3}{\overset{CH_3}{N}}$	Trimethyl amine	(N,N - dimethyl amino) methane
 $C_2H_5-\underset{CH_3}{\overset{CH_3}{N}}$	Ethyldimethyl amine	(N,N - dimethyl amino) ethane

www.tntextbooks.in

Nitro compounds

These compounds are represented by the general formula RNO_2. IUPAC names are obtained by adding the prefix "**nitro**" to the alkane.

	Structural formula	**Common/IUPAC name**
1.	$CH_3 - NO_2$	Nitromethane
2.	$CH_3 – CH_2 – NO_2$	Nitroethane
3.	$CH_3 – CH_2 – CH_2 - NO_2$	1-Nitropropane
4.	 $\underset{\displaystyle NO_2}{\underset{\vert}{CH_3 – CH – CH_3}}$	2-Nitropropane

15.5 Isomerism

The molecular formula of an organic compound represents only the number of different atoms present in a molecule. But the molecular formula does not tell about the arrangement of atoms. A given molecular formula may lead to more than one arrangement of atoms such that there are many compounds which may have same molecular formula but with different physical and chemical properties. This phenomenon in which the same molecular formula may exhibit different structural arrangement is called isomerism.

Compounds that have the same molecular formula but different structural formulae are called isomers (from the Greek word isos + meros, "made of the same parts").

There are two types of isomerism, namely,

1. Structural isomerism 2. Stereoisomerism

Structural isomerism

When two or more compounds possess the same molecular formula but different structural formulae, they are said to exhibit structural isomerism. Structural isomerism is divided into.

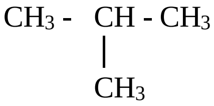
1. Chain isomerism or Nuclear isomerism

Chain isomers are compounds that have the same molecular formula but have different carbon skeletons.

Examples

$CH_3 - CH_2 - CH_2 - CH_3$ and

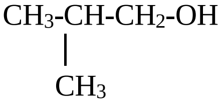
n-butane


$CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$

isobutane

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$ and

n-butyl alcohol


$CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}OH$

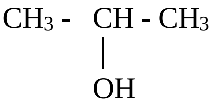
isobutyl alcohol

2. Position Isomerism

Position isomers are compounds that have the same formula, carbon skeleton and functional groups but have the functional groups located at different positions along the carbon skeleton.

$CH_3 - CH_2 - CH_2 - OH$ and

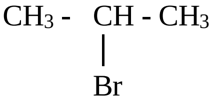
1-Propanol


$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$

2-Propanol

$CH_3 - CH_2 - CH_2 - Br$ and

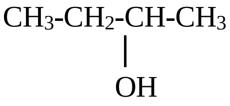
n-propyl bromide


$CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$

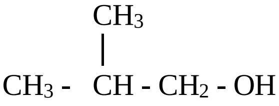
Isopropyl bromide

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$ and

n-butyl alcohol

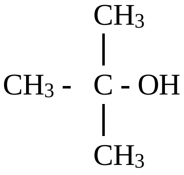

$CH_3\text{-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_3$

Sec - butyl alcohol


$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{CH}} - CH_2 - OH$

Isobutyl alcohol

and


$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - OH$

ter - butyl alcohol

$CH_3 - CH_2 - CH = CH_2$ $CH_3 - CH = CH - CH_3$

1-Butene 2-Butene

www.tntextbooks.in

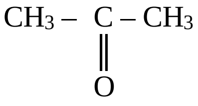
Functional isomerism

Functional isomers are compounds that have the same molecular formula but have different functional groups.

Examples

1. CH_3-CH_2-OH and CH_3-O-CH_3

   Ethyl alcohol Dimethyl ether

2.  $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$ and CH_3-CH_2-CHO

   Acetone Propionaldehyde

3. CH_3-CH_2-COOH and $CH_3-COO-CH_3$

   Propionic acid Methyl acetate

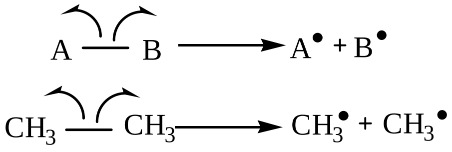
15.6 Fission of bonds

How bond fission occurs?

A covalent bond (σ bond) joining two atoms exist because of the shared pair of electrons. When two atoms are separated from each other, bond fission is said to have taken place. The fission process can take place in two ways.

Homolytic fission

A covalent bond between two atoms A and B may be shown as A· · B or A–B. This bond may undergo fission in such a way that each atom retains the electrons of the shared pair. Such species are known as **free radicals** or odd electron molecules.



$$A-B \longrightarrow A^\bullet + B^\bullet$$

$$CH_3-CH_3 \longrightarrow CH_3^\bullet + CH_3^\bullet$$

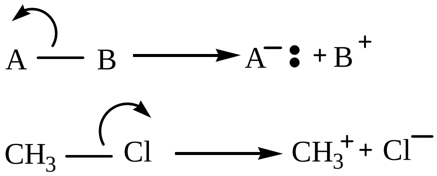
Ethane Methyl free radicals

Heterolytic fission

A covalent bond breaks in such a way that the shared pair of electron

www.tntextbooks.in

stay on any one of the atoms. Breaking of the bond in this manner is known as heterolytic fission or heterolysis.



$$A - B \longrightarrow A^{-}: + B^{+}$$

$$CH_3 - Cl \longrightarrow CH_3^{+} + Cl^{-}$$

The atom or group which carries the unshared pair of electrons are represented with a negative sign as A^{-}: is known as anions. The carbonium ion carries the positive charge which lacks a pair of electrons. Heterolysis occurs only when the initially bonded atoms are of different in electronegativities and in that the electron pair becomes attached to the more electronegative atom.

An organic reaction may be represented as :

Reactants + attacking agent → [intermediate] → product

Depending upon the nature of the reaction which the intermediate species undergo, the reactions of the organic compounds are classified as substitution reactions, addition reactions, elimination reactions, polymerisation reactions, condensation reaction, hydrolysis, oxidation and reduction reactions.

15.7 Types of Reactions

Substitution or Displacement reactions

Displacement reaction is one in which an atom or group linked to a carbon atom is removed and in its place another atom or group is attached.

The substitution reactions are classified into three types.

a) Nucleophilic substitution reaction (S_N)

When a substitution reaction is brought about by a nucleophile, the reaction is termed as S_N (S stands for substitution and N for nucleophile). These reactions are divided into two classes :

(1) S_N^1 (substitution, nucleophilic, unimolecular)

$$\underset{\text{tert-butyl chloride}}{(CH_3)_3C\ Cl} + KOH \xrightarrow{\text{aqueous}} (CH_3)_3C\ OH + KCl$$

www.tntextbooks.in

(2) S_N^2 (Substitution, nucleophilic, bimolecular)

$$\underset{\text{(Methyl Chloride)}}{CH_3Cl} + KOH \xrightarrow{\text{aqueous}} CH_3OH + KCl$$

b) Electrophilic substitution reaction (S_E)

When a substitution reaction involves an attack by an electrophile, the reaction is referred to as S_E (S - stands for substitution and E for electrophile).

c) Free radicals substitution reaction

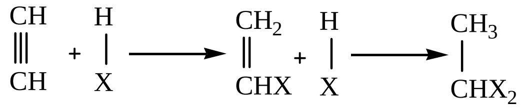
These reactions are initiated by free radicals.

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \quad \text{(Free radical)}$$

$$\underset{\text{Methane}}{CH_4} + 2Cl\cdot \rightarrow CH_3Cl + HCl$$

Addition Reactions

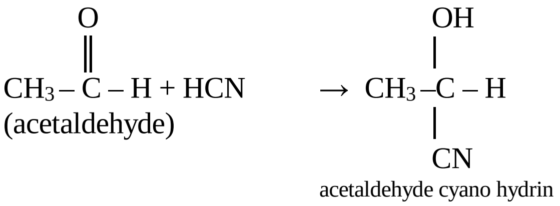
All organic compounds having double or triple bond adopt addition reactions in which two substances unite to form a single compound.



$$\begin{matrix} CH \\ ||| \\ CH \end{matrix} + \begin{matrix} H \\ | \\ X \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ || \\ CHX \end{matrix} + \begin{matrix} H \\ | \\ X \end{matrix} \longrightarrow \begin{matrix} CH_3 \\ | \\ CHX_2 \end{matrix}$$

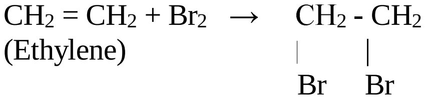
Depending on the type of reagent initiating these reactions, addition reactions are classified into three types.

(a) Nucleophilic addition



$$\underset{\text{(acetaldehyde)}}{CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - H} + HCN \rightarrow \underset{\text{acetaldehyde cyano hydrin}}{CH_3 - \overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}} - H}$$

(b) Electrophilic addition



$$\underset{\text{(Ethylene)}}{CH_2 = CH_2} + Br_2 \rightarrow \underset{\underset{\displaystyle Br}{|}}{CH_2} - \underset{\underset{\displaystyle Br}{|}}{CH_2}$$

www.tntextbooks.in

(c) Free radical addition

$$CH_3 - CH = CH_2 \xrightarrow[H_2O]{HBr} CH_3 - CH_2\text{-}CH_2 - Br$$

Elimination reactions

In these reactions, two atoms or groups are removed from a molecule without being substituted by other atoms (or) groups. The reverse of addition reactions are eliminations. These reactions are classified into two types.

(a) Unimolecular elimination (E_1)

$$(CH_3)_3C\text{-}Br \xrightarrow[KOH]{alcoholic} (CH_3)_2C{=}CH_2 + H_2O + Br^-$$

2-Methyl propene

(b) Bimolecular elimination (E_2)

$$CH_3 - CH_2 - CH_2 - Br \xrightarrow[KOH]{alcoholic} CH_3 - CH = CH_2 + KBr + H_2O$$

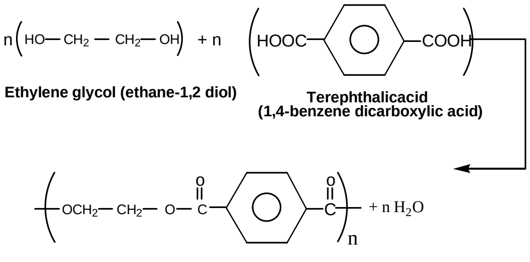
Polymerisation

The union of two or more molecules to form a large single molecule is called **polymerisation** and the product is a polymer.

Examples

$$n\,CH_2 = CH_2 \xrightarrow{473K,1000\ atm} (-\,CH_2 - CH_2\,-)_n$$

Ethylene (Monomer) → Polyethene (Polymer)



Terylene

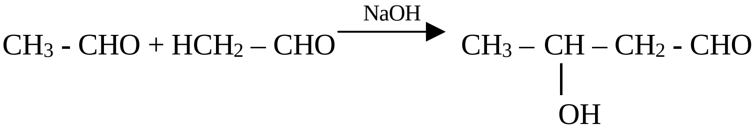
www.tntextbooks.in

Condensation reactions

When two molecules (similar or different) combine to form a single molecule with or without the elimination of simple molecules like H_2O, NH_3, HCl, CO_2, it is called a **condensation** reaction.

Example

Aldol condensation reaction



$$CH_3-CHO + HCH_2-CHO \xrightarrow{NaOH} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CHO$$

(acetaldehyde) (aldol)

Hydrolysis

Esters are hydrolysed by boiling with mineral acids or alkalis.

a) Acid hydrolysis

An ester can be hydrolysed to give the parent carboxylic acid and alcohol by using mineral acid (H_2SO_4 or HCl) as catalyst.

$$\underset{\text{Ethylacetate}}{CH_3-COOCH_2-CH_3} + H_2O \overset{H^+}{\rightleftharpoons} \underset{\text{acetic acid}}{CH_3-COOH} + \underset{\text{Ethyl alcohol}}{CH_3-CH_2-OH}$$

The above reaction is reversible and is exactly opposite of esterification. In order to hydrolyse most of the ester, the equilibrium must be pushed to the right by using large excess of water.

b) Basic hydrolysis

When an ester is treated with an alkali (NaOH or KOH) as catalyst, the hydrolysis yields the parent alcohol and sodium salt of the carboxylic acid.

$$\underset{\text{Ethyl propionate}}{CH_3-CH_2-COOC_2H_5} + NaOH \rightarrow \underset{\text{Sodium propionate}}{CH_3-CH_2-COONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

Reduction and oxidation reactions

A reaction which proceeds by the addition of hydrogen is termed

www.tntextbooks.in

Reduction and the one that involves the addition of oxygen is called **Oxidation**. For example,

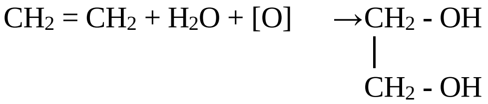
1) Clemmensen Reduction

Ketones can be reduced to their corresponding hydrocarbons by the mixture of Zn/Hg and conc. HCl.

$$C_6H_5COCH_3 \xrightarrow[HCl]{Zn/Hg} C_6H_5 - CH_2 - CH_3$$

acetophenone Ethyl benzene

2) Very mild oxidising agent such as $KMnO_4$, causes a spliting of the molecule at the double bond.



$$CH_2 = CH_2 + H_2O + [O] \rightarrow \begin{array}{l} CH_2 - OH \\ | \\ CH_2 - OH \end{array}$$

Ethylene Ethylene glycol

15.7.1 Types of Reagents

Electrophilic reagents

These reagents are electron deficient. This deficiency accounts for their affinity for electrons (electro = electron, philic = loving). They are also called cationic reagents and may carry positive charge or have incomplete valence shells. These reagents can therefore, be of two types.

(i) Positive electrophiles (or) Ionic electrophiles

(ii) Neutral electrophiles

Some common electrophiles are given in the table

S. No.	Ionic electrophiles	Neutral electrophiles (Lewis acids)
1.	H^+ (proton)	$AlCl_3$
2.	Cl^+ (chloronium)	BF_3
3.	Br^+ (bromonium)	$ZnCl_2$
4.	No_2^+ (Nitronium)	$FeCl_3$
5.	$>C^+$ carbonium	SO_3

Nucleophilic reagents

Nucleophiles or nucleophilic reagents are electron rich substances containing atoms which have at least an unshared pair of electron. These reagents are nucleus loving (nucleo = nucleus, philic = loving). Nucleophiles can be (i) negatively charged (or) Ionic (ii) neutral species (Lewis bases). Some of the common nucleophiles are reported in table

S. No.	Neutral nucleophiles (Lewis bases)	Ionic nucleophiles
1.	NH_3	X^- (halide ions)
2.	H_2O	OH^- (hydroxide)
3.	R-OH	RO^- (alkoxide)
4.	$R\text{-}NH_2$	CN^- (cyanide)
5.	$R_3\text{-}N$	$< C^-$ (carbanion)

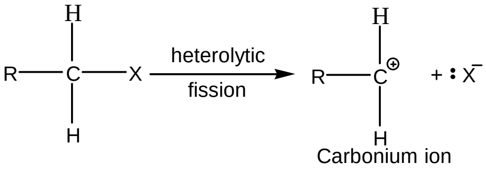
The differences between these reagents are summarised in the following table.

S. No.	Electrophiles	Nucleophiles
1.	are electron deficient	are electron rich
2.	are cations	are often anions
3.	are Lewis acids	are Lewis bases
4.	accept an electron pair	donate an electron pair
5.	attack on electron rich sites	attack on electron deficient sites
6.	possess an empty orbital to house the lone pair from the nucleophiles	possess a minimum of one lone pair of electron.

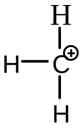
15.7.2 Carbonium ions

Let us consider the heterolytic fission of the bond C – X present in an organic molecule. If the atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomes negatively charged while the carbon will lose its electron and thus acquire a positive charge. Such cationic species carrying a positive charge on carbon are known as carbonium ions.

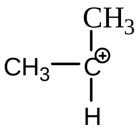
For illustration



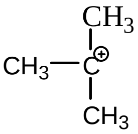
These carbonium ions are called primary, secondary and tertiary depending up on the nature of the carbon atom bearing the charge.



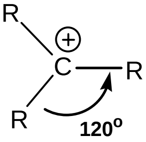
Carbonium ion (primary)



Methyl carbonium ion (secondary)



Trimethyl carbonium ion (tertiary)



The geometry of alkyl carbonium ion

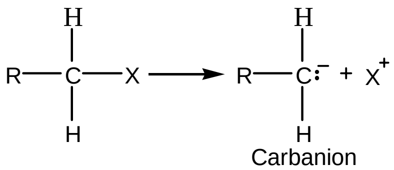
Since the carbon of the carbonium ion is in sp^2 hybridised state, the ion is planar with a vacant p orbital perpendicular to the plane of the three covalent bonds to carbon.

Carbanion

Let us consider the heterolytic fission of the bond C - X present in an organic molecule. If the carbon atom has greater electronegativity than the atom X, the former takes away the bonding electron pair and acquires a negative charge. The resulting carbon anion is known as carbanion.

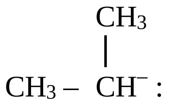
www.tntextbooks.in

For illustration



Examples

$CH_3 - CH_2^{-}:$ methyl carbanion



$CH_3 - \underset{}{\overset{\overset{CH_3}{|}}{CH^{-}}}:$ dimethyl carbanion

15.8 Free Radicals

Free radicals are species with one or more unpaired electrons obtained by the homolytic fission of covalent bond. The free radicals themselves are electrically neutral. The free radicals are denoted by putting a dot against the atom or group of atoms.

Few examples : $Cl\cdot$, $CH_3\cdot$, $C_6H_5\cdot$

They are classified as short lived free radicals and long lived free radicals on the basis of their life time.

Formation of free radicals

(a) Photochemical fission : When an organic compound is exposed to ultraviolet region it under goes bond fission.

Example : $Cl \cdot \cdot\, Cl \xrightarrow{uv} Cl\cdot + Cl\cdot$

(b) Thermal fission : All organic compounds on heating yield free radicals.

$(C_2H_5)_4Pb \xrightarrow{\Delta} Pb + 4C_2H_5\cdot$

Polar Effects

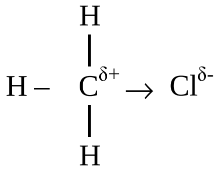
Inductive Effect

If a covalent bond is formed by two atoms differing much in electronegativity then the bond is said to be polarised. The electron pair

www.tntextbooks.in

shifts towards the more electronegative atom resulting in the origin of fractional charges on the atoms.

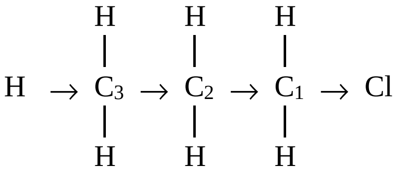
Consider methyl chloride,



$$\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}{}^{\delta+}\rightarrow \mathrm{Cl}^{\delta-}$$

In this molecule, chlorine atom is more electronegative than the carbon atom. Due to this, chlorine pulls the electron pair and acquires a small negative charge.

Let us consider, 1 - chloropropane



$$\mathrm{H}\rightarrow \underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C_3}}}\rightarrow \underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C_2}}}\rightarrow \underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C_1}}}\rightarrow \mathrm{Cl}$$

As C_1 is positively charged, it attracts towards itself the electron pair shared between C_1 and C_2. This causes C_2 to acquire a small positive charge but the charge is smaller than the charge on C_1. This type of electron displacement occuring in saturated compounds along a carbon chain is termed, inductive effect.

It is a permanent effect and decreases rapidly as the distance from the electronegative atom increases. It is represented by → the arrow head pointing towards the more electronegative atom. This effect operates in the case of σ - electrons only.

For measurements of relative inductive effect, atoms or groups having greater electron affinity than hydrogen are said to have - I effect. Similarly, atoms or groups having lesser electron affinity than hydrogen are said to have + I effect. Some of the atoms and groups arranged in the increasing order of inductive effect are given as

Groups having - I effect [electron - attracting].

- C_6H_5, ^{-}OH, -I, -Br, -Cl, -F

Groups having + I effect [electron pumping]

www.tntextbooks.in

CH_3 -,	$CH_3 - CH_2$ - ,	$(CH_3)_2CH$-,	$(CH_3)_3C$ -
(Methyl)	(Ethyl)	Isopropyl	tertiarybutyl

Resonance (Mesomeric) Effect

When several structures may be assumed to contribute to the true structure of a molecule but none of them can be said to represent it uniquely, then the molecule is referred to as a resonance hybrid and the phenomenon is termed as resonance.

It is somewhat abstract, but it can be better understood if we consider the structure of a simple molecule carbon dioxide.

$$O = C = O$$

(I)

The above structure does not account for all observed properties although it can explain many. The C-O bond length in CO_2 molecule is 1.15 Å where as it is expected to be 1.22 Å on the basis of the above structure.

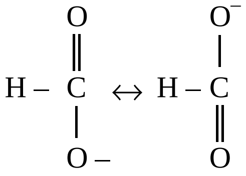
Again, the heat of formation of carbon dioxide is 1592 $kJ.mol^{-1}$ where as on the basis of the above structure it is expected to be approximately 1466 $kJ.mol^{-1}$. These discrepancies can be explained only if we assume the following resonance hybrid for carbon dioxide.

$$O^+ \equiv C - O^- \leftrightarrow O = C = O \leftrightarrow {}^-O - C \equiv O^+$$

The difference in energy i.e. 126 $KJ.mol^{-1}$ is regarded as resonance energy.

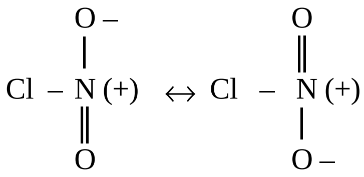
Few other examples

1. Formate ion, $HCOO^-$



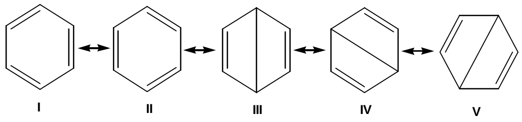
$$H - \overset{\overset{O}{\|}}{\underset{\underset{O\,-}{|}}{C}} \leftrightarrow H - \overset{\overset{O^-}{|}}{\underset{\underset{O}{\|}}{C}}$$

2. Nitryl chloride, NO_2Cl



$$Cl-\overset{\substack{O-\\|}}{\underset{\substack{\|\\O}}{N}}(+) \leftrightarrow Cl-\overset{\substack{O\\\|}}{\underset{\substack{|\\O-}}{N}}(+)$$

3.

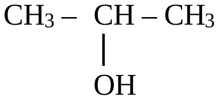


Benzene

Questions

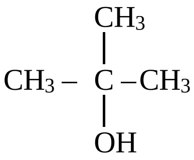
A. Write IUPAC name of the following

(a)



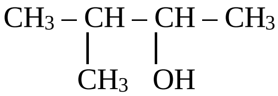
$CH_3-\underset{\substack{|\\OH}}{CH}-CH_3$

(b)



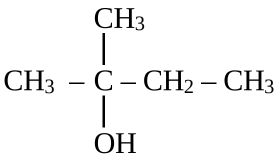
$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\OH}}{C}}-CH_3$

(c)



$CH_3-\underset{\substack{|\\CH_3}}{CH}-\underset{\substack{|\\OH}}{CH}-CH_3$

(d)

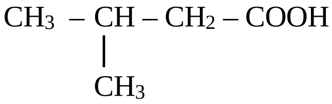


$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\OH}}{C}}-CH_2-CH_3$

(e) $CH_2=CH-COCH_2CH_3$

(f) CH_3CH_2CHO

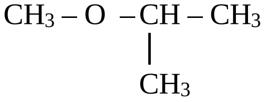
www.tntextbooks.in

(g) 

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COOH$$

(h) $CH_3CH_2OCH_2CH_3$

(i) $CH_3OCH_2CH_2CH_3$

(j) 

$$CH_3-O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

(k) $CH_3CH_2CH_2CH_2NH_2$

B. Explain briefly on the following

1. Homolytic and heterolytic fission.
2. Substitution reaction.
3. Addition reaction.
4. Elimination reaction.
5. Polymerisation reaction.
6. Condensation reaction.
7. Hydrolysis.
8. Reduction and oxidation reactions.
9. Electrophilic and Nucleophilic reagents.
10. Carbonium ions and carbanions.
11. Free radicals.
12. Inductive effect.
13. Resonance effect.

SUMMARY

- This chapter explains the ability of carbon atoms to form long chains held together by strong carbon-carbon bonds, catenation.
- Characteristics of homologous series and structural isomers are explained.

www.tntextbooks.in

- Method of writing IUPAC names of different organic compounds are explained with suitable examples.
- All types of organic reactions, like substitution, addition, elimination, condensation, polymerisation, hydrolysis, oxidation and reduction reactions are explained with suitable examples.
- Different types of isomerism and the representations are explained.
- Nature of fission of bonds, reagents, carbonium ions carbanions and free radicals are structurally explained with suitable examples.
- Notable electron displacements in organic chemistry like inductive and mesomeric effect in covalent bond are explained.

REFERENCES

1. Advanced Organic Chemistry by I.L.Finar.
2. Organic Chemistry by Bahl and Arun Bahl.

www.tntextbooks.in

16. PURIFICATION OF ORGANIC COMPOUNDS

OBJECTIVES

The main objectives of this chapter are to provide

- * *Characteristics of organic compounds*
- * *Need for purification*
- * *Methods of purifying organic substances like crystallisation, distillation, fractional distillation, steam distillation, distillation under reduced pressure and various methods of chromatography.*

16.1 Characteristics of organic compounds

Organic compounds have the following general characteristics.

i) Organic compounds are generally covalent and hence they do not dissolve in water (polar solvents) but dissolve in organic solvents (non-polar solvents) such as ether, alcohol, benzene etc.

ii) Due to maximum catenation and tetravalency of carbon, they have tendency to form long open and closed chain compounds.

iii) They are volatile, inflammable and possess low boiling points and melting points.

iv) Some organic compounds exhibit the phenomenon of polymerisation. For example, ethylene polymerises to poly ethylene.

v) They exhibit isomerism.

vi) They contribute homologous series.

vii) They are non-conductors of electricity.

Need for purification of organic compounds

The organic compounds obtained from natural sources are not pure. They contain a number of other compounds which occur with them. Similarly, the organic compounds prepared in the laboratory are also not pure. They are found to contain other products formed during the reaction. In order to investigate the structure and properties of an organic compound, it should be in the purest form. Hence purification of organic compounds become essential.

www.tntextbooks.in

Various methods used for purification and separation of organic compounds are:

i) Crystallisation
ii) Fractional Crystallisation
iii) Sublimation
iv) Distillation
v) Extraction with solvents
vi) Chromatography

16.2 Crystallisation

Crystallisation is carried out in four stages (a) preparation of the solution of the substance in a suitable solvent (b) filtration of the hot solution (c) crystallisation by cooling the hot filtrate (d) isolation and drying of the purified substance.

a) Preparation of the solution : The powdered organic substance is taken in a semi-micro round bottom flask and the solvent is added little by little with constant stirring and heating till the amount added is just sufficient to dissolve the solute, when the solution is just boiled. If the solvent is non-inflammable, heating may be done on the wire gauze, while in the case of inflammable solvents, heating should be done on a water bath.

b) Filtration of the Solution : The hot saturated solution obtained is filtrated through a fluted filter paper placed in a hot water funnel.

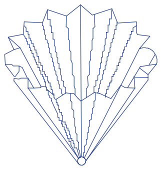


Fig. 16.1 Fluted Filter paper

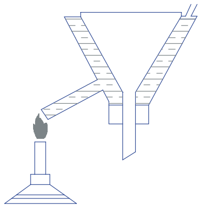


Fig. 16.2 Water funnel

www.tntextbooks.in

c) Crystallisation : When the filtration is over, the beaker containing the solution is allowed to cool when pure crystals separate. Sometimes the crystals do not separate due to super cooling of the solution. Crystallisation can be started in such cases by scratching the sides of the vessel containing the solution with a glass rod or seeding with a tiny crystal of the substances.

d) Isolation and drying of the purified crystals : The purified crystals are separated from the mother liquor by filtration using Buchner funnel and a suction pump.

When the whole of the mother liquor has been drained off, the crystals are washed with small amounts of cold solvent thrice. The crystals are then transfered to a porous plate, pressed by using filter paper and then dried by using infra-red light or by keeping in sunlight. If the crystals are coloured, decolourisation is effected by using animal charcoal.

Fractional Crystallisation

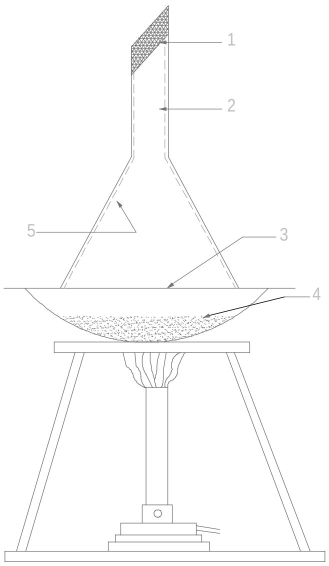
When the solubility of two substances in any solvent is not much different from one another, then the two compounds can be separated by fractional crystallisation, involving a series of repeated crystallisations. For example, when a solution containing two substances A and B is subjected to crystallisation, the slightly less soluble substances (say A) containing a small amount of the other substance (B) crystallises out. The mother liquor when subjected to crystallisation gives crystals of B containing a small amount of A.

Now, if these crystals are subjected to recrystallisation separately and the process is repeated number of times to get pure A and pure B.

16.3 Sublimation

Certain solid substances like Naphthalene or camphor when heated pass directly from solid to the vapour state without melting. The vapours when cooled give back the solid substance. This process is known as sublimation.

www.tntextbooks.in



1. Cotton
2. Inverted funnel
3. Perforated asbestos sheet
4. Mixture
5. Sublimate

Fig. 16.3

This process is very helpful in separating a volatile solid from a non-volatile solid. The powdered substance is taken in a China dish and covered with a perforated filter paper and an inverted funnel. The dish is carefully heated on a sand bath.

The vapours passing through the holes in the paper condense on the inner sides of the funnel. The non-volatile impurities remain in the dish.

16.4 Methods for the purification of liquids Distillation

Distillation is used for separating the constituents of a liquid mixture which differ in their boiling points. Depending upon the difference in the boiling points of the constituents, different types of distillation are employed. These are described below.

i) Simple Distillation

Liquids with boiling points widely apart (about 40K and above) can be purified by simple distillation if they do not decompose under ordinary pressure. Simple distillation involves conversion of a liquid into its vapour by heating in a distilling flask and then condensation of the vapour into a liquid in the receiver.

Mixtures like the following can be separated by this simple distillation.

a Nitro benzene (b.p 484K) and benzene (b.p.354K)

b. Diethyl ether (b.p.308K) and ethyl alcohol (b.p.351K)

Note : Simple distillation is also helpful in separating non-volatile impurities from liquids.

16.4.1 Fractional Distillation

This method is applicable for the separation and purification of a mixture of two or more miscible liquids whose boiling points lie very close to each other.

This is similar to the ordinary distillation method with the only exception that a fractionating column is introduced in-between the distillation flask and the condenser.

The process of separation of the components in a liquid mixture at their respective boiling points in the form of vapours and the subsequent condensation of those vapours is called fractional distillation.

The fractionating columns used for the purpose are of different shapes.

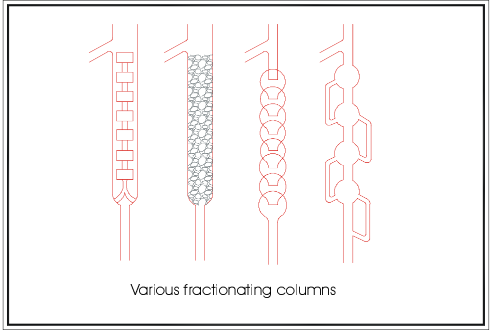


Fig. 16.4

16.4.2 Steam Distillation

In steam distillation impure compounds are distilled in a current of steam. This method is applicable to solids as well as liquids. For purification by steam distillation, an impure compound must satisfy the following conditions:

i) It should not decompose at the steam temperature.

ii) It should have a fairly high vapour pressure at 373 K.

iii) It should be insoluble in water.

iv) The impurities present should be non-volatile

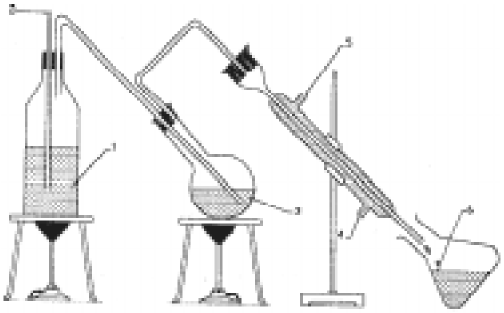


Fig. 16.5

1. Water 2. Protective tube 3. Flask 4. Inlet for water
5. Outlet for water 6. Pure liquid

The apparatus used for steam distillation is shown in the figure (16.5). The impure compound is taken in the round bottomed flask and a small quantity of water is added. The flask is then heated gently. Now steam is bubbled through the contents in the flask. The vapours of the compound mix up with steam and escape into the condenser. The condensate thus obtained is a mixture of water and the organic compound which can be separated.

Theory of steam distillation

Let p_1 represent the vapour pressure of water and p_2 the vapour pressure of the organic liquid. In steam distillation the liquid boils at a temperature at which

$$p_1 + p_2 = \text{Atmospheric Pressure}$$

This temperature must be lower than the normal boiling point of water or the organic liquid. The reason that $p_1 + p_2$ becomes equal to the atmospheric pressure must earlier than p_1 or p_2 alone. Thus in steam distillation, the impure liquid boils at a temperature which is lower than its normal boiling point. Hence, steam distillation serves the same purpose as

www.tntextbooks.in

distillation under reduced pressure. However, the former is cheaper but less useful than the latter.

16.4.3 Distillation under reduced pressure

This technique is used for purifying or separating thermally unstable liquid compounds which decompose at their normal boiling points.

Principle : Lowering of pressure on the surface of a liquid lowers its boiling point. As a result, a liquid can be boiled and distilled at a temperature much below the normal boiling point without any decomposition.

Procedure : Distillation under reduced pressure or vacuum is carried out in a specially designed glass apparatus as shown in (Fig.17.6).

The receiver is attached to a vacuum pump to reduce pressure. The pressure is measured with the help of a manometer.

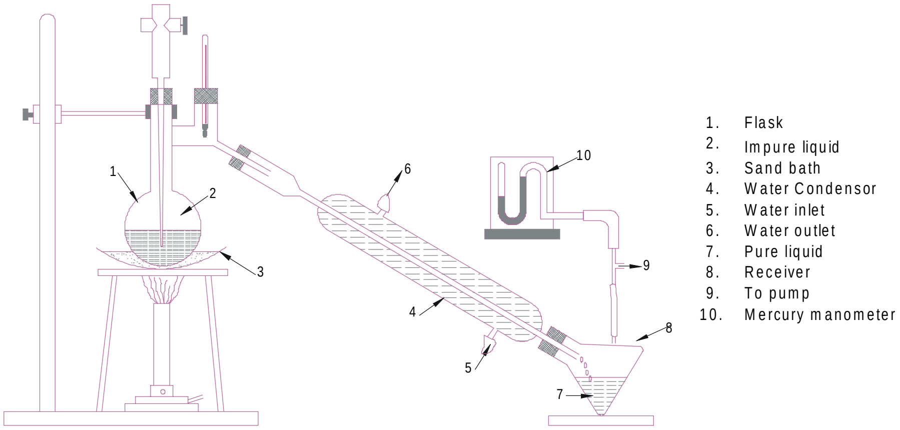


Fig.16.6 Distilation under reduced pressure

Advantages of distillation under reduced pressure

Distillation under reduced pressure has the following advantages:

www.tntextbooks.in

i) The compounds which decompose on heating to their boiling points under normal pressure can be purified by distillation under reduced pressure. This is because at a reduced pressure, a liquid would boil at temperature much below its normal boiling point.

ii) In distillation under reduced pressure, a liquid boils at temperature well below the normal boiling point. So, the distillation under reduced pressure is more fuel-economical.

16.4.4 Extraction with solvents

This method is based on the fact that organic substances are more soluble in organic solvents than in water.

The organic substance is extracted from its aqueous solution adopting the following procedure.

a. The aqueous solution containing organic substance is shaken with a suitable organic solvent which dissolves the substance but is immiscible with water. Two layers are formed; the organic layer and aqueous layer.
b. The solvent layer containing the organic substance (organic layer) is separated using a `separating funnel'. The impurities remain in the aqueous layer removed by distillation to obtain the organic substance.
c. The organic solvent is removed by distillation to obtain the organic substance.

16.5 Chromatography

This technique was introduced by M.S.Tswett, a Russian botanist in 1906 when he reported the separation of different coloured constituents of chlorophyll. He achieved it by passing a petroleum ether solution of the chlorophyll present in leaves through a column of calcium carbonate firmly packed into a narrow glass tube. Different components of the pigment got separated into band or zones of different colours.

Chromatography is based on the general principle of distributing the components of a mixture of organic compounds between two phases - a stationary phase and a moving phase. The stationary phase can be a solid or liquid supported on a solid, while the moving phase is a liquid or a gas. When the stationary phase is a solid, the basis of separation is adsorption; when it is a liquid, the basis is partition.

Hence, chromatography can be defined as the technique for the separation of a mixture of compounds where the separation is brought about by the differential movement of the individual compounds through a porous medium under the influence of a moving solvent. The technique has now a days undergone tremendous modification and is widely used for the separation and purification of different types of organic compounds.

The different chromatographic techniques used are : column chromatography (CC), thin-layer chromatography (TLC), paper chromatography (PC), gas-liquid chromatography (GLC) and ion-exchange chromatography.

a) Column Chromatography

The simplest chromatographic method is column chromatography. It is carried out in a long glass column having a stop-cock near the bottom. To start the operation, a plug of cotton or glass wool is placed at the bottom of the column to support the adsorbent powder. The tube is packed uniformly with suitable adsorbent. This constitutes what is known as the stationary phase. The commonly employed adsorbents are activated aluminium oxide (alumina), magnesium oxide, silica gel and starch. A loose plug of cotton or glass wool is then placed at the top of the adsorbent column.

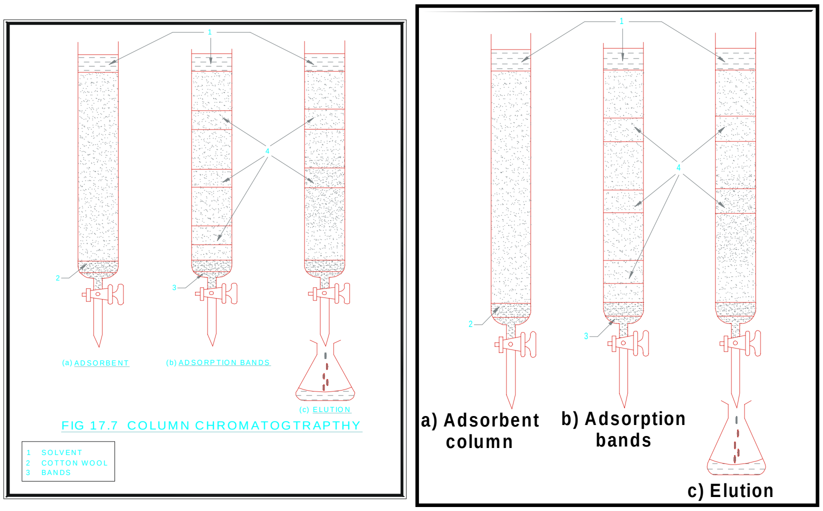


Fig. 16.7 Column chromatography

www.tntextbooks.in

The substance to be purified is added, as such if it is a liquid or in the form of its solution in some suitable solvent if it is a solid, at the top of the column and allowed to pass slowly through it. As it passes through the column, the different components of a mixture (Say A, B and C) got adsorbed to different extent and are thus retained by the adsorbent at different levels of the column. The components which are adsorbed very strongly are retained at the top while others are retained at lower levels. In this way different zones or bands are formed in the column which contain different components of a mixture. As soon as the last portion of the substances enter the column, a selected solvent, known as eluent, is added to the column. This acts as moving phase. The elements dissolve out the different components from the various zones selectively and thus `take out' the different bands in the form of fractions which are collected separately.

b) Thin Layer Chromatography (TLC)

Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of the substances of a mixture over a thin layer of an adsorbent. A thin layer (about 0.2mm thick) of an adsorbent (Silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The glass plate is then placed in a closed jar containing the solvent (Below 2cm height). As the solvent jar moves up the plate, the components of mixture move up along the plate to different distances depending on this degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its retention factor ie., R_f Value.

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

c) Paper Chromatography

It is an important and useful class of partition chromatography. In this technique, the stationary phase is considered to be made up of water molecules bound to the cellulose network (inert support) of the paper. The mobile phase, known as the developing solvent consists of either one solvent or a mixture of different solvents. Separation of the mixture into pure compounds takes place by the partitioning of different compounds between these two liquid phases. The mobile phase travels by capillary action through the paper. Depending upon the way the solvent travels on the paper, there are three types of paper chromatography.

i) Ascending Paper Chromatography : The mobile phase moves upwards on the paper strip in this case.

ii) Descending Paper Chromatography : The mobile phase in this case moves downward on the paper strip.

iii) Circular or radial paper chromatography: The mobile phase moves horizontally along a circular sheet of paper in this case.

In the ascending paper chromatography, the mixture of compounds is applied on the paper as a spot little above the lower end and then this end is dipped in the solvent. When the solvent has risen more than two third length of the paper, then it is removed from the solvent. The paper is dried and is known as chromatogram.

Now the spots for different compounds can be visualised using some suitable chemicals. The ratio of the distance travelled by the compound in a particular solvent to that the distance travelled by the solvent is a constant and is known as retention factor (R_f). This value is used in identifying the compounds.

$$R_f = \frac{\text{Distance travelled by the compound}}{\text{Distance travelled by the solvent}}$$

Type of Chromatography	**Stationary Phase**	**Mobile Phase**
1. Column Chromatography	Solid	Liquid
2. Thin Layer Chromatography (TLC)	Solid	Liquid
3. Paper Chromatography	Liquid	Liquid
4. Gas Liquid Phase Chromatography	Liquid	Gas

www.tntextbooks.in

Difference between paper chromatography and thin layer chromatography

Paper Chromatography	Thin Layer Chromatography
(i) Separation based on partition	Separation is based on partition, adsorption and ion exchange.
(ii) Stationary phase is the water molecules bound on the paper.	Stationary phase is a layer of silica gel or alumina on glass plate.

Questions

A. Choose the best answer

1. Organic compounds are soluble in
   a) Non-polar Solvents b) Polar solvents c) Water d) HCl
2. Decolourisation of coloured compounds can be effected by using
   a) Animal charcoal b) Carbon c) Coke d) Infra-red rays
3. Compounds having boiling points widely apart 40 K and above can be purified by
   a) Crystallisation b) Simple distillation
   c) Fractional distillation d) Sublimation
4. Nitrobenzene and benzene can be separated by the method of
   a) Steam distillation b) Crystallisation
   c) Fractional crystallisation d) Chromatography
5. Purification of two miscible liquids possessing very close boiling points can be separated using
   a) Fractional distillation b) Sublimation
   c) Simple distillation d) Steam distillation
6. Purification of mixture of compounds can be done by steam distillation only if the impurities are
   a) Non-volatile b) Volatile c) Insoluble in Water d) both a & c
7. When the stationary phase is solid, then the compounds can be separated on the basis of
   a) Adsorption b) Partition c) Both partition and adsorption d) Either
8. Column Chromatography is based on the principle of
   a) Adsorption b) Partition c) Absorption d) Distribution
9. In Ascending paper Chromatography, the solvent moves
   a) Upwards b) Downwards c) Horizontally d) None
10. The existence of wide range of organic compounds is due to their, property of
    a) Extensive catenation b) Lower boiling points
    c) Polymerisation d) Isomerism

B. Fill in the blanks

1. The Compounds separated and purified by crystallisation can be dried over ________
2. Camphor can be purified by the process of ________________ .
3. In simple distillation the compounds should not decompose at ________
4. Water insoluble compounds can be purified by __________ .
5. In T.L.C the stationary phase is a _______________ .
6. Chromatographic technique was first introduced by ____________ .
7. In paper chromatography, the mobile phase travels by __________action through the paper.
8. The adsorbent used in column Chromatography method is__________ .
9. In Chromatographic technique, the separation of compounds are brought about by _______________ movement of the compounds.
10. Paper Chromatography is _______________ Chromatography.

C. Write in one or two sentence

1. What are the different stages followed during Crystallisation?
2. Define steam distillation.
3. What are different types of distillation?
4. Give the advantages of distillation under reduced pressure.
5. What are the types of paper chromatography?

D. Explain briefly on the following

1. Explain the method of purifying a solid organic compound.
2. Write short notes on
   a) Fractional crystallisation b) Solvent extraction
3. Explain the purification of compounds by using thin layer chromatography.
4. What are the various principles used in chromatographic separation?
5. Write down the general characteristics of organic compounds.

SUMMARY

All organic compounds must be purified before study. There are various purification methods adopted. Depending on the physical and chemical properties of the organic compounds, purification methods are done. Methods like crystallization, sublimation, distillation, solvent extraction and chromatographic techniques are dealt in detail in this chapter.

REFERENCES

1. Organic Chemistry by Bahl and Arun Bahl.
2. Organic Quantitative Analysis by Arthur I Vogel, ELBS edition.

www.tntextbooks.in

17. DETECTION AND ESTIMATION OF ELEMENTS

OBJECTIVES

The main objectives of the chart are to provide

- *Detection and estimation of carbon, hydrogen, nitrogen, sulphur and halogens.*
- *The various methods for the detection and estimations are discussed in detail.*

17.1 Qualitative Analysis

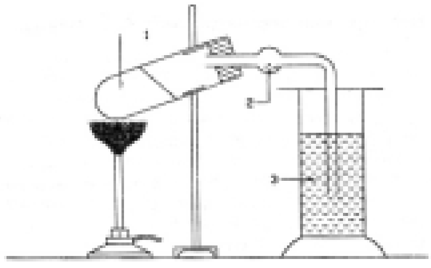
Qualitative analysis of an organic compound involves the detection of various elements present in it. The elements commonly present in organic compounds are carbon, hydrogen, oxygen, nitrogen, halogens and sulphur and sometimes phosphorous. The carbon and hydrogen are present in almost all the organic compounds.

A) Detection of carbon and hydrogen

The detection of carbon and hydrogen in an organic compound is done by a single experiment.

A small quantity of pure and dry compound is mixed with about ten times its weight of copper oxide (CuO). The mixture is taken in a hard glass test tube fitted with a delivery tube having a small bulb. The other end of the tube is immersed in freshly prepared lime water. In the bulb of delivery tube, a small amount of anhydrous copper sulphate (white) is placed. The mixture is heated strongly when carbon and hydrogen present are oxidised to carbon dioxide and water respectively.

$$\boxed{\begin{array}{c} C + 2CuO \rightarrow CO_2 + Cu \\ 2H + CuO \rightarrow H_2O + Cu \end{array}}$$



1. Organic Compound + Copper (II) oxide
2. Anhydrous copper sulphate
3. Lime water

Fig. 17.1

Carbon dioxide turns **lime water milky** and the water vapour turns colourless copper sulphate, blue.

$$\begin{array}{ll} Ca(OH)_2 + CO_2 \rightarrow & CaCO_3 \downarrow + H_2O \\ & \text{(White ppt)} \end{array}$$

$$\begin{array}{ll} CuSO_4 + 5H_2O \rightarrow & CuSO_4 \, . \, 5H_2O \\ \text{(colourless)} & \text{(blue)} \end{array}$$

Turning of lime water milky and of colourless copper sulphate blue shows the **presence of carbon and hydrogen** respectively.

B. Detection of Oxygen

There is no direct method for the detection of oxygen in organic compounds. It is detected indirectly. For example,

a) If any organic compound on heating in a dry test tube, gives out water vapour, then the presence of oxygen in the organic compound is indicated.

b) If any organic compound is found to contain any oxygen containing functional groups such as - OH, -CHO, -COOH, $-NO_2$ etc., then the compound contains oxygen.

c) If the sum of the percentages of various elements present in the compound is less than 100, then the compound contains oxygen.

C) Detection of nitrogen, sulphur and halogens

All these can be detected by **Lassaigne's Test**.

Lassaigne's Test : The organic compound is taken in an ignition tube. A pea-size sodium metal is added to it and heated to red hot. The hot tube is crushed to powder under a few ml of water in a mortar. The solution is filtered and the filtrate is known as `sodium extract' or **`lassaigne's filtrate'**. The filtrate is used for the detection of the elements.

Nitrogen : During fusion, the carbon and nitrogen of the organic compound combine with sodium metal forming sodium cyanide.

$$Na + C + N \rightarrow NaCN$$

The unreacted sodium combines with water forming caustic soda, so the solution becomes alkaline.

Test : To the extract, ferrous sulphate solution is added and warmed. Sodium ferrocyanide is formed.

$FeSO_4 + 2NaCN \rightarrow Fe(CN)_2 + Na_2SO_4$

$Fe(CN)_2 + 4\ NaCN \rightarrow Na_4[Fe(CN)_6]$

sodiumferrocyanide

A few drops of **ferric chloride** are added to it and the solution is **acidified with dilute sulphuric acid**. The ferric ions react with sodium ferrocyanide giving a bright blue (prussion blue) coloration

$3\ Na_4\ [Fe(CN)_6]+4Fe^{+3} \rightarrow Fe_4[Fe(CN)_6]+ 12Na^+$

ferric ferrocyanide
(prussion blue)

Test : If an organic compound contains nitrogen along with sulphur, a blood red colour will be obtained in the above test.

$Na + C + N + S \rightarrow Na\ CNS$

$3NaCNS + FeCl_3 \rightarrow Fe\ (CNS)_3 + 3NaCl$

(Ferric sulphocyanide)
(blood red colour)

Sulphur

Organic compounds containing sulphur give sulphide on fusion with sodium.

$2Na + S \rightarrow Na_2S$

Test : To the Lassaigne's filtrate, sodium nitroprusside is added. **Purple colour** is developed.

$Na_2S + Na_2\ [Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5\ NOS]$

sodium nitroprusside purple

Halogens : In sodium extract, the halogen is present as sodium halide.

$$\boxed{Na + X \rightarrow NaX \ (X = Cl, Br, I)}$$

Test : The extract is acidified with dilute nitric acid and silver nitrate solution is added. Formation of precipitate indicates the presence of halogen.

$$\boxed{NaX + AgNO_3 \rightarrow AgX \downarrow + NaNO_3}$$

The halogen is identified from the **colour** and the **solubility** of the precipitate in ammonium hydroxide.

Sl. No.	Colour of the precipitate	Halogen present	Solubility in ammonium hydroxide
1.	White	chlorine	Easily soluble
2.	Pale yellow	bromine	Sparingly soluble
3.	Yellow	iodine	Insoluble

17.2 Quantitative analysis of organic compounds

Once we have known the various elements present in any organic compound, the next point of interest is to know how much of each element is present in the compound. Determination of the relative proportions (generally as percentages) of various elements present in an organic compound is called **quantitative analysis of that compound**. For quantitative analysis, the percentages of the various elements present in any compound are estimated by suitable chemical methods.

(a) Estimation of carbon and hydrogen (liebig's combustion method)

The estimation of carbon and hydrogen is carried out in one experiment.

A known weight of the organic compound is strongly healed with excess of dry copper oxide in an atmosphere of dry and pure oxygen or air. Carbon of the compound is oxidised to carbon dioxide and hydrogen to water.

www.tntextbooks.in

$$\boxed{\begin{array}{l} C + 2CuO \rightarrow CO_2 \uparrow + Cu \\ 2H + CuO \rightarrow H_2O \uparrow Cu \end{array}}$$

The CO_2 and H_2O are absorbed by a strong solution of **caustic potash** and **anhydrous calcium chloride** respectively. The percentage of carbon and hydrogen is calculated from the weights of CO_2 and H_2O obtained. These weights are obtained by finding the weights of caustic potash and calcium chloride tubes before and after the experiment.

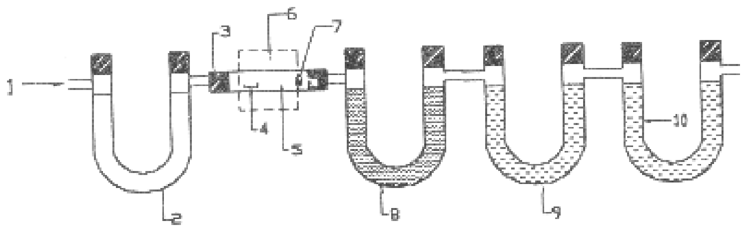


Fig.17.2

1. Oxygen supply 2. Drying tube 3. Glass joints
4. Platinum boat with organic compound 5. CuO
6. Combustion tube 7. Copper coil to remove nitrogen oxide
8. $CaCl_2$ guard tube 9. KOH tube 10. To prevent the incoming CO_2 and H_2O

Calculation

Let, weight of organic compound = wg
Increase in weight of $CaCl_2$ tube
(weight of water formed) = w_1g
Increase in weight of potash bulbs
(weight of carbon dioxide formed) = w_2g

Percentage of carbon

Molecular weight of CO_2 = (12 + 32) = 44
44 g of carbon dioxide contains, carbon= 12 g
w_2g of carbon dioxide contains,

$$= \frac{12}{44} \times w_2 g \text{ carbon}$$

wg of compound contains

$$= \frac{12}{44} \times w_2 \text{ g of carbon}$$

$\therefore$ 100 g of compound contains

$$= \frac{12}{44} \times \frac{w_2}{w} \times 100 \text{ g of carbon}$$

Percentage of carbon in the compound $= \frac{12}{44} \times \frac{w_2}{w} \times 100$

Percentage of hydrogen

Molecular weight of H_2O = (2 + 16) = 18

18 g of water contains, hydrogen = 2 g

w_1 g of water contains, hydrogen $= \frac{2}{18} \times w_1$ g

wg of compound contains

$$= \frac{2}{18} \times w_1 \text{ g of hydrogen.}$$

$\therefore$ 100 g of compound contains

$$= \frac{2}{18} \times \frac{w_1}{w} \times 100$$

Example 1

0.30 g of a substance gives 0.88 g of carbon dioxide and 0.54 g water. Calculate the percentage of carbon and hydrogen in it.

Solution

Weight of organic compound = 0.30 g
Weight of carbon dioxide = 0.88 g
Weight of water = 0.54 g

Percentage of carbon

44 g of carbondioxide contains, carbon = 12 g

0.88 g of carbon dioxide contains, carbon = $\frac{12 \text{ x } 0.88}{44}$ g

0.30 g substance contains, carbon = $\frac{12 \text{ x } 0.88}{44}$ g

100 g substance contains

$= \frac{12 \text{ x } 0.88}{44} \text{ x } \frac{100}{0.30} = 80$ g of carbon

Percentage of carbon = 80

Percentage of hydrogen

18 g of water contains, hydrogen = 2 g

0.54 g of water contains, hydrogen = $\frac{2 \text{ x } 0.54}{18}$ g

0.30 g of substance contains hydrogen = $\frac{2 \text{ x } 0.54}{18 \text{x} 0.30}$ g

100 g of substance contains = $\frac{2 \text{ x } 0.54}{18 \text{x} 0.30} \text{ x } 100$ g

= 20 g of hydrogen

Percentage of hydrogen = 20

(b) Estimation of oxygen

Oxygen is commonly estimated by the method of difference. The percentage of all other elements are added together and then subtracted from 100. The balance is the percentage of oxygen.

Example 2

0.2004 g of glucose gave on combustion 0.2940 g of CO_2 and 0.1202 g of H_2O. Find the percentage composition.

Solution

Weight of organic compound = 0.2004 g

Weight of carbon dioxide = 0.2940 g

Weight of water = 0.1202 g

Percentage of carbon

44 g of CO_2 contains, carbon = 12 g

www.tntextbooks.in

0.2940 g of CO_2 contains, carbon = $\frac{12 \text{ x } 0.2940}{44}$ g

Percentage of carbon = $\frac{12 \text{ x } 0.2940}{44} \text{ x } \frac{100}{0.2004} = 40.01$

Percentage of hydrogen

18 g of H_2O contains, hydrogen = 2 g

0.1202 of H_2O contains, hydrogen = $\frac{2 \text{ x } 0.1202}{18}$

Percentage of hydrogen = $\frac{2 \text{ x } 0.1202}{18} \text{ x } \frac{100}{0.2004} = 6.66$

Percentage of oxygen is therefore by difference,

= [100 - (40.01 + 6.66)] = 53.33

Estimation of nitrogen

c) Kjeldahl Method

This method is based on the fact that many nitrogenous organic compounds when heated with con. H_2SO_4, are quantitatively converted into ammonium sulphate. The ammonium sulphate so obtained is heated with excess NaOH and the ammonia liberated is absorbed in a known volume of standard acid.

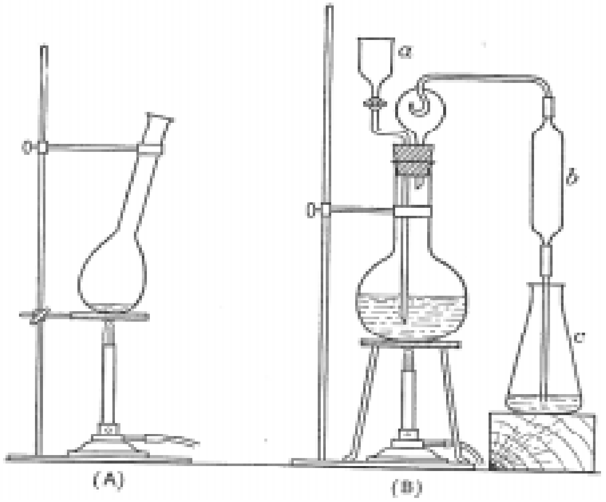


Fig. 17.3 Kjeldahl's method

www.tntextbooks.in

From the volume of standard acid used by ammonia and the mass of organic compound taken for the experiment, we can calculate the mass of nitrogen in the compound.

Organic compound $\xrightarrow{H_2SO_4}$ $(NH_4)_2$
SO_4 $\xrightarrow{NaOH}$ NH_3 $\xrightarrow{H_2SO_4}$ $(NH_4)_2\,SO_4$
with nitrogen

Note : 1000 ml 1N acid ≡ 17 g NH_3 ≡ 14 g nitrogen.

Calculation

Mass of the nitrogenous substance = W g

Volume of acid used up by NH_3 = V_1 ml

Normality of acid = N_1

Volume of 1 N acid = V_1 N

$$\text{Mass of nitrogen} = \frac{14 \text{ x } V_1 N_1}{1000}$$

$$\text{\% of nitrogen} = \frac{14 \text{ x } V_1 N_1 \text{ x } 100}{1000 \text{ x } w}$$

Example 1

The ammonia evolved from 0.21 g of an organic compound by Kjeldahl method neutralised 15 ml of N/20 sulphuric acid solution. Calculate the percentage of nitrogen.

Weight of organic compound = 0.21 g

$$\text{Normality of acid} = \frac{N}{20}$$

Volume of standard acid
neutralised by ammonia = 15 ml

www.tntextbooks.in

1000 ml of 1N ammonia contains = 14 g of nitrogen

15 ml of ammonia of normality

$$\frac{N}{20} \text{ contains nitrogen } = \frac{14 \text{ x } 15 \text{ x } 1}{1000 \text{ x } 20}$$

0.21 g of compound contains nitrogen

$$= \frac{14 \text{ x } 15}{1000 \text{ x } 20}$$

100 g of compound contains nitrogen

$$= \frac{14 \text{ x } 15 \text{ x } 100}{1000 \text{ x } 20 \text{ x } 0.21} = 5\text{g}$$

$\therefore$ Percentage of nitrogen = 5

Example 2

0.35 g of an organic substance was Kjeldahlised and the ammonia obtained was passed into 100 ml of N/5 H_2SO_4. The excess acid required 154 ml of N/10 NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

Solution

Volume of N/5 H_2SO_4 solution taken = 100 mL

The volume of N/5 H_2SO_4 neutralised by N/10 NaOH can be obtained as follows :

$$N_{acid} \text{ x } V_{acid} = N_{alkali} \text{ x } V_{alkali}$$

$$\frac{N}{5} \text{ x } V_{acid} = \frac{N}{10} \text{ x } 154 \text{ mL}$$

$$V_{acid} = \frac{154}{10} \text{ x } 5 \text{ mL}$$

www.tntextbooks.in

= 77 mL

Therefore,

Volume of N/5 H_2SO_4 used for
neutralising ammonia = (100 - 77) mL
= 23 mL

Then,

Percentage of nitrogen in the sample

$$= \frac{1.4 \times \text{Normality volume of acid used for neutralising } NH_3}{\text{Mass of the compound taken}}$$

Percentage of nitrogen in the sample

$$= \frac{1.4 \times 1/5 \times 23}{0.35} = 18.4$$

d) Estimation of sulphur

Carius method

A known mass of the organic compound is heated in a sealed tube with fuming nitric acid. The sulphur present in the organic compound will be oxidised to sulphuric acid. The tube is cooled and broken in dilute hydrochloric acid. Then excess of barium chloride solution is added. The precipitate of barium sulphate obtained is filtered, washed, dried and weighed accurately.

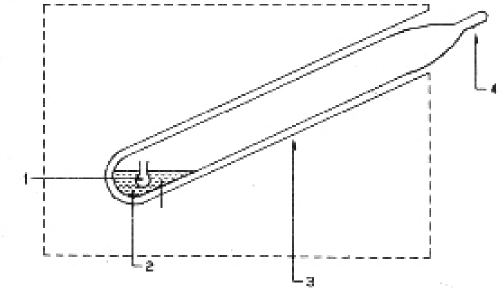


Fig.17.4

1. Organic compound 2. Nitric acid 3. Iron tube 4. Carius tube

Calculations

Mass of the organic compound = w g

Mass of barium sulphate = w_1 g

233.4 g $BaSO_4$ contains 32 g sulphur

$\therefore$ w_1 g $BaSO_4$ will contain $\dfrac{32 \text{ x } w_1}{233.4}$ g sulphur

Percentage of sulphur

$$= \frac{32 \text{ x } w_1}{233.4 \text{ x } w} \text{ x } 100$$

Example

0.316 g of an organic compound, after heating with fuming nitric acid and barium nitrate crystals in a sealed tube gave 0.466 g of the precipitate of barium sulphate. Determine the percentage of sulphur in the compound.

(Atomic masses : Ba = 137, S = 32, O = 16, C = 12, H = 1).

Solution

Mass of the substance taken = 0.316 g

Mass of $BaSO_4$ formed = 0.466 g

Molecular mass of $BaSO_4$ = 137 + 32 + 64 = 233

Then, mass of S in 0.466 g of $BaSO_4$

$$= \frac{0.466 \text{ x } 32}{233} \text{ g}$$

Percentage of S in compound

$$= \frac{0.466 \text{ x } 32 \text{ x } 100}{233 \text{ x } 0.316}$$

$$= 20.25$$

e) Estimation of halogens

Carius Method

Principle : The organic compound is heated with silver nitrate and fuming nitric acid. The halogen in the organic compound becomes the halide ion and this reacts with silver ion of the silver nitrate solution. The silver halide is precipitated. The precipitate is filtered, washed, dried and then weighed accurately.

Procedure

About 0.2 g of the organic compound is weighed accurately in a small glass tube. The tube is introduced into the Carius tube containing fuming nitric acid and silver nitrate crystals. The upper end of the tube is sealed. The tube is then heated in a furnace for 5 to 6 hours. The organic compound breaks up and the halogen present gives a precipitate of silver halide. The Carius tube is cooled and then broken. The precipitate of silver halide is washed, dried and weighed accurately.

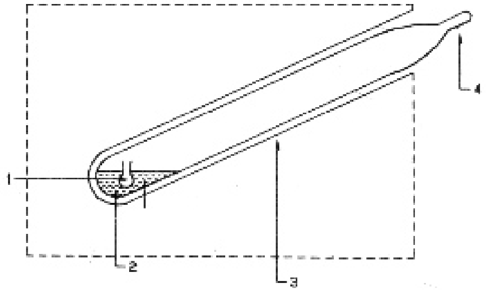


Fig.17.5

1. Organic compound	2. Nitric acid + Silver nitrate
3. Iron tube	4. Carius tube

Calculation

Mass of organic compound = w g

Let the mass of silver halide be w_1 g

143.5 g of silver chloride contains

35.5 g Cl_2

$$w_1 \text{ g of AgCl contains } \frac{35.5 \times w_1}{143.5} \text{ g of } Cl_2$$

$$\text{Percentage of chlorine} = \frac{35.5 \times w_1 \times 100}{143.5 \times w}$$

similarly,

Percentage of bromine

$$= \frac{80}{188} \times \frac{w_1}{w} \times 100$$

Percentage of iodine

$$= \frac{127}{235} \times \frac{w_1}{w} \times 100$$

Example

0.15 g of iodoform gave 0.2682 g of AgI. Calculate the percentage of iodine.

Weight of compound = 0.15 g

Weight of silver iodide = 0.2682 g

Molecular weight of silver iodide = 108 + 127 = 235

235 g of silver iodide contains 127 g of iodine

$$\text{0.2682 g of AgI contains} = \frac{127 \times 0.2682}{235}$$

$$= 0.144 \text{ g iodine}$$

0.15 g of compound contains 0.144 g of iodine

$$\text{100 g of compound contains} = \frac{100 \times 0.1449}{0.15} = 96.6 \text{ g}$$

$\therefore$ Percentage of iodine = 96.6

Problems

Estimation of carbon and hydrogen

1. 0.12 g of an organic compound gave on combustion 0.18 g of water and 0.11 g of CO_2. Calculate the percentage of C and H in the organic compound. [Ans : C = 25%, H = 16.66%]
2. An organic compound contains C, H and O. 0.2475 g of the organic compound yielded on combustion 0.4950 g of CO_2 and 0.2025 g of H_2O. Find the percentage composition of the organic compound.
   [Ans : C = 54.54%, H = 9.09%, O = 36.37%]

3. 0.2004 g of glucose gave on combustion 0.2940 g of CO_2 and 0.1202 g of H_2O. Find the percentage composition.
   [Ans : C = 40.01%, H = 6.66%, O = 53.33%]
4. 0.2056 g of an organic compound gave on combustion 0.114 g of H_2O and 0.880 g of CO_2. Find the percentage of hydrogen and carbon in the organic compound. [Ans : C = 93.76%, H = 6.128]
5. On complete combustion, 0.246 g of an organic compound gave 0.198 g of CO_2 and 0.1014 of H_2O. Find the percentage composition of the organic compound. [Ans : C = 21.95%, H = 4.58%]

Estimation of nitrogen

1. 1.15 g of an organic compound was analysed by Kjeldahl's method and the ammonia produced was collected in 30 mL of normal HCl solution. The excess of acid consumed 18.4 mL of normal sodium hydroxide solution for back titration. Calculate the percentage of nitrogen in the substance. [Ans : N = 14.12%]
2. 0.80 g of a substance was digested with sulphuric acid and then distilled with an excess of caustic soda. The ammonia gas evolved was passed through 100 ml of 1N H_2SO_4. The excess of the acid required 80 ml of 1N caustic soda solution for its complete neutralisation. Calculate the percentage of nitrogen in the organic compound.
   [Ans : N = 35%]
3. 0.36 g of a nitrogeneous organic compound was Kejldahilised and the ammonia liberated was exactly neutralised by 20 ml of 0.3 N H_2SO_4. Calculate the percentage of nitrogen in the compound.
4. 0.257 g of an organic substance was Kjeldahlised and ammonia evolved was absorbed in 50 mL of N/10 HCl which required 23.2 ml of N/10 NaOH for neutralization. Determine the percentage of nitrogen in the compound. [Ans : N = 14.6%]
5. During nitrogen estimation present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen neutralised 10 ml of 1 M H_2SO_4. Find the percentage of nitrogen in the compound. [Ans : N = 56%]

Estimation of sulphur

1. 0.4037 g of an organic substance containing sulphur was heated with conc. nitric acid in a carius tube. On precipitation with $BaCl_2$, 0.1963 g of $BaSO_4$ was produced. Determine the percentage of sulphur in the compound. [Ans : S = 7.66%]

2. 0.316 g of an organic compound gives 0.466 g of barium sulphate by carius method. Calculate the percentage of sulphur?
   [Ans : S = 20.25%]
3. 0.530 g of an organic compound gave 0.90 g of $BaSO_4$ in carius determination of sulphur. Calculate the percentage of sulphur.
   [Ans : S = 23.32%]

Estimation of halogens

1. 0.24 g of an organic compound gave 0.287 g of AgCl in the carius method. Calculate the percentage of chlorine in the compound.
   [Ans : Cl = 25%]
2. In carious method of estimation of halogen 0.15 g of an organic compound gave 0.12 g of AgBr. Find the percentage of bromine in the compound. [Ans : Br = 34.04%]
3. 0.301 g of an organic compound gave 0.282 g of silver bromide by carius method. Find the percentage of bromine. [Ans : Br = 39.83%]
4. 0.196 g of an organic compound gave 0.22 g of CO_2 and 0.0675 g of H_2O. In carius determination, 0.3925 g of the substance gave 0.717 g of dry AgCl. Find the percentage composition of the substance.
   [Ans : C = 30.6%, 4 = 3.8%, Cl = 45.2%, O = 20.4%]
5. 0.25 g of an organic compound was found to produce 0.35 g of AgCl after heating with fuming HNO_3 and $AgNO_3$ in a sealed carius method. Determine the percentage of chlorine in the compound.
   [Ans : Cl = 34.75%]

SUMMARY

This chapter explains various methods of detection and estimation.

The principles behind various methods of detection and estimation are explained.

REFERENCES

1. I.L. Finar organic chemistry Vol.1, ELBS edition.
2. Vogel's Organic quantitative analysis ElBS.

www.tntextbooks.in

18. HYDROCARBONS

OBJECTIVES

The main objectives of this chapter is to give

- * *knowledge on sources, classification and nomenclature of hydrocarbons.*
- * *general methods of preparation of alkanes, alkenes and alkynes and their chemical properties.*

18.1 Classification of Hydrocarbons

Hydrocarbons are made of only carbon and hydrogen. They are obtained mainly from petroleum, natural gas and coal. They are divided into two main categories :

- * aliphatic hydrocarbons
- * aromatic hydrocarbons

The aliphatic hydrocarbons are further classified into saturated (alkanes), unsaturated (alkenes and alkynes) and alicyclic (cycloalkanes) hydrocarbons.

Aliphatic Saturated Hydrocarbons

These are otherwise called alkanes. Alkanes are often referred to as paraffins. Alkanes show little chemical affinity towards other compounds and are chemically inert to most reagents.

18.2 IUPAC nomenclature

With the exception of the first four compounds (methane, ethane, propane and butane) whose names have historical roots, other alkanes are named from Greek number according to the number of carbon atoms present.

Table 18.1

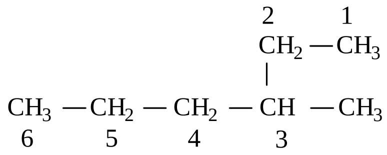
Number of Carbon atoms	Name	Molecular formula C_nH_{2n+2}
1	Methane	CH_4
2	Ethane	C_2H_6
3	Propane	C_3H_8
4	Butane	C_4H_{10}
5	Pentane	C_5H_{12}
6	Hexane	C_6H_{14}

www.tntextbooks.in

The suffix `ane' is added to the end of the each name to indicate that the molecule identified is an alkane. Thus, pentane is a five-carbon alkane and hexane is a six carbon alkane and so on. According to IUPAC rules, branched chain alkanes can be named by the following four steps:

Step 1 Finding out the parent hydrocarbon

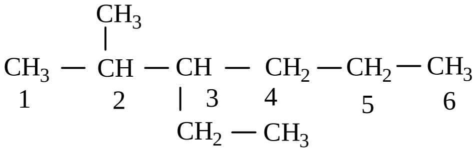
a. Find the longest continuous carbon chain present in the molecule and use the name of that chain as the parent name.



$$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{2}{C}H_2-\overset{1}{C}H_3}{\overset{|}{CH}}}-CH_3$$

Named as a substituted hexane.

b. If two different chains of equal length are present, select the chain with the larger number of branch points as the parent.



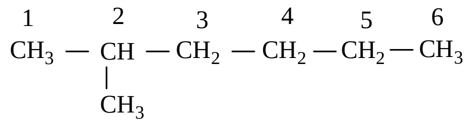
$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{CH_2-CH_3}{\underset{|\ 3}{CH}}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_3}$$

3-ethyl-2-methyl hexane
(correct name)
4- is opropylhexane
(wrong name)

The above compound is named as hexane with two substituents and not as hexane with one substituent.

Step 2 Numbering the carbon atoms in the main chain

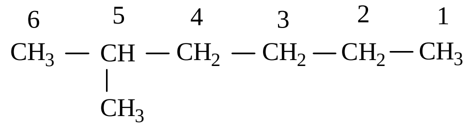
a. Beginning either from the left or from the right nearer the first branch point, give the number to each carbon atom in the longest chain, you have identified.



$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_3}$$

2-methylhexane (correct)

(Not as)



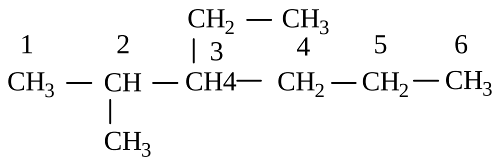
$$\overset{6}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{5}{CH}}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

5-methylhexane (wrong)

b. If there are branchings at equal distance from both ends of the parent chain, give numbering from the end which is nearer to the second branch point.

Step 3 Identifying and numbering the substituents

a. Using the correct numbering system, assign a number to each substituent according to its point of attachment to the main chain e.g.

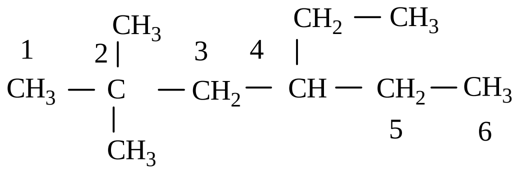


$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{\overset{CH_2-CH_3}{|\,3}}{CH}4-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH_3}$$

Substituents : On C_2, there is a methyl group, and write it as 2-methyl.

On C_3, there is a ethyl group, and write it as 3-ethyl.

b. If there are two substituents on the same carbon, give them the same number. There must always be as many numbers in the name as there are substituents :



$$\overset{1}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{2\,|}}{C}}-\overset{3}{CH_2}-\overset{\overset{CH_2-CH_3}{4\;|}}{CH}-\underset{5}{CH_2}-\underset{6}{CH_3}$$

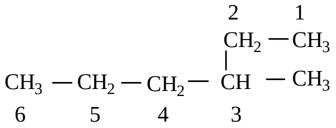
www.tntextbooks.in

Substituents : On C_2 there are two methyl groups, they are written as 2,2 dimethyl, on C_4 there is an ethyl group, it is written as 4-ethyl.

Step 4 Final naming

Write out the name as a single word, using hyphens to separate the different prefixes and using commas to separate numbers. If two or more different substituents are present, write them in alphabetical order. If two or more identical substituents are present use one of the prefixes di-, tri-, tetra- and so on. Don't use those prefixes for alphabetising purposes. The following are a few examples adopting the above IUPAC nomenclature.

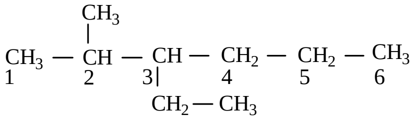
1)



$$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{CH_2}-\underset{3}{\overset{\overset{2}{CH_2}-\overset{1}{CH_3}}{\overset{|}{CH}}}-CH_3$$

3-methylhexane and not
as 2-ethylpentane

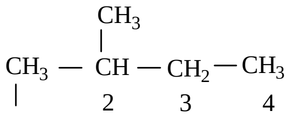
2)



$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{\underset{CH_2-CH_3}{3|}}{CH}-\underset{4}{CH_2}-\underset{5}{CH_2}-\underset{6}{CH_3}$$

3-ethyl-2-methylhexane
(correct)
4-ethyl-5-methylhexane
(or) 4-isopropylhexane
(wrong)

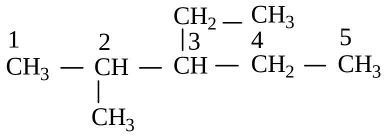
3)



$$CH_3-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{3}{CH_2}-\underset{4}{CH_3}$$

2-methylbutane

4)

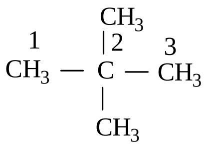


$$\overset{1}{CH_3}-\overset{2}{\underset{\underset{CH_3}{|}}{CH}}-\overset{\overset{CH_2-\overset{4}{CH_3}}{|3}}{CH}-CH_2-\overset{5}{CH_3}$$

3-ethyl-2- methylbutane

www.tntextbooks.in

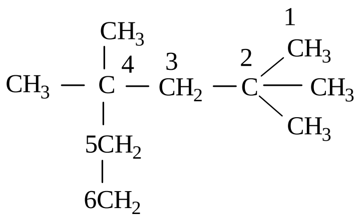
5)



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

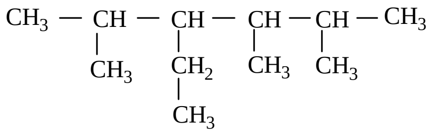
2,2-dimethylpropane

6)



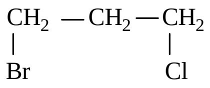
2,2,4,4,-tetramethylhexane

7)



4-ethyl -2, 3-5-
trimethlyhexane

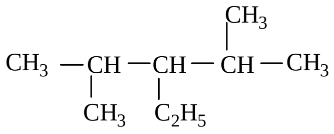
8)



$$\underset{Br}{CH_2}-CH_2-\underset{Cl}{CH_2}$$

1-bromo-3-chloropropane

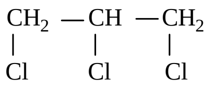
9)



$$CH_3-\underset{CH_3}{CH}-\underset{C_2H_5}{CH}-\overset{CH_3}{CH}-CH_3$$

3-ethyl1-2,4-dimethylpentane

10)



$$\underset{Cl}{CH_2}-\underset{Cl}{CH}-\underset{Cl}{CH_2}$$

1,2,3-trichloropropane

18.3 Sources of alkanes (petroleum)

The major sources of alkanes are natural gas and petroleum deposits, which are derived from the decomposition of marine organic matter. Natural gas consists chiefly of methane but ethane, propane, butane and isobutane are also present. Petroleum is a highly complex mixture of hydrocarbons that must be refined into different fractions to get various lower member hydrocarbons.

Cracking

When higher alkanes are passed through a chamber heated to 400-600°C in the presence of a catalyst (metallic oxides), the products are alkanes with less number of the carbon atoms and this is known as cracking.

18.4 General methods of preparation of alkanes

(i) By catalytic reduction of alkenes

Many alkenes (olefins) may be reduced by passing their vapours with hydrogen over finely divided nickel supported on Kieselguhr at 200-300°C. This reaction is referred to as the Sabatier-Senderens reduction.

$$CH_2 = CH_2 \xrightarrow[H_2]{Ni/300^\circ C} CH_3 - CH_3$$

$$CH_3CH = CH_2 \xrightarrow[H_2]{Ni/300^\circ C} CH_3CH_2CH_3$$

Nickel adsorbs, activates and dissociates molecular hydrogen for addition to olefins.

Finely divided nickel may be replaced by Raney nickel introduced by Raney (1927). It is more active than finely divided nickel. It is active even at room temperature. It is prepared by removing aluminium from Al-Ni alloy using sodiumhydroxide. Olefins can also be hydrogenated at room temperature over platinum or palladium.

Unsaturated edible oils are hydrogenated to Vanaspathi ghee with nickel catalyst at 300°C.

www.tntextbooks.in

(ii) Wurtz reaction

An ethereal solution of an alkyl halide is treated with sodium to obtain an alkane.

$CH_3CH_2\,Br + 2Na + Br - CH_2.CH_3 \rightarrow CH_3(CH_2)_2\,CH_3 + 2NaBr$

The reaction can be applied to mixed alkyl halides. The products are mixed alkanes.

$$CH_3CH_2Br + 2Na + BrCH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3 + CH_3CH_2CH_2CH_2CH_2CH_3 + CH_3CH_2CH_2CH_2CH_3$$

(iii) From Grignard reagents

Alkyl magnesium halides (RMgX, X = halogen) are known as Grignard reagents. Alkyl halides (chloride, bromide or iodide) react with magnesium in dry ether to give Grignard reagents. Grignard reagents react with water or dilute acids to give alkanes.

$$CH_3CH_2Br + Mg \xrightarrow{\text{Ether}} CH_3CH_2MgBr$$

$$CH_3CH_2MgBr + H_2O \longrightarrow CH_3CH_3 + MgBr(OH)$$

(iv) By decarboxylation of carboxylic acids

When sodium salts of carboxylic acids are heated with soda lime, alkanes are obtained.

$$CH_3CH_2COONa + NaOH \xrightarrow{\text{CaO / 350°C}} CH_3CH_3 + Na_2CO_3$$

Sodalime is a 3:1 mixture of NaOH and CaO. The role of CaO is to fuse sodium hydroxide.

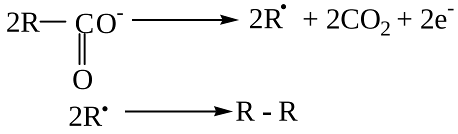
(v) Kolbe's electrolytic method

When a concentrated solution of sodium or potassium salt of carboxylic acid is electrolysed, a higher homologue of the alkane series is obtained. During electrolysis, the anions ($RCOO^-$) migrate towards the anode where they get decomposed to alkanes and carbon dioxide.

$$2RCOOK \xrightarrow{\text{Electrolysis}} 2RCOO^- + 2K^+$$

www.tntextbooks.in

At Anode



$$2R-\underset{\substack{\| \\ O}}{C}O^- \longrightarrow 2R^\bullet + 2CO_2 + 2e^-$$

$$2R^\bullet \longrightarrow R-R$$

Example

$$2CH_3COONa \longrightarrow 2CH_3COO^- + 2Na^+$$

At Anode

$$CH_3COO^- + CH_3COO^- \longrightarrow \underset{\text{ethane}}{CH_3-CH_3} + 2CO_2 \uparrow$$

(vi) From alcohols

Alcohols on heating with concentrated hydroiodic acid and red phosphorous at 150°C under pressure in a sealed tube get reduced to alkanes.

$$ROH + 2HI \xrightarrow{P/\Delta} RH + H_2O + I_2$$

18.5 Physical Properties

The dipole moment of all alkanes, whether straight or branched-chain is zero. Hence the alkanes have very weak force of attraction (Vanderwaals forces) between them. The Vanderwaals force increases with increase in the area of contact. Hence in the n-alkanes, owing to their large surface area due to their linear structure, the Vanderwaals force is large. In the branched alkanes the molecules tend to become spherical hence they have less surface area and contact, and less Vanderwaals force. As a consequence these, C_1-C_4 hydrocarbons are gases, C_5 - C_{17} liquids, and from C_{18} onwards are solids. The boiling points rise fairly regularly as the number of carbon atoms in the compound increases. Other physical properties such as melting point, density, viscosity etc., also changes, as the chain length of the compound increases.

Account for the following

(i) The boiling point of butane (0°C) is more than 2-methyl propane(-120.0°C).

www.tntextbooks.in

(ii) The melting point of n-pentane (-129.7°C) is less than neopentane (-17°C).

Solution

(i) Due to more Vanderwaal's force of butane.

(ii) The melting point of alkanes depends on the packing of the molecules in the crystal lattice. Packing in turn depends on molecular size. As neopentane is spherical in shape it will be better packed in the crystal lattice than n-butane. Hence the melting point of n-butane is less than neopentane.

All of them are colourless. Methane is soluble in water, but others are insoluble. Solubility of methane is due to its small molecular size. Due to its small size it can easily diffuse and dissolve in water. An useful rule in organic chemistry with respect to solubility is that `like dissolves like', e.g., if a compound contains a hydroxyl group, then the best solvents usually contain the hydroxyl groups.

18.5.1 Chemical Properties

(i) Halogenation

Chlorination and bromination of alkanes may be brought about by light, heat or catalysts. In the presence of ultraviolet light ($\lambda < 400$ nm λ = wavelength of light) or at high temperature all the four hydrogen atoms of CH_4 may be substituted. The reaction is of free radical type.

$$CH_4 + Cl_2 \xrightarrow{h\upsilon} CH_3Cl + HCl$$

Methyl chloride

$$CH_3Cl + Cl_2 \xrightarrow{h\upsilon} CH_2Cl_2 + HCl$$

Methylene chloride

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\upsilon} CHCl_3 + HCl$$

Chloroform

$$CHCl_3 + Cl_2 \xrightarrow{h\upsilon} CCl_4 + HCl$$

Carbon tetrachloride

Iodides are prepared by treating the chloro- or bromoderivative with sodium iodide in methanol or acetone

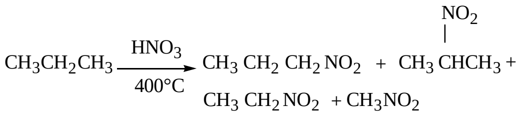
$$RCl + NaI \xrightarrow[CH_3OH]{} RI + 2NaCl$$

It is easy to separate the product from NaCl as the later is insoluble in methanol or acetone. This reaction is known as the **Finkelstein** or **Conant-Finkelstein** reaction.

Direct fluorination is usually explosive in nature. The great reactivity of fluorine is due to its low dissociation energy (150.6 kJ mol^{-1}). Also, one of the termination step is $R^{\bullet} + F^{\bullet} \rightarrow RF$. This reaction is very strongly exothermic (447.7 kJ). The energy liberated is larger than that required to break a C-C single bond (347.3 kJ), thereby resulting in the fragmentation of the organic molecule.

(ii) Nitration

Nitration of alkanes is carried out between 150 and 475°C, and the reaction yields a complex mixture of products. The reaction may be of free radical type.



$$CH_3CH_2CH_3 \xrightarrow[400°C]{HNO_3} CH_3\,CH_2\,CH_2\,NO_2 + CH_3\overset{\overset{NO_2}{|}}{C}HCH_3 + CH_3\,CH_2\,NO_2 + CH_3NO_2$$

(iii) Oxidation

Alkanes readily burn in excess air to form CO_2 and H_2O.

$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$$

At controlled oxygen supply methane forms carbon black used in the manufacturing of ink and black pigments. It is also used as fillers.

Oxidising agents such as $KMnO_4$ readily oxidise isobutane into tertiary butyl alcohol.

$$(CH_3)_3CH + [O] \xrightarrow{KMnO_4} (CH_3)_3COH$$

Molybdenum trioxide oxidises methane to formaldehyde

$$CH_4 + O_2 \xrightarrow{MoO_3} HCHO + H_2O$$

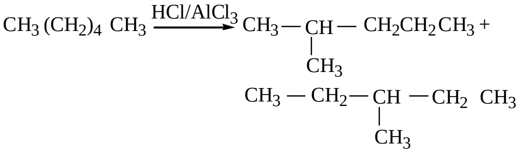
Ag_2O oxidises ethane to acetic acid

www.tntextbooks.in

$$2CH_3CH_3 + 3O_2 \xrightarrow{Ag_2O} 2CH_3COOH + H_2O$$

(iv) Isomerization

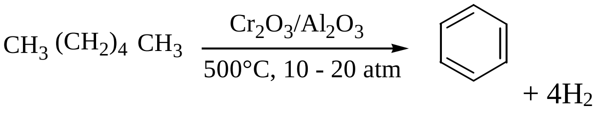
n-Alkanes can be isomerized into branched chain alkanes when heated with anhydrous aluminium chloride and hydrogen chloride at 300°C. The presence of an alkene impurity is shown to be important to initiate isomerization.



$$CH_3(CH_2)_4CH_3 \xrightarrow{HCl/AlCl_3} CH_3-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_2CH_2CH_3 + CH_3-CH_2-\underset{\underset{\textstyle CH_3}{|}}{CH}-CH_2CH_3$$

(v) Aromatization

When alkanes with six or more carbon atoms are passed over hot alumina supported chromium, vanadium or molybdenum oxide, dehydrogenative cyclization to yield aromatic compounds occurs.



Cr_2O_3 is the catalyst, and Al_2O_3 merely disposes Cr_2O_3 on it.

18.6 Alkenes

Alkenes are hydrocarbons that contain carbon-carbon double bond as functional group. They are otherwise known as olefins. Alkenes occur abundantly in nature. Following table contains details of a few simple alkenes.

Table 18.2

Molecular formula	Structural formula	Common name	IUPAC name
C_2H_4	$CH_2 = CH_2$	Ethylene	Ethene
C_3H_6	$CH_3 - CH = CH_2$	Propylene	Propene
C_4H_8	$CH_3-CH_2-CH = CH_2$	Butylene	1 - Butene

IUPAC Nomenclature : Alkenes are named systematically by following a series of rules similar to those followed for alkanes, with the suffix -ene instead of -ane. The following three basic steps are used.

Step 1 Name the parent hydrocarbon

Find the longest chain containing the double bond and name the compound accordingly using the suffix -ene.

Step 2 Number the carbon atoms in the chain beginning from the end which is nearer the double bond, e.g:

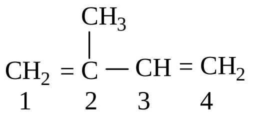
$$\overset{6}{CH_3}-\overset{5}{CH_2}-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_3}$$

Hex-2-ene (or) 2-hexene (correct)
4-hexene (wrong)

If the double bond is equidistant from the two ends, give the number from the end which gives the lowest number to the substituent.

Step 3 If more than one double bond is present, indicate the position of each double bond and use the suffices as -diene, -triene, -tetrene etc.

Example



$$\underset{1}{CH_2}=\underset{2}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{3}{CH}=\underset{4}{CH_2}$$

2-methyl-1,3-butadiene

18.7 General methods of Preparation of alkenes

i. By dehydration of alcohols

Alcohols can be dehydrated to olefins by heating with sulphuric acid.

$$CH_3-CH_2-OH \xrightarrow[160\text{-}170°C]{H_2SO_4} CH_2=CH_2$$

The mechanism is as follows

$$CH_3-CH_2-OH+H^+ \longrightarrow CH_3CH_2-\overset{+}{O}H_2$$

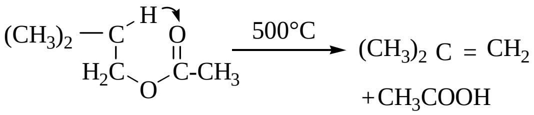
$$\xrightarrow{-H_2O} CH_3-CH_2 \xrightarrow{-H^+} CH_2=CH_2$$

www.tntextbooks.in

Sulphuric acid is a catalyst. For this reaction H_3PO_4, anhydrous zinc chloride and alumina can also be used as catalysts.

ii. By pyrolysis of esters

Esters with more than one carbon in the alkyl portion of the esters can be pyrolysed to get olefins.



iii. Dehydrohalogenation of alkyl halides

When an alkyl halide is treated with alcoholic potassium hydroxide, hydrogen halide is removed resulting in the formation of an alkene. For example

$$CH_3-CH_2Br \xrightarrow[\text{Dehydrohalogenation}]{\text{Alcoholic KOH}} CH_2=CH_2 + H_2O + KBr$$

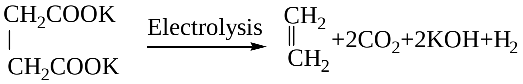
iv. Hydrogenation of alkynes

Alkynes on controlled reduction with palladium and hydrogen give alkenes. For example

$$\underset{\text{Acetylene}}{HC\equiv CH}+2[H] \xrightarrow[\text{Controlled Reduction}]{\text{Pd}} \underset{\text{Ethylene}}{CH_2=CH_2}$$

v. By electrolysis of salts of dicarboxylic acids

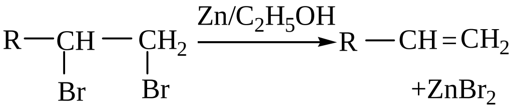
Alkenes are formed by the electrolysis of the aqueous solutions of potassium salts of dibasic acids of the succinic acid series.



$$\begin{array}{l}CH_2COOK\\|\\CH_2COOK\end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{l}CH_2\\\|\\CH_2\end{array} + 2CO_2 + 2KOH + H_2$$

vi. Dehalogenation of vicinal halides

Treatment of vicinal dihalides with zinc dust and ethyl alcohol gives the alkenes.



$$R-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2} \xrightarrow{Zn/C_2H_5OH} R-CH=CH_2 + ZnBr_2$$

www.tntextbooks.in

18.8 Physical Properties

The olefins with two to four carbon atoms are gases; five to seventeen liquids, eighteen on wards solids at room temperature and they burn in air with luminous smoky flame.

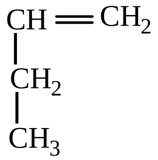
The exhibit isomerism

i. Position isomerism : It arises due to position of the double bond in a molecule. Ethene and propene do not show position isomerism, but butene shows.

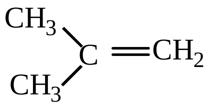
$CH_3CH_2CH=CH_2$	But - 1 - ene
$CH_3 - CH = CH - CH_3$	But - 2 - ene

ii. Chain isomerism

It is due to branching of the linear chain



But-1-ene

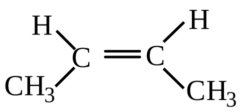


2-Methyl propene-1

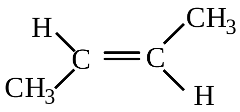
iii. Geometrical Isomerism

When two isomers differ in their spatial arrangement of atoms or groups, they are said to be stereoisomers. This type of isomerism is called stereoisomerism. Types of stereoisomerism : 1. Optical isomerism, 2. Geometrical isomerism

Geometrical isomers are named as cis and trans compounds depending on whether the identical groups are on the same or opposite sides of the bonds.



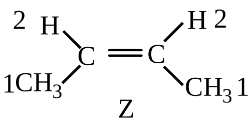
Cis-isomer

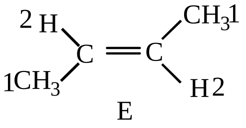


Trans-isomer

www.tntextbooks.in

The necessary and sufficient condition for geometrical isomerism is that the two groups or atoms attached to the same carbon must be different. When the two groups or atoms of highest priority are on the same side of the double bond, the isomer is designated as Z (Zusammen in German means together), and when they are on the opposite sides, the isomer is designated as E (Entegen in German meaning opposite). The priority is decided by the atomic number of atoms to which the olefinic carbons are bonded. The sequence rules given by Cahn - Ingold and Prelog are applied.





The atoms with the high atomic number is given the number 1 and other 2.

18.9 Chemical Properties

i. Hydrogenation of alkenes

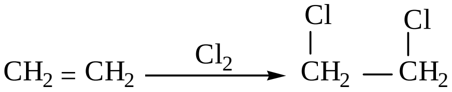
Alkenes can be readily hydrogenated under pressure in the presence of a catalyst.

$$CH_2{=}CH_2 + H_2 \xrightarrow[\text{Room Temp}]{\text{Pt or Pd}} CH_3-CH_3$$

Nickel supported on alumina is effective between 200 and 300°C (Sabatier -senderens reduction). Raney nickel is effective at room temperature and atmospheric pressure.

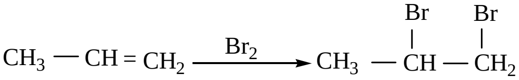
ii. Addition of halogens

Bromine and chlorine add readily to alkenes to yield dihaloalkanes.



$$CH_2 = CH_2 \xrightarrow{Cl_2} \underset{\displaystyle CH_2}{\overset{\displaystyle Cl}{|}} - \underset{\displaystyle CH_2}{\overset{\displaystyle Cl}{|}}$$

1,2-dichloroethane



$$CH_3 - CH = CH_2 \xrightarrow{Br_2} CH_3 - \underset{\displaystyle CH}{\overset{\displaystyle Br}{|}} - \underset{\displaystyle CH_2}{\overset{\displaystyle Br}{|}}$$

1,2-dibromopropane

In this reaction bromine will be decolourised and this test is used to detect unsaturation.

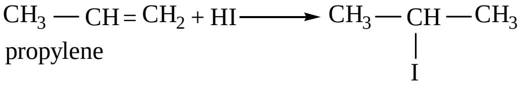
www.tntextbooks.in

iii. Hydrohalogenation

An alkene is converted into the corresponding alkyl halide by HX. The reaction is frequently carried out by passing dry gaseous HX directly into the alkene. For example,

$$\underset{\text{ethylene}}{CH_2 = CH_2} \xrightarrow{\text{dry HCl}} \underset{\text{ethyl chloride}}{CH_3CH_2Cl}$$

Propylene can yield two possible products namely n-propyl iodide or isopropyl iodide with HI, depending upon the orientation of addition. Actually it is found that isopropyl iodide is the only product obtained.

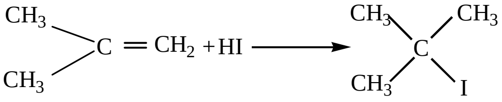


$$CH_3-CH=CH_2 + HI \longrightarrow CH_3-\underset{\displaystyle I}{\underset{|}{CH}}-CH_3$$

propylene

isopropyl iodide

In the same way, isobutylene can yield either of the two products, isobutyl iodide or tertiary butyl iodide. Here the orientation or addition is such that the tertiary butyl iodide is the only product.



isobutylene

tert-butyl iodide

In the above two reactions, though two products are possible, only one of the products is obtained. The Russian chemist Vladimir Markovnikov, explained the reason which is known as Markovnikov's rule, which states that, the negative part of addendum attaches itself to the carbon atom carrying less number of hydrogen atoms.

Carbocations are involved as intermediates in these reactions. Highly substituted carbocation is formed as an intermediate in preference to the less substituted one due to stability.

Order of stability

3° carbocation > 2° carbocation > 1° carbocation]

Hence in the above two reactions the formation of only one of the products can be accounted on the basis of the stability of the carbocation

www.tntextbooks.in

intermediate. When HBr adds to alkene under normal conditions, we know that an intermediate carbocation is formed and Markovnikov's orientation will be observed (electrophilic addition). But in the presence of peroxides the electrophilic addition does not take place and the addition takes place through free radical mechanism.

iv. Hydration

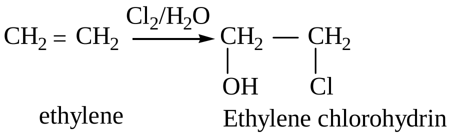
Water can be added to simple alkenes to yield alcohols. This hydration reaction takes place on treatment of the alkene with water in presence of a strong acid-catalyst.

$$\underset{\text{ethylene}}{CH_2 = CH_2} + H_2O \xrightarrow{H^+} \underset{\text{ethyl alcohol}}{CH_3 - CH_2OH}$$

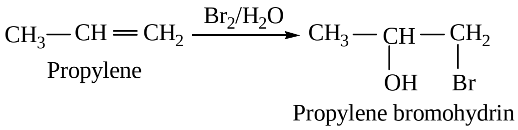
v. Halohydrin formation

Alkenes can add HOCl or HOBr under suitable conditions to yield 1,2 haloalcohols or halohydrins. Halohydrin formation does not take place by direct reaction of an alkene with the reagents (HOCl or HOBr). But the addition is done indirectly by the reaction of the alkene with either Br_2 or Cl_2 in presence of water.

Example



$$\underset{\text{ethylene}}{CH_2 = CH_2} \xrightarrow{Cl_2/H_2O} \underset{\text{Ethylene chlorohydrin}}{\underset{OH}{\underset{|}{CH_2}} - \underset{Cl}{\underset{|}{CH_2}}}$$

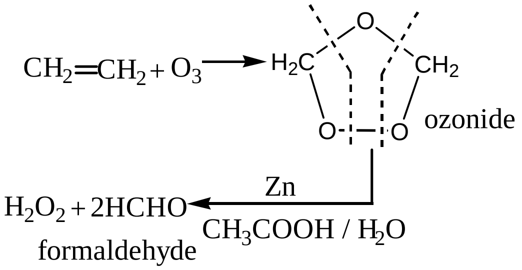


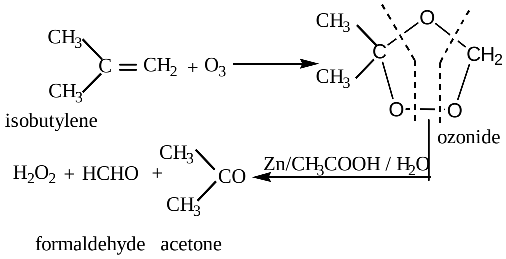
$$\underset{\text{Propylene}}{CH_3 - CH = CH_2} \xrightarrow{Br_2/H_2O} \underset{\text{Propylene bromohydrin}}{CH_3 - \underset{OH}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH_2}}}$$

vi. Ozonolysis

Ozone is the most useful double bond cleavage reagent. When added to an alkene first an ozonide intermediate is formed. When the ozonide is further treated with a reducing agent such as zinc metal in acetic acid, it is converted into carbonyl compounds.

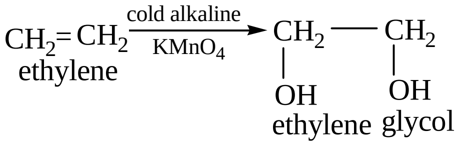
www.tntextbooks.in





vii. Hydroxylation

The addition of an -OH group to each of the two alkene carbons can be carried out with alkaline potassium permanganate. This reagent is known as Baeyer's reagent. Ethylene or any alkene decolourises potassium permanganate and this is a test for unsaturation.



$$\underset{\text{ethylene}}{CH_2=CH_2} \xrightarrow[KMnO_4]{\text{cold alkaline}} \underset{\text{ethylene glycol}}{\underset{OH}{CH_2}-\underset{OH}{CH_2}}$$

viii. Hydroboration

Alkenes readily react with diborane to form trialkyl boranes which on oxidation with alkaline hydrogen peroxide yield primary alcohols.

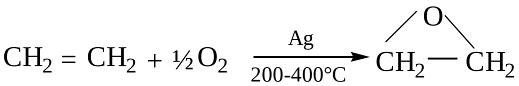
$$3CH_2=CH_2 + (BH_3)_2 \rightarrow 2(CH_3\text{-}CH_2)_3B$$

$$(CH_3\text{-}CH_2)_3B \xrightarrow{H_2O_2} 2CH_3CH_2OH$$

www.tntextbooks.in

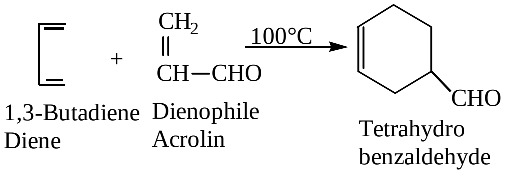
ix. Epoxidation

When ethylene is mixed with oxygen, under pressure passed over at 200 - 400°C, epoxide is obtained.



$$CH_2 = CH_2 + \tfrac{1}{2}O_2 \xrightarrow[200\text{-}400°C]{Ag} CH_2 - CH_2 \text{ (bridged by O)}$$

x. Diels - Alder reaction



Polymerisation : A polymer is simply a large molecule built up by many smaller units called "monomers". Conversion of a large number of monomers into a single polymer is known as polymerisation.

When ethylene is heated under pressure in presence of oxygen, a compound of high molar mass known as polyethylene or polythene is formed.

$$nCH_2{=}CH_2 \xrightarrow[\text{under pressure}]{O_2,\ \Delta} \underset{\text{polythene}}{(\text{-}CH_2\text{-}CH_2)_n}$$

18.10 Uses of Alkenes

(i) Ethylene is used for ripening of fruits.

(ii) Ethylene is used to prepare industrial solvents like ethylene dichloride, glycol, dioxan etc.,

(iii) Ethylene and propylene are important industrial organic chemicals. They are used in the synthesis of polymers like polythene, polypropylene, pvc, polystyrene, teflon, orlon, acrilan, polyvinyl acetate, polyvinyl alcohol etc.,

(iv) Ethylene dichloride which is prepared from ethylene is used in the preparation of a synthetic rubber called thiokol.

www.tntextbooks.in

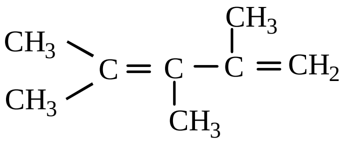
18.10.1 Test for ethylene

(i) Rapid decolourisation of bromine in carbontetrabromide without evolution of hydrogen bromide.

(ii) Decolourisation of cold dilute aqueous potassium permanganate solution.

18.11 Unsaturated compounds with two or more double bonds

If a hydrocarbon contains two double bonds it is called diolefin or alkadiene. Alkadienes have general formula C_nH_{2n-4}. In the chain containing the maximum number of double bonds is chosen as the parent hydrocarbon, and the chain is so numbered as to give the lowest possible numbers to the double bonds.



2,3,4 - Trimethyl penta - 1,3-diene

Preparation of alkadiene

i. Alkadienes with isolated double bonds

$$CH_2=CH\ CH_2Cl + Mg$$
$$\Big\downarrow \text{Ether}$$
$$CH_2=CH(CH_2)_2CH=CH_2 + MgCl_2$$

Hexa 1,5-diene

ii. Alkadienes with cumulative double bonds

By heating 1,2,3-tribromopropane with solid KOH and then treating the resulting 2,3- dibromopropene with zinc dust in methanol.

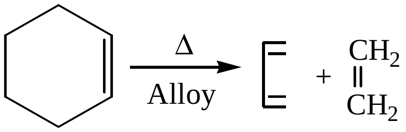
$$Br\ CH_2\ CH\ Br-CH_2Br \xrightarrow{KOH} Br\ CH_2\ CBr=CH_2$$

$$\xrightarrow{Zn/CH_3OH} CH_2=C=CH_2$$

Allene gas

iii. Preparation of alkadienes with conjugated double bonds.

Buta - 1,3 - diene can be obtained by passing cyclohexene over a heated nichrome wire (an alloy of Ni, Cf and Fe).



Butadiene is used in the manufacture of Buna rubber.

18.12 Alkynes

Alkynes are also called acetylenes. They are hydrocarbons that contain a carbon-carbon triple bond. The first and the most important member of this series is acetylene and hence these are called acetylenes.

IUPAC nomenclature of alkyenes : Alkynes follow the general rule of hydrocarbon nomenclature. The suffix -yne is substituted for `-ane' in the base hydrocarbon name to denote alkyne and the position of the triple bond is indicated by its number in the chain. Numbering begins from the chain end which is nearer the triple bond.

The following table contains details along a few of the simple alkynes.

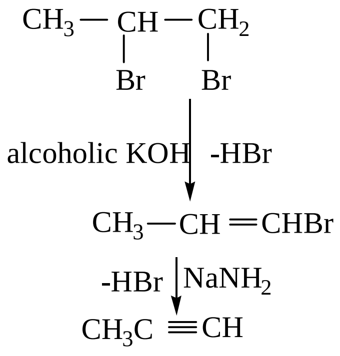
Table 18.3

Structural formula	Common name	IUPAC name
$CH \equiv CH$	acetylene	ethylene
$^3CH_3{}^2C \equiv {}^1CH$	methyl acetylene	1-propyne
$^4CH_3{}^3CH_2\ {}^2C{\equiv}{}^1CH$	ethyl acetylene	1-butyne
$CH_3 - C \equiv C - CH_3$	dimethyl acetylene	2-butyne

General methods of preparation

(i) Dehydrohalogenation of vicinal dihalides : Compounds that contain halogen atoms on adjacent carbon atoms are called vicinal dihalides. Alkynes are obtained by treatment of vicinal dihalides with alcoholic KOH followed by treatment with sodamide ($NaNH_2$). For example

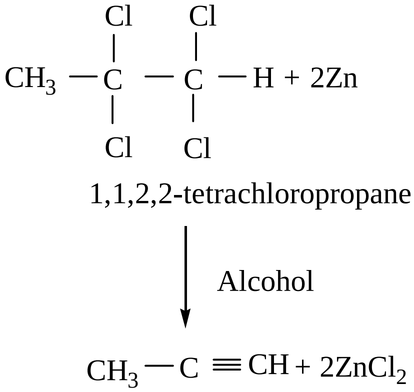
www.tntextbooks.in



$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} \xrightarrow[\text{-HBr}]{\text{alcoholic KOH}} CH_3-CH=CHBr \xrightarrow[\text{-HBr}]{NaNH_2} CH_3C\equiv CH$$

methyl acetylene

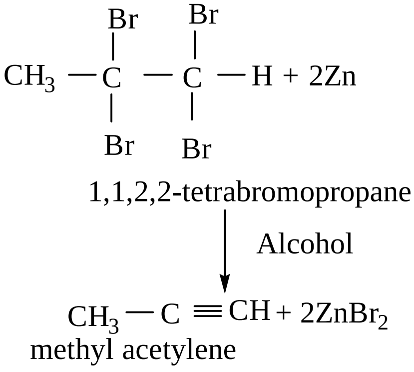
(ii) Dehalogenation of tetrahalides : When 1,1,2,2-tetrahalide is heated with zinc dust in alcohol, alkyne is formed. For example,



$$CH_3-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-H + 2Zn \xrightarrow{\text{Alcohol}} CH_3-C\equiv CH + 2ZnCl_2$$

1,1,2,2-tetrachloropropane

methyl acetylene



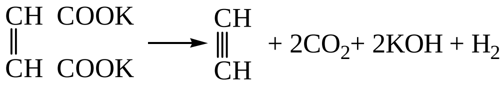
$$CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-H + 2Zn \xrightarrow{\text{Alcohol}} CH_3-C\equiv CH + 2ZnBr_2$$

1,1,2,2-tetrabromopropane

methyl acetylene

www.tntextbooks.in

Electrolysis of salts of unsaturated dicarboxylic acids.



$$\begin{matrix}\text{CH COOK}\\ \|\\ \text{CH COOK}\end{matrix} \longrightarrow \begin{matrix}\text{CH}\\ |||\\ \text{CH}\end{matrix} + 2CO_2 + 2KOH + H_2$$

18.13 Physical properties of alkynes

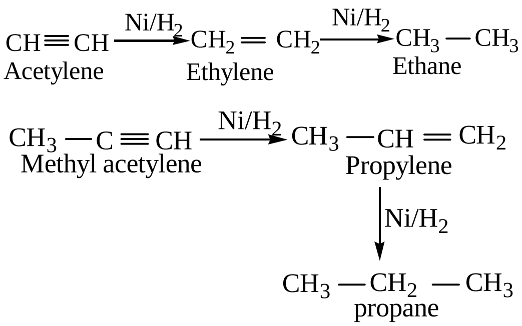
Alkynes have physical properties that are essentially the same as those of alkanes and alkenes. They are insoluble in water but quite soluble in organic solvents like benzene, carbon tetrachloride, ether etc. They are less dense than water. Their boiling points and melting points show a regular increase with increasing carbon number and the usual effects of chain branching are also observed.

18.14 Reactions of alkynes

Alkynes contain carbon-carbon triple bond. One of them is strong carbon-carbon sigma (σ) bond and the other two are weak carbon-carbon pi (π) bonds. Alkynes undergo addition reactions with other compounds due to the cleavage of these weak pi (π) bonds.

(i) Addition of hydrogen : Alkynes are easily converted to alkanes by addition of hydrogen in the presence of metal catalyst like nickel, platinum or palladium.

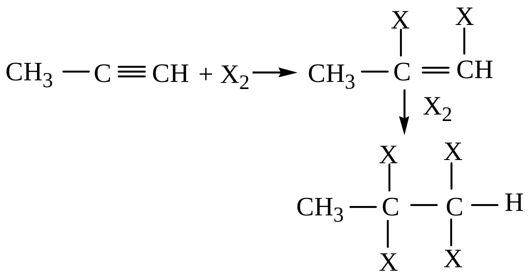
Example



$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow{Ni/H_2} \underset{\text{Ethylene}}{CH_2 = CH_2} \xrightarrow{Ni/H_2} \underset{\text{Ethane}}{CH_3-CH_3}$$

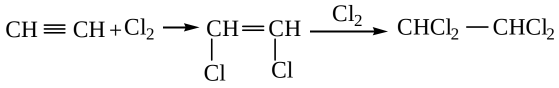
$$\underset{\text{Methyl acetylene}}{CH_3-C\equiv CH} \xrightarrow{Ni/H_2} \underset{\text{Propylene}}{CH_3-CH=CH_2} \xrightarrow{Ni/H_2} \underset{\text{propane}}{CH_3-CH_2-CH_3}$$

(ii) Addition of halogens : Two molecules of halogens add to alkynes in two steps forming dihalides and then tetrahalides



$$CH_3-C\equiv CH+X_2\rightarrow CH_3-\overset{X}{\overset{|}{C}}=\overset{X}{\overset{|}{C}}H\xrightarrow{X_2}CH_3-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H$$

Direct combination of C_2H_2 with chlorine may explode and this is prevented by using a metal chloride catalyst.



$$CH\equiv CH+Cl_2\rightarrow \underset{Cl}{CH}=\underset{Cl}{CH}\xrightarrow{Cl_2}CHCl_2-CHCl_2$$

Acetylene 1,2-dichloroethylene 1,1,2,2-tetrachloroethane

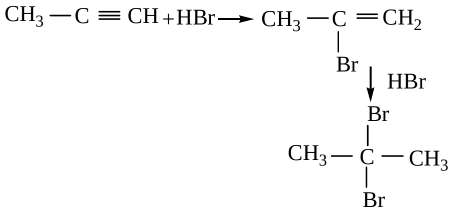
(iii) Addition of halogen acids : Halogen acids add to alkynes in the same way as in alkenes and give the expected addition product. Halogen acids add to symmetrical alkynes in two stages. After one molecule of the acid is added to a symmetrical alkyne, the product is an unsymmetrical derivative of alkene. The addition of a second molecule of the acid takes place in accordance with Markonikov's rule.

Example

$$CH\equiv CH+HBr\rightarrow H_2C=CHBr\xrightarrow{HBr}CH_3-CHBr_2$$

1,1-dibromoethan

The addition of halogen acid to unsymmetrical alkynes follows Markonikov's rule both in the first and second steps.



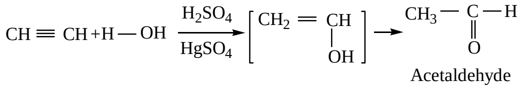
$$CH_3-C\equiv CH+HBr\rightarrow CH_3-\underset{Br}{C}=CH_2\xrightarrow{HBr}CH_3-\underset{Br}{\overset{Br}{C}}-CH_3$$

2,2-dibromopropane

Peroxides have the same effect on the addition of hydrogen bromide to alkynes as in alkenes.

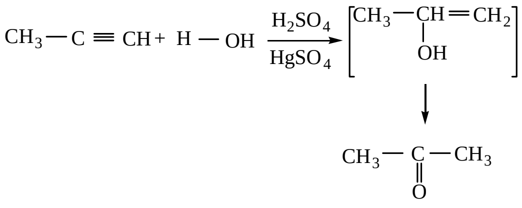
(iv) Addition of water : When alkynes are passed into dilute sulphuric acid in presence of mercuric sulphate as catalyst at 60°C one molecule of water is added to the alkyne resulting in the formation of either an aldehyde or a ketone.

Example



$$CH\equiv CH + H-OH \xrightarrow[HgSO_4]{H_2SO_4} \left[CH_2=\underset{\displaystyle OH}{\underset{|}{CH}}\right] \rightarrow CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-H$$

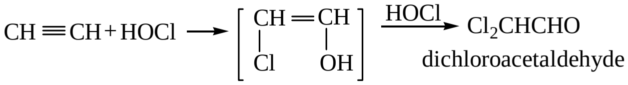
Acetaldehyde



$$CH_3-C\equiv CH + H-OH \xrightarrow[HgSO_4]{H_2SO_4} \left[CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}=CH_2\right] \downarrow CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3$$

Acetone

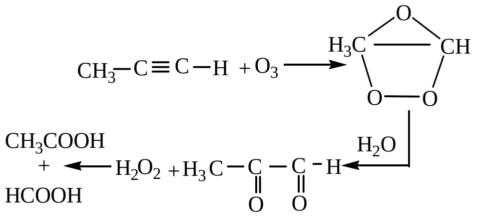
(v) Addition of HOCl : When acetylene is passed into hypochlorous acid solution, dichloroacetaldehyde is formed.



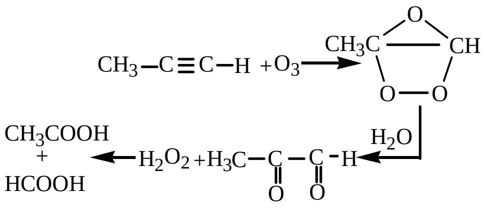
$$CH\equiv CH + HOCl \longrightarrow \left[\underset{\displaystyle Cl}{\underset{|}{CH}}=\underset{\displaystyle OH}{\underset{|}{CH}}\right] \xrightarrow{HOCl} Cl_2CHCHO$$

dichloroacetaldehyde

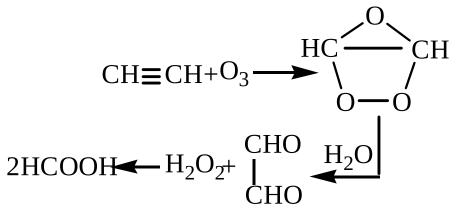
(vi) Addition of ozone : Alkynes react with ozone to give ozonides. These ozonides get decomposed with water to yield diketones. Diketones are oxidised to acids by hydrogen peroxide produced in the reaction.



Acetylene is an exception as it gives both glyoxal and formic acid with ozone.



www.tntextbooks.in



(vii) Reactions of acidic hydrogen : The most striking difference between alkenes and alkynes is that terminal alkynes are weakly acidic. In alkyenes sp hybridization is taking place in carbon atoms and so they exhibit. 50% s character. Hence an alkyne attracts the electrons towards itself and therefore the terminal H can be removed as H^+. When acetylene is passed into ammoniacal silver nitrate solution silver acetylide (white) is precipitated respectively.

Example

$$CH\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\text{Sliver-acetylide}}{AgC\equiv CAg\downarrow} + 2NH_4NO_3 + 2H_2O$$

$$CH\equiv CH + Cu_2Cl_2 + 2NH_4OH \xrightarrow{Cu_2Cl_2} \underset{\text{Copper acetylide}}{CuC\equiv CCu\downarrow} + 2NH_4Cl + 2H_2O$$

Dry copper and silver acetylides are very sensitive to shock and may explode violently. However, they can be decomposed by nitric acid to regenerate alkynes. This type of reaction is possible with only terminal alkynes. Non-terminal alkynes will not give this reaction.

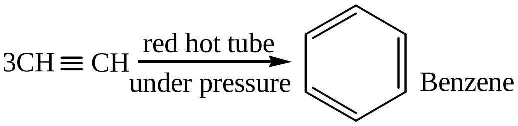
$$\underset{\text{(A terminal alkyne)}}{\underset{\text{(1-butyne)}}{CH_3-CH_2-C\equiv CH}} + AgNO_3 \xrightarrow{NH_4OH} CH_3-CH_2-C\equiv CAg$$

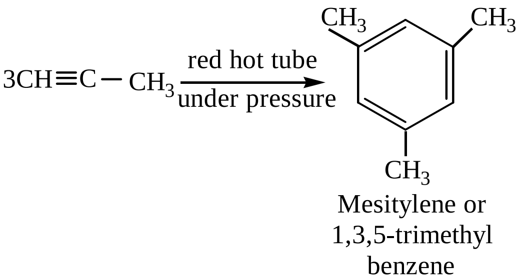
$$\underset{\text{(A non-terminal alkyne)}}{CH_3-C\equiv C-CH_3} + AgNO_3 \xrightarrow{NH_4OH} \text{No reaction}$$

Thus this reaction can be used to differentiate terminal alkynes and non-terminal alkynes.

www.tntextbooks.in

(viii) Polymerisation : When alkynes are passed through red hot iron tube under pressure they polymerise to aromatic compounds. For example acetylene polymerises to benzene and propylene polymerises to mesitylene.





18.14.1 Tests for acetylene

(i) Acetylene decolourises bromine water.

(ii) Acetylene decolourises alkaline potassium permanganate solution

(iii) With ammoniacal solution of cuprous chloride it gives a red precipitate of cuprous acetylide.

(iv) With ammoniacal solution of silver nitrate it gives a white precipitate of silver acetylide. The tests (iii) and (iv) will not be answered by ethylene and these two tests can be used to distinguish ethylene from acetylene.

18.14.2 Uses of alkynes

(1) Acetylene is used as a starting material for manufacture of industrially important compounds like acetaldehyde, acetone and benzene.

(2) Acetylene is used in oxyacetylene torch used for welding and cutting metals.

(3) Westron, a solvent which is tetrachloro derivative of acetylene is prepared from acetylene.

(4) Acetylene is used as a starting material for the manufacture of PVC, polyvinyl acetate and synthetic rubber.

Questions

A. Choose the correct answer

1) Alkanes can be represented by the formula

   a) C_nH_{2n+2} c) C_nH_{2n-2}

   b) C_nH_{2n} d) C_nH_{2n-3}

2) Alkenes are represented by the formula

   a) C_nH_{2n+2} c) C_nH_{2n-2}

   b) C_nH_{2n} d) C_nH_{2n-3}

3) Alkynes are represented by the formula

   a) C_nH_{2n+2} c) C_nH_{2n-2}

   b) C_nH_{2n} d) C_nH_{2n-3}

4) The type of substitution reaction that takes place when methane is treated with Cl_2 in presence of light

   a) ionic c) nucleophilic

   b) electrophilic d) radial

5) When n-hexane is passed over hot alumina supported chromium, vanadium or molybdenum oxide the compound formed is

   a) cyclopentaene c) toluene

   b) cyclohexane d) benzene

6) When the identical groups are on the same or opposite sides of the bonds in alkenes the isomerism is called as

   a) chain isomerism b) geometrical isomerism

   c) position isomerism d) optical isomerism

7) Diels-Alder reaction is the reaction between

   a) diene and dienophile

   b) electrophile and nucleophile

   c) oxidant and reductant

   d) none.

8) Unsaturated compounds with two double bonds are called as

   a) diene c) olefins

   b) alkadiene d) paraffins.

9) The hybridization of carbons in ethylene is

   a) sp^2 c) sp^3

   b) sp d) dsp^2

www.tntextbooks.in

10) Alcohols can be dehydrated to olefins using

a) H_2SO_4 c) Pd
b) $SOCl_2$ d) Zn/Hg

11) When alkyl halides are treated with alcoholic KOH, the products are

a) olefins c) alcohols
b) alkanes d) aldehydes

12) Witting reaction is used to prepare

a) an alkene c) an alkane
b) an alkyne d) none of the above.

13) Electrolysis of potassium succinate gives

a) ethylene c) acetylene
b) ethane d) none of the above.

B. Fill up the blanks

1) In alkanes, the carbon atoms are connected by _____ bonds.
2) Treatment of 1,2-dibromopropane with zinc and ethanol gives _____.
3) Cis But-2-ene is an _______ isomer.
4) Addition of HCl to an olefin follows ______ rule.
5) An alkene reacts with ozone to form
6) CaC_2 on hydrolysis gives
7) Ethylenedibromide on treatment with KOH gives
8) Electrolysis of sodium maleate gives

C. Explain briefly on the following

1) Mention any five chemical properties of alkanes.
2) Discuss the general methods of preparing alkanes.
3) What is hydroboration?
4) What is ozonolysis?
5) What is witting reaction?
6) What is polymerisation?
7) How is ethylene hydrated?
8) What is the action of ozone on acetylene.
9) What happens when acetylene is passed through red-hot tube?

SUMMARY

- Hydrocarbons are broadly classified into aliphatic and aromatic hydrocarbons.
- Petroleum is the main source of alkanes.
- The alkanes have very weak force of attraction between them.
- In alkanes the carbon atoms are connected by sigma bonds.
- Alkenes and alkynes under go addition reactions.

REFERENCES

1) Organic Chemistry, I.L. Finar, ELBS Edition.

2) Organic Chemistry Morrison and Boyd.

3) Organic Chemistry, Daniel S. Kemp, Frank Vellaccio, Worth Publishers INC, 1980.

19. AROMATIC HYDROCARBONS

OBJECTIVES

The main objectives of this chapter are to provide

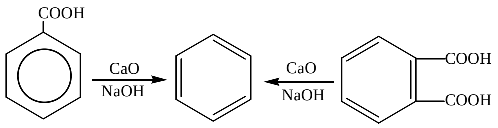
- *Details of nomenclature of aromatic hydrocarbons.*
- *Detail discussion on structure of benzene*
- *Explanatory note on aromaticity*
- *A discussion on orientation in aromatic electrophilic substitution*
- *General methods of preparation of benzene homologues*
- *Some examples for electrophilic substitution and some preliminary discussion of poly cyclic aromatic hydrocarbons.*

Natural sources like resins, balsams, aromatic oils etc., contain aliphatic compounds, and also a group of compounds with pleasant odour. These odorous compounds were arbitrarily classified as aromatic (Greek : aroma : pleasant smell). Most of the simple aromatic compounds were found to contain six carbon atoms. Further when aromatic compounds were subjected to various methods of treatment, they often produced benzene or a derivative of benzene. Hence these aromatic compounds are called benzenoid compounds.

Benzene, C_6H_6, was first isolated by Faraday (1825) from cylinders of compressed illuminating gas obtained from the pyrolysis of whale oil. In 1845, benzene was found in coal-tar by Hofmann, and this is still a source of benzene and its derivatives. Benzene was first synthesised by Berthelot (1870) by passing acetylene through a red-hot tube.

$$3C_2H_2 \longrightarrow C_6H_6 + \text{Other products.}$$

It may be prepared in the laboratory by decarboxylation of aromatic acids.



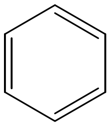
In the early days of organic chemistry the word aromatic was used to describe fragrant substances such as benzaldehyde, toluene etc. It was soon realised that substances grouped as aromatic behaved in a chemically different manner from other organic compounds. Today, we use the term aromatic to refer to benzene and its structural homologues. In this section,

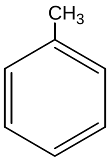
www.tntextbooks.in

aromatic compounds showing chemical properties quite different from that of aliphatic compounds are dealt with.

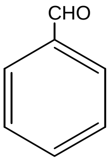
Many compounds isolated from natural sources are aromatic in part. In addition to benzene, toluene and benzaldehyde, complex compounds such as the female steroidal harmone estrone and the well known analgesic, morphine have aromatic rings. Many synthetic drugs used medicinally are also aromatic in part.

Benzene is the first member in the aromatic series of compounds. The whole series of compounds which contain one or more benzene rings in their molecules are called aromatic compounds. Certain heterocyclic compounds like pyridine which do not have benzene rings also come under this classification.

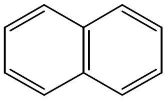

Benzene

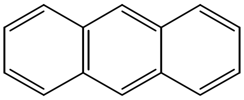


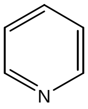
Toluene



Benzaldehyde


Naphthalene


Anthracene



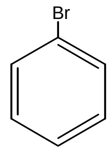
Pyridine

Commercial preparation of benzene from coal tar

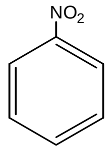
The two main sources of aromatic hydrocarbons are coal and petroleum. Coal is a complex substance made of primarily large arrays of highly unsaturated benzene like rings linked together. When coal is heated to 1000°C in the absence of air, thermal break down of coal molecules occur and a mixture of volatile products called "coaltar" distills off. The coaltar forms the source of many organic compounds. Further distillation of coaltar yields benzene, toluene, xylene, naphthalene and a host of other aromatic compounds.

19.1 Nomenclature of aromatic compounds

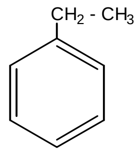
Aromatic compounds acquired a large number of common, nonsystematic names. Although the use of such names is discouraged, IUPAC rules allow for some of the more widely used ones to be retained. eg. methyl benzene is familiarly known as toluene, hydroxy benzene as phenol, aminobenzene as aniline and so on. Mono substituted benzene derivatives are systematically named in the same manner as other hydrocarbons with benzene as the parent name.



Bromobenzene

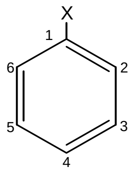


Nitrobenzene

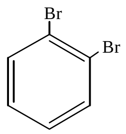


Ethyl benzene

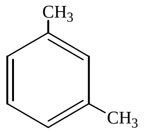
Disubstituted benzene derivatives are named using one of the prefixes ortho, meta or para. In a benzene ring there are six carbon atoms and they can be numbered as follows :



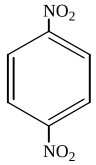
The 2 and 6 positions or the adjacent positions are known as ortho-positions. 3 and 5 or the alternate positions are known as meta-positions and the only one 4th position is known as para- position.



o-dibromobenzene or 1,2-dibromobenzene



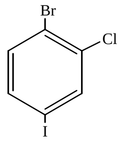
m-xylene or m-dimethylbenzene or 1,3-dimethylbenzene



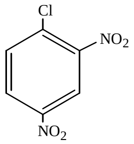
p-dinitro benzene (or) 1,4-dinitro benzene

Benzene with more than two substituents must be named by numbering the position of each substituent on the ring. The numbering should be done in such a way that the lowest possible numbers are given to the substituents and the substituents are listed alphabetically.

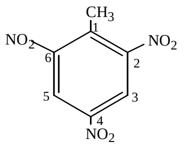
Example



1-bromo-2-chloro-4-iodo-benzene



1-chloro-2,4-dinitro benzene



2,4,6 -Trinitro Toluene

19.1.1 Aromaticity

Compounds which contain benzene rings or a condensed system of benzene rings have the following properties which are not shown by the analogous aliphatic and alicyclic compounds.

- They readily undergo substitution reactions.
- They are thermally stable.
- They resist addition and oxidation reactions.
- With respect to benzene the enthalpy of hydrogenation, the enthalpy change, when one mole of an unsaturated compound is hydrogenated is much smaller (-208.5kJ mol^{-1}) than the corresponding calculated value for hypothetical 1,3,5 - cyclohexatriene (-359.1 -kJ mol^{-1})

These distinguishing properties led to seek an explanation and define the term aromaticity.

Aromaticity in other related systems

The modern theory of aromaticity was introduced by Huckel in the year 1937. Delocalized electronic cloud and coplanar structure the compound are important for aromaticity. Any polynuclear compound, heterocyclic rings or cyclic ions may be aromatic if they are planar and have $4n + 2$ ($n = 0,1,2,3$ etc) delocalized π electrons in a closed shell. Thus to be aromatic, a molecule must have 2(n=0), 6(n=1), 10 (n=2)..... π electrons.

19.1.2 Orientation in aromatic electrophilic substitution

Orientation in aromatic electrophilic substitution reactions of benzene aims at locating the position of the incoming substituent with respect to the one that is already present. The substituent which is already present in the ring directs the incoming group either to ortho and para or to meta position, and changes the reaction rate higher or lower than benzene.

If a substituent directs the incoming group to ortho and para positions, it is called ortho, para - directing, and if it directs to meta position it is called meta-directing. The substituents that increase the rate of substitution compared to benzene are called activating and those decreasing the rate are called deactivating. The activating groups increase the rate by increasing the electron density of ring, but the deactivating groups decrease the rate by decreasing the electron density of the ring.

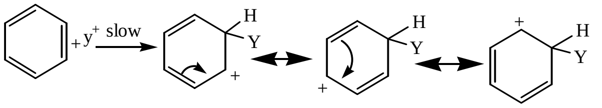
Ortho and Para Directing Groups

R, OH, OR, NH_2, NHR, $NHCOCH_3$, Cl, Br, I, F, SH etc.

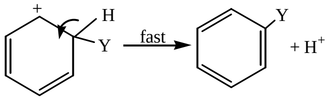
Meta-Directing Groups

NO_2, CHO, COOH, COOR, SO_3H, CN, NH_3^+ etc. The directive influence of these groups are found to be predominant but not exclusive. Halogens behave in a different way, they are ortho, para-directing but deactivating as they withdraw electronic cloud from the ring.

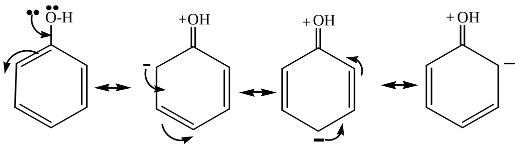
The orientation and activating or deactivating influence of the substituents can be explained based on the resonance and inductive effect of the substituents on the stability of the intermediate arenium ions formed in electrophilic substitution reactions as shown below.



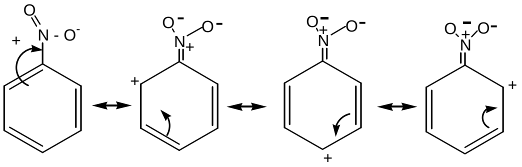
Arenium ion



With ortho and para directing groups, for example, OH, there is increased negative charge on the ortho and para positions as shown below. Hence electrophilic substitution predominantly occurs at these positions.



With meta directing groups positive charge is created on the ortho and para positions, but the meta positions are free of such charges, and hence these positions are more reactive than the ortho and para position.



19.2 General methods of preparation of benzene and its homologous series

(i) From aromatic acids : When sodium salt of aromatic acids are heated with sodalime, the corresponding aromatic hydrocarbon is formed.

Example

$$\underset{\text{Sodium benzoate}}{C_6H_5COONa} \xrightarrow[\Delta]{NaOH + CaO} \underset{\text{Benzene}}{C_6H_6} + Na_2CO_3$$

(ii) When phenol is dry distilled with zinc dust benzene is formed.

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[Zn]{\text{dry distillation}} \underset{\text{Benzene}}{C_6H_6} + ZnO$$

(iii) Wurtz-Fittig reaction : The derivatives of benzene can be prepared by a reaction known as Wurtz-Fittig reaction. When a mixture of aryl halide and an alkyl halide is treated with metallic sodium the derivatives of benzene are formed.

Example

$$\underset{\text{Bromobenzene}}{C_6H_5Br} + 2Na + \underset{\text{Methyl bromide}}{BrCH_3} \rightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + 2NaBr$$

(iv) Friedel-Craft's reaction : Benzene reacts with alkyl halides in presence of anhydrous aluminium chloride as catalyst to form alkyl benzenes.

Example

$$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl \xrightarrow[AlCl_3]{\text{anhydrous}} \underset{\text{Toluene}}{C_6H_5CH_3} + HCl$$

19.2.1 Commercial preparation of benzene

From Petroleum

Naphtha obtained by fractional distillation of petroleum is passed over platinum supported on alumina catalyst, benzene, toluene and other homologous of benzene are produced.

This process is now used for the large scale production of benzene and its homologous (toluene xylene). Benzene is separated from the resulting mixture by solvent extraction and by fractional distillation. 90% of commercial benzene is obtained from petroleum.

19.3 Physical Properties

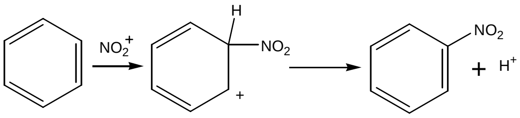
They are colourless liquids or solids with characteristic. They are insoluble in water but are miscible in all proportions with organic solvents such as ethanol, ether etc. They are inflammable, and burn with sooty flame. They are toxic and carcinogenic in nature. The boiling points increase with increase in molecular weight, but their melting points do not exhibit regular gradation Melting point seems to depend on molecular symmetry than on molecular weight.

19.4 Chemical Properties : Reactions of aromatic compounds

Aromatic compounds readily undergo electrophilic substitution reactions. The reactions are normally irreversible and the products formed are kinetically controlled. Sulphonation of aromatics is reversible and at high temperature thermodynamically stable products predominate. There are three steps in electrophilic substitution on aromatics. In the first step an electrophile is produced, in the second step the electrophile attacks the aromatic ring to give an arenium ion, and in the third step the arenium ion gives out a proton to form the final product.

(1) Nitration

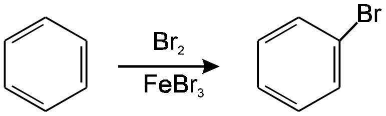
It is carried out in most of the cases with concentrated sulphuric acid and nitric acid. The temperature is between 30-40°C. HNO_3 acid gives nitronium ion after protonation.



NO_2^+ is an electrophile. It attacks the benzene to give an arenium ion, and the later gives out a proton to yield nitrobenzene.

(ii) Halogenation

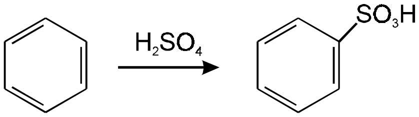
Benzene can be halogenated with chlorine and bromine in the presence of Lewis acid which, assists polarization of the attacking halogen molecule, thereby making it more reactive.



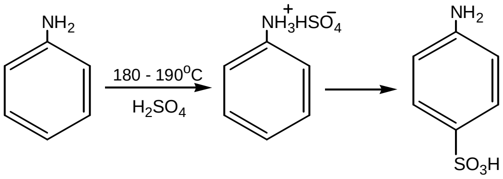
Fluorine reacts vigorously with aromatic hydrocarbons even in the absence of catalyst, however, iodine is very un reactive even in the presence of a catalyst.

(iii) Sulphonation

Aromatic compounds react with concentrated sulphuric acid to give arene sulphonic acid. The electrophile is SO_3. Although it does not have positive charge, it is a strong electrophile. This is because the octet of electrons around the sulphur atom is not reached.



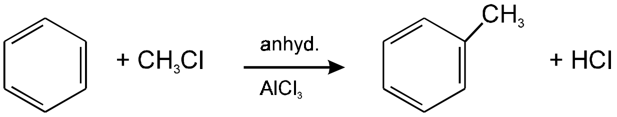
Aniline reacts with sulphuric acid to give a salt, which on strong heating rearranges to sulfanilic acid.



Sulphanilic acid

(iv) Friedel Crafts Alkylation

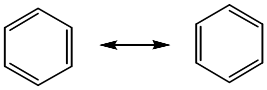
It is an important reaction to prepare alkyl aromatics. Alkylation of aromatic hydrocarbon is achieved using alkylhalide and aluminium trihalide (Lewis Acid).



Toluene

19.5 Resonance in benzene

1) The phenomenon in which two or more structures can be written for substance which involve identical position of atoms is called resonance. A double headed arrow (⟷)used to represent the resonance hybrid.



2) Structure of benzene is a single, unchanging hybrid structure that combines the characteristics of both resonance forms.
3) Resonance structures differ only in the position of their electrons. Different resonance structures of a substance need not be equivalent.
4) The resonance hybrid is more stable than any individual resonance structure.
5) More the resonance structures for a molecule more stable the molecule is.

19.6 Structure of benzene

The unusual stability of benzene was a great puzzle in the early days.

1) Although benzene with the molecular formula, C_6H_6 indicates the presence of unsaturation and the Kekule's structure proposes three carbon-carbon double bonds, it does not show any of the characteristic behaviour of alkenes.
2) For example, alkenes react readily with potassium permanganate to give cleaved products, undergo addition reactions with acids followed by hydrolysis to give alcohols and react with HCl to give saturated alkyl chlorides. However benzene does not exhibit any of the above reactions.
3) In the presence of platinum benzene reacts with hydrogen to give cyclohexane, six membered ring. This proves that benzene is a hexagonal molecule with three double bonds.
4) However, benzene reacts with bromine in the presence of iron to give substituted C_6H_5Br rather than the possible addition product of $C_6H_6Br_2$. Further only one monobromo substitution product was formed. No isomers of C_6H_5Br was identified.
5) On further reaction with bromine three isomeric disubstituted products. $C_6H_4Br_2$ are formed. On the basis of these results Kekule proposed that benzene consists of ring of carbon atoms with alternate single and double bonds.

www.tntextbooks.in

6) The structure can readily account for the formation of a single mono substituted product and three disubstituted isomers (o-, m- and p-) since all six carbon atoms and all six hydrogen atoms are equivalent.

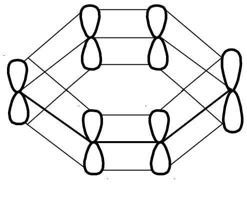
7) X-ray and electron diffraction studies inidicated that all carbon-carbon bonds are of equal length 1.39 Å which is in between that of a single bond (1.54 Å) and that of a double bond (1.34 Å).

8) Localised chemical bonding may be defined in which the electrons are shared by two nuclei only. The delocalised chemical bonding is one in which electrons are shared by more than two nuclei. Certain compounds contain one or more bonding orbitals that are not restricted to two atoms, but spread over three or more atoms. Such bonding is said to be delocalised bonding.

9) Benzene is a flat hexagonal molecule with all carbons and hydrogen lying in the same plane with a bond angle of 120°. Each carbon atom has sp^2 hybridisation.

10) The sp^2 hybrid orbitals of carbon overlap with each other and with 's' orbitals of six hydrogen atoms forming six sigma (σ) C-H bonds and six sigma (σ) C-C bonds.

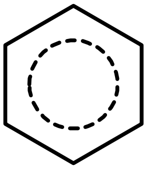
11) There are six p orbitals perpendicular to the plane containing six carbon atoms. Since all the six p orbitals are parallel to each other in benzene and are equivalent, it is not possible to define three localised alkene type pi (π) bonds, in which a p orbital overlaps with only one neighbouring p orbital. In benzene each p orbital overlaps equally well with both neighbouring p orbitals leading to a picture of benzene in which the six pi (π) electrons are completely delocalised around the ring. Thus benzene has two clouds of electrons one above and one below the ring. This is represented as follows.



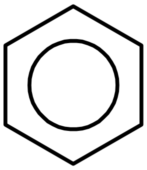
www.tntextbooks.in

The delocalisation of π orbitals in benzene

12) Thus the structure of benzene is now represented with either a full or a dotted circle to indicate the equivalence of all carbon-carbon bonds.



or

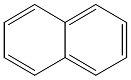


19.7 Uses

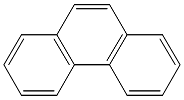
1. Benzene is used as a solvent for the extraction of fats and oils.
2. It is used as fuel along with petrol.
3. It is used for the production of maleic anhydride

19.8 Polynuclear aromatic hydro carbons

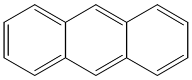
They have two or more fused aromatic rings. They have at least two adjacent carbons shared by aromatic rings. Some examples of these compounds which are carcinogenic.



naphthalene



phenanthrene



Anthracene

Questions

A. Choose the best answer :

1. Aromatic compounds are
   a) benzenoid compounds b) non-benzenoid compounds
   c) aliphatic compounds d) alicyclic compounds
2. Benzene was first isolated by
   a) Huckel b) Faraday c) Hofmann d) Barthelot
3. Benzene undergoes
   a) addition reactions b) oxidation reactions
   c) polymerisation reactions d) electrophilic substitution reactions

www.tntextbooks.in

4. The modern theory of aromaticity was introduced by
   a) Faraday c) Hofmann
   b) Huckel d) Berthelot
5. Any compound can be aromatic if they have __________ delocalised π electrons.
   a) 4n + 2 b) 4n + 1 c) 4n d) 4n - 2
6. The function of $FeCl_3$ in chlorination of benzene is to produce
   a) Cl b) Cl^+ c) Cl^- d) C
7. The ortho and para directing groups are
   a) activating group b) deactivating group c) both d) none
8. The purpose of adding conc. H_2SO_4 in nitration of benzene is to produce
   a) NO_2 b) NO_2^- c) NO_2^+ d) NO_3^-
9. An example of polycyclic aromatic hydrocarbon
   a) pyridine b) pyrole c) naphthalene d) cyclohexane
10. The compound which is used as a solvent for the extraction of fats and oils
    a) naphthalene b) benzene c) cyclohexane d) butane

B. Fill in the blanks

1. Many synthetic drugs used are ________ in part.
2. The _________ forms the source of many organic compounds.
3. The modern theory of aromaticity was introduced by______.
4. Ortho and para directing groups are called as __________ groups.
5. Meta directing groups are called as _______ groups.
6. Alkyl substituted benzenes are prepared by _________ reaction.
7. Naphtha obtained by fractional distillation of _________ is passed over platinum.
8. Aromatic compounds readily undergo ________________ substitution reactions.
9. ___________ reacts vigorously with aromatic hydrocarbons even in the absence of catalyst.
10. In the presence of ____________ benzene reacts with hydrogen to give cyclohexane.

www.tntextbooks.in

C. Explain briefly on the following

1. How is benzene is prepared commercially?
2. Explain the term aromaticity.
3. Write a note an activating groups in benzene.
4. How would you convert the following?
   a) sodium benzoate to benzene
   b) phenol to benzene
   c) benzene to toluene
5. Write briefly on resonance in benzene.

SUMMARY

- Aromatic compounds are called as benzenoid compounds.
- Benzene is the first member in the aromatic series of compounds.
- Coal is a complex substance made of primarily large arrays of highly unsaturated benzene like rings linked together.
- Delocalized electronic cloud and coplanarity of the compound are important for aromaticity.
- Aromatic compounds readily undergo electrophilic substitution reactions.

REFERENCES

1. Organic Chemistry, I.L. Final volume 1, ELBS Edition.
2. Organic Chemistry, Morrison and Boyd.

www.tntextbooks.in

20. ORGANIC HALOGEN COMPOUNDS

OBJECTIVES

The main objectives of this chapter are

* *to highlight the medicinal importance of certain halogenated compounds.*

* *to understand the physical and chemical properties of the organic halogen compounds.*

* *to give brief account of classification and nomenclature of these compounds.*

* *to discuss mechanisms of substitution and elimination reactions which are important to halogen compounds.*

* *to provide students more exposure to named organic reactions.*

* *to raise the capability of students to design new synthetic routes for interested target materials.*

* *to provide proof that how much important these compounds are as intermediates in the synthesis of wide variety of organic compounds.*

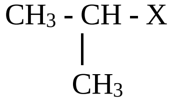
In organic halogen compounds F, Cl, Br and I are bonded to the carbons of the aliphatic, aromatic and aralkyl hydrocarbons. Many organic halogen compounds occur in nature and some of them have medicinal value. Chloromycetin is a naturally occurring halogen compound used in the treatment of typhoid fever. Thyroxine is yet another one used in the treatment of goitre. There are many synthetic organic halogen compounds few of which are important in health care and medicine. Two such compounds to cite are chloroquine and halothane. The former is used in the treatment of malaria and the later is used as an anaesthetic during surgery. There are also compounds which are important in agriculture and industry, as intermediates in the synthesis of wide variety of other organic compounds.

20.1 Classification of halogen compounds

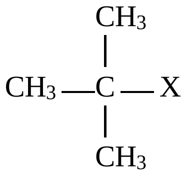
Depending on the type of halogen present, the halohydrocarbons are classified as follows.

Based on the number of alkyl groups bonded to the carbon that carries the halogen, the classification may be as follows.

Primary halides $CH_3CH_2 - X$

Secondary halides 

$$\begin{array}{c} CH_3 - CH - X \\ \quad | \\ \quad CH_3 \end{array}$$

Tertiary halides 

$$\begin{array}{c} CH_3 \\ | \\ CH_3 - C - X \\ | \\ CH_3 \end{array}$$

Where X = Halogen

In the primary halides, the carbon bonded to the halogen is connected to one alkyl group, in the secondary halides two alkyl groups in the tertiary halides three alkyl groups.

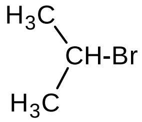
20.2 Nomenclature of alkyl halides : common and IUPAC

In this section the nomenclature of alkyl halides alone is presented, and the same for aryl halides and aralkyl halides are presented in their respective sections.

The common names of the monohalogen derivatives are derived by naming the alkyl group first and the halogen second.

CH_3CH_2Cl

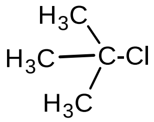
Ethyl chloride



Isopropyl brom ide

$CH_3CH_2CH_2CH_2Cl$

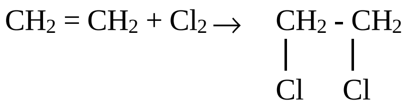
n-butyl chloride



tert butylchloride

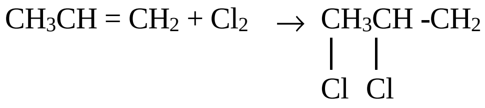
If two halogen atoms are bonded to the same carbon, they are named as the alkylidene halides. CH_3CHBr_2 Ethylidene bromide. If the two halogen atoms are bonded to adjacent carbons, they are named as the dihalides of the alkenes from which they are formed.

www.tntextbooks.in



$$CH_2 = CH_2 + Cl_2 \rightarrow \underset{\underset{Cl}{|}}{CH_2} - \underset{\underset{Cl}{|}}{CH_2}$$

Ethylene dichloride



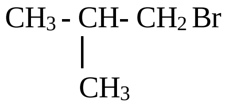
$$CH_3CH = CH_2 + Cl_2 \rightarrow CH_3\underset{\underset{Cl}{|}}{CH} - \underset{\underset{Cl}{|}}{CH_2}$$

Propylene dichloride

Trihalomethane and tetrahalomethanes are named as haloforms and carbon tetra halides respectively.

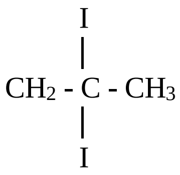
Example

Write the common names of the following halides

a) 

$$CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2Br$$

b) $CH_3\,CH_2\,CH\,Cl_2$

c) 

$$CH_2 - \overset{\overset{I}{|}}{\underset{\underset{I}{|}}{C}} - CH_3$$

d) $CH\,Br_3$ e) CCl_4

Solution

a. Isobutyl bromide b. Propylidene chloride

c. Propylidene iodide d. Bromoform

e. Carbon tetra chloride.

More complex halogen compounds are named according to IUPAC system.

i. If any halogen is at the end of the chain, the carbon bearing the halogen is to be given the number 1.

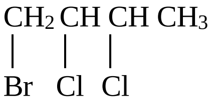
ii. If the halogen is present in the second or third carbon, numbering is to be started from that side of the chain which gives the least number for carbon bonded to halogen.

www.tntextbooks.in

iii. When two different halogens are present, the carbon bonded to higher atomic number halogen is to be given priority.

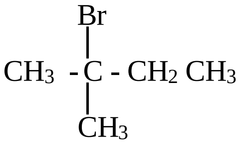
iv. The names of the halogens and other substituents are to be arranged alphabetically.

$CH_3CH_2CH_2Br$ 1 - Bromobutane



$$\underset{Br}{CH_2}\underset{Cl}{CH}\underset{Cl}{CH}CH_3$$

1-Bromo-2,3- dichlorobutane



$$CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2CH_3$$

2 - Bromo-2-methylbutane

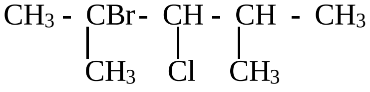
Example

Write the IUPAC names of the following halides.

a. $CH_2Br.CHCl.CH_2CH_2Cl$

b. $CH_3CCl_2.CHBr.CH_3$

c.



$$CH_3-\underset{CH_3}{CBr}-\underset{Cl}{CH}-\underset{CH_3}{CH}-CH_3$$

Solution

a. 1 - Bromo - 2,4 - dichlorobutane

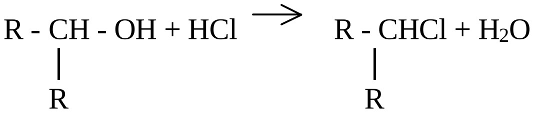
b. 2 - Bromo - 3,3 - dichlorobutane

c. 2-Bromo-3-chloro-2,4-dimethylpentane

20.3 General methods of preparation

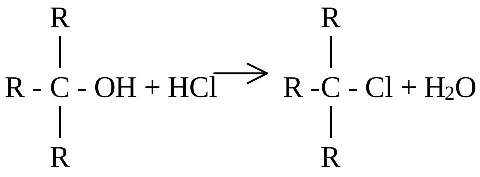
i. From alcohols : Preparation of alkyl halides from alcohols involves replacement of the hydroxyl group with halogen. It is done by using halogen acids.

$$RCH_2OH + HCl \xrightarrow{ZnCl_2} RCH_2Cl + H_2O$$



$$R-\underset{R}{CH}-OH + HCl \rightarrow R-\underset{R}{CHCl} + H_2O$$

www.tntextbooks.in



$$R-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-OH + HCl \rightarrow R-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-Cl + H_2O$$

$ZnCl_2$ is the Lewis acid catalyst. It is required for both primary and secondary alcohols as they are not rapidly reacting. Tertiary alcohols do not require this reagent as they are more reactive.

ii. From alkenes : Alkenes reacts with halogen acids to give alkyl halides. The addition of HCl occurs with first proton and second with halogen.

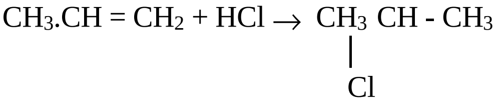
$CH_2 = CH_2 + H^+ \rightarrow CH_3\ CH_2^+$

$CH_3\ CH_2^+ + Cl^- \rightarrow CH_3CH_2Cl$

Hence $CH_2 = CH_2 + HCl \rightarrow CH_3CH_2Cl$

HBr and HI are added in a similar manner

When a hydrogen halide is added to an unsymmetrical olefin, the position of the halogen in the product is predicted by Markovnikoff's rule : It states that when a hydrogen halide is added to an unsymmetrical olefin, the negative part of it is added to the carbon that carries least number of hydrogens.



$$CH_3.CH = CH_2 + HCl \rightarrow CH_3\ \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_3$$

It is based on the stability of the carbonium ion formed after the addition of the proton. The order of the stability of the carbonium ion is

tertiary carbonium ion > secondary carbonium ion > primary carbonium ion

The stability of the carbonium ion depends on the extent to which the degree of the positive charge is decreased. In the tertiary carbonium ion the positive charge is more decreased by inductive effect and hyper conjugation and hence its degree of positive charge is more decreased than the secondary and primary carbonium ions.

www.tntextbooks.in

iii. From hydrocarbons

By treating alkanes with chlorine (or bromine) at room temperature in the presence of light, chloroalkanes are obtained. The reaction follows a free radical mechanism.

Chlorine molecule decomposes into chlorine atoms by absorption of light and the atoms then react with hydrocarbons.

$$Cl_2 \xrightarrow[\text{light}]{h\upsilon} Cl^{\bullet} + Cl^{\bullet}$$

$$CH_3CH_2 - H + Cl^{\bullet} \rightarrow CH_3CH_2^{\bullet} + HCl$$

$$CH_3CH_2^{\bullet} + Cl_2 \rightarrow CH_3CH_2Cl + Cl^{\bullet}$$

$$ClCH_2CH_3 + Cl^{\bullet} \rightarrow ClCH_2CH_2\,Cl + HCl$$

It is a chain reaction with the formation of several products. The reaction may be stopped by absorption of the chlorine atoms on the wall, or by reaction if two chlorine atoms to form a chlorine molecule.

iv. Hunsdiecker or Borodine - Hunsdiecker reaction

Silver carboxylates in carbon tetrachloride are decomposed by chlorine or bromine to form alkyl halide.

$$CH_3CH_2COO\,Ag + Br_2 \rightarrow CH_3CH_2Br + CO_2 + AgBr$$

Bromine is better than chlorine as the later gives poor yield.

v. By halogen exchange : Finkelstein reaction

Alkyl iodides are prepared by treating the corresponding chloride or bromide with a solution of sodium iodide in acetone. The exchange of halogen between alkyl halide and sodium iodide occurs.

$$RCl + NaI \xrightarrow{\text{Acetone}} RI + NaCl$$

$$RBr + NaI \xrightarrow{\text{Acetone}} RI + NaBr$$

Alkyl fluorides are obtained by treating alkyl chloride or bromide with metallic fluoride, such as AgF or SbF_3. It is the Swarts reaction.

$$CH_3\,CH_2\,Br + AgF \rightarrow CH_3CH_2F + AgBr.$$

www.tntextbooks.in

vi. Preparation of dihalogens

$CH_3COCH_3 + PCl_5 \rightarrow CH_3CCl_2.CH_3$,

$CH \equiv CH + 2HBr \rightarrow CH_3CHBr_2$

$CH_3CH = CH_2 \xrightarrow{Br_2} CH_3CHBr\ CH_2Br$

20.4 Properties

20.4.1 Physical properties

The lower members CH_3Cl, CH_3Br and CH_3CH_2Cl are gases. CH_3I and the majority of higher members are sweet-smelling liquids. For a given alkyl group the boiling point of halides increases with increase in the atomic weight of the halogens.

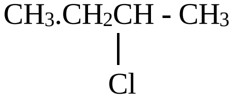
Halide	CH_3F	CH_3Cl	CH_3Br	CH_3I
B.P (°C)	-78	-24	4.0	92

It is due to increase in the Vanderwaals force with increase in the molecular size (molecular weight).

For a given halide, the boiling point increases with the length of the alkyl chains.

Halide	CH_3Cl	CH_3CH_2Cl	$CH_3CH_2CH_2Cl$
B.P (°C)	-22	12.5	47

It is due to increase in the Vanderwaals force with increase in the chain length. In a similar manner the boiling point of isomeric alkyl halides decreases in the order as shown below.

Halide	B.P (°C)
$CH_3CH_2CH_2CH_2Cl$	21.5
 $CH_3.CH_2\underset{\displaystyle Cl}{\underset{\vert}{CH}} - CH_3$	68
$(CH_3)_3\ C\text{-}Cl$	51

Organic halides are insoluble in water, as they are unable to form strong hydrogen bonds with water. They are less inflammable than the hydrocarbons. It is due to dilution of oxygen during combustion by the released halogen. Carbon tetrachloride is used in fire extinguishers and as solvent. Tri- and tetrachloroethylenes are widely used as solvents, and they are good solvents for fats and oils. They do not catch fire easily.

20.5 Nucleophilic substitution reactions

The alkyl halides are important reagents in organic synthesis. The halogen can be displaced by other groups by which variety of other organic compounds can be prepared. The reaction can be written as

$$\underset{\text{nucleophile}}{Y^-} + \underset{\text{substrate}}{RX} \rightarrow \underset{\text{product,}}{RY} + \underset{\text{leaving group}}{X^-}$$

The nucleophile may be negatively charged or a neutral species with a lone pair of electrons.

Nucleophiles : OH^-, RO^-, HS^-, NO_2^-, CN^- etc.
Neutral : H_2O, NH_3 CH_3NH_2 etc.

The R-X bond is polar with partial positive charge on carbon as shown below. It is due to more electronegativity of halogen than carbon.

$$CH_3 - \overset{\delta+}{CH_2} - \overset{\delta-}{X}$$

The nucleophile attacks on the carbon (CH_2) and displaces the leaving group. This reaction can occur by the following mechanisms.

20.6 Mechanism of nucleophilic substitution reactions

When a substitution reaction involves the attack of a nucleophile, the reaction is referred to as S_N (S-stands for substitution and N for nucleophile). The hydrolysis of alkyl halides by aqueous NaOH is an example of nucleophilic substitution.

$$R - X + \underset{\text{nucleophile}}{OH^-} \rightarrow R - OH + \underset{\text{leaving group}}{X^-}$$

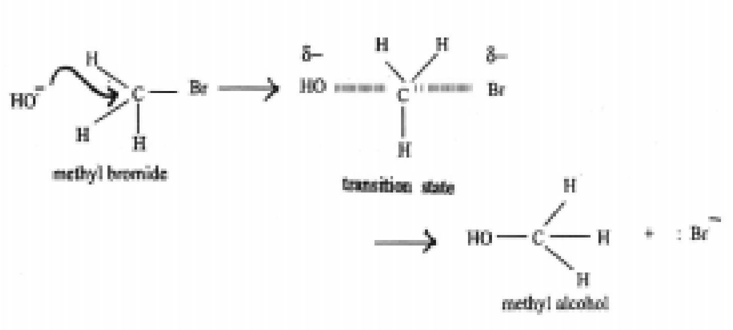
The nucleophilic substitution reactions are divided into two classes : (1) S_N2 reactions (2) S_N1 reactions.

S_N2 reactions : S_N2 stands for bimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends on the

www.tntextbooks.in

concentration of both the substrate and the nucleophile, the reaction is of second order and is represented as S_N2.

Consider the hydrolysis of methyl bromide by aqueous NaOH. The reaction is represented below.



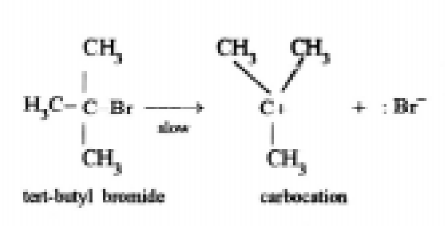
The hydroxide ion approaches the substrate carbon from the side opposite to the bromine atom. This is backside attack. This is because both hydroxide ion and the bromine atom are electron rich. They stay as far apart as possible. The transition state may be pictured as a structure in which both OH and Br are partially bonded to the substrate carbon. The C-Br bond is not completely cleaved and C-OH bond is not completely formed. Hydroxide ion has a diminished negative charge because it has started to share its electrons with the substrate carbon. The bromine atom also carries a negative charge because it has started removing its shared pair of electrons from the carbon atom. In the transition state the three C-H bond lie in one plane. The C-OH and C-Br bonds are perpendicular to the plane of the C-H bonds.

S_N1 reactions: S_N1 stands for unimolecular nucleophilic substitution. When the rate of nucleophilic substitution reaction depends only on the concentration of the substrate (alkyl halide), the reaction is first order and is represented as S_N1.

Consider the hydrolysis of tertiary butyl bromide. The reaction consists of two steps.

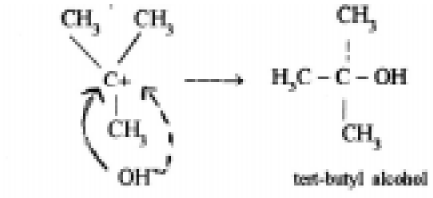
Step 1: The alkyl halide ionises to give the carbocation (carbonium ion). This step is the slow rate determining step.

www.tntextbooks.in



The carbocation is planar. This is because the central positively charged carbon atom is sp^2 hybridised.

Step 2 : The nucleophile can attack the planar carbocation from either side to give tertiary butyl alcohol.



Primary alkyl halides undergo hydrolysis by S_N2 mechanism. The tertiary alkyl halides undergo hydrolysis by S_N1 mechanism. Secondary alkyl halides may undergo hydrolysis by both S_N1 and S_N2 mechanism.

20.7 Mechanism of elimination reaction

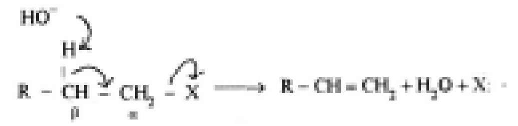
Elimination reactions are reverse of addition reactions. Here atoms or group attached to the adjacent carbon atoms in the substrate molecule are eliminated to form a double bond. Example, dehydrohalogenation of alkyl halides with alcoholic alkalis.

$$R-CH_2-CH_2-X \xrightarrow[\text{alcoholic alkali}]{OH^-} R-CH=CH_2 + H_2O + X^-$$

These reactions are divided into two classes

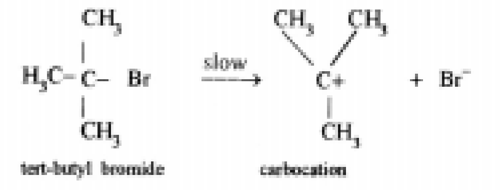
1) E2 reaction2) E1 reactions

E2 reactions: E2 stands for bimolecular elimination. When the rate of an elimination reaction depends on the concentration of substrate and nucleophile, the reaction is second order and is represented as E2. E2 is a one step process in which the abstraction of the proton from the beta carbon and expulsion of the halide ion from the alpha carbon occur simultaneously. The mechanism is shown below :

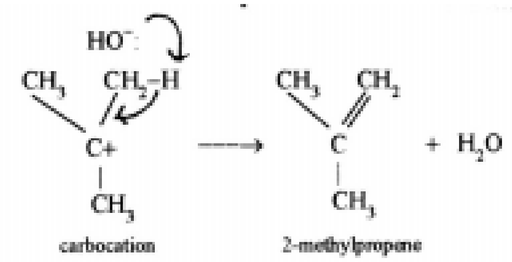


E1 reactions: E1 stands for unimolecular elimination. when the rate of an elimination reaction depends only on the concentration of the substrate, the reaction is of first order and is designated as E1. E1 reactions are two step processes.

Step 1 : The alkyl halide ionise to give the carbocation.



Step 2 : The nucleophile (OH^-) abstracts a proton and forms an alkene.



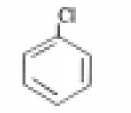
Uses of alkyl halides

1) Alkyl chlorides such as trichloromethane (chloroform) and tetra chloromethane (carbon tetrachloride) are widely used as industrial solvents. 2) Chloroform is used as anaesthetic 3) Iodoform is used as an antiseptic 4) Carbon tetrachloride is used as a fire extinguisher 5) dichlorodifluoromethane (a freon) is used as a refrigerant 6) Alkyl halides are used for the preparation of Grignard reagents.

www.tntextbooks.in

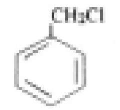
20.8 Aryl halides

When the halogen atom is substituted in the place of a hydrogen atom in an aromatic ring, the compound is called aryl halide. Example,



chlorobenzene

The halogen atom may be linked to carbon atom in the side chain of an aromatic hydrocarbon. Such a compound is called aralkyl halide. Example,



benzyl chloride

20.8.1 General methods of preparation, properties and uses of aryl halides

The methods of preparation of chlorobenzene can be taken as general methods of preparation of aryl halides.

1. Direct halogenation : Aryl chlorides and aryl bromides are generally prepared from arenes by action with chlorine or bromine in presence of a catalyst such as $FeCl_3$ or $FeBr_3$.

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} \underset{\text{chlorobenzene}}{C_6H_5Cl} + HCl$$

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} \underset{\text{bromobenzene}}{C_6H_5Br} + HBr$$

2. Decomposition of diazonium salts : Aryl halides can be prepared by the decomposition of aryldiazonium salts in the presence of appropriate metal halides.

www.tntextbooks.in

$$C_6H_5N_2^+Cl^- \xrightarrow[HCl]{Cu_2Cl_2} C_6H_5Cl + N_2$$

$$C_6H_5N_2^+Cl^- \xrightarrow[HBr]{Cu_2Br_2} C_6H_5Br + N_2$$

20.9 General properties :

The molecule of an aryl halide is made of (i) an aromatic ring and (ii) halogen atom directly bonded to the ring. The reactions of aryl halides are, therefore, due to the aromatic ring and the halogen atom.

Reactions involving the halogen atom : Nucleophilic aromatic substitution : 1) Aryl halides do not readily undergo nucleophilic substitution reactions, as those of alkyl halides. The reason for such low reactivity is given below. One reason is that the C-X bond in aryl halides is short and strong compared to that of alkyl halides. Another reason is that the aromatic ring is a centre of high electron density because of the delocalised π electrons. However nucleophilic substitution of halogen of aryl halides can take place under vigorous conditions. Example,

$$C_6H_5Cl + NaOH \xrightarrow[300\ atm]{623K} \underset{phenol}{C_6H_5OH} + NaCl$$

$$C_6H_5Cl + 2NH_3 \xrightarrow[50\ atm]{523K} \underset{aniline}{C_6H_5NH_2} + NH_4Cl$$

$$C_6H_5Cl + \underset{cuprous\ cynide}{CuCN} \xrightarrow[pyridine]{523K} \underset{phenyl\ cyanide}{C_6H_5CN} + CuCl$$

2) Wurtz-Fittig reaction : Aryl halides react with alkyl halides when heated with sodium in ether solution to form alkylbenzene.

$$C_6H_5Br + 2Na + C_2H_5Br \xrightarrow{ether} \underset{ethyl\ benzene}{C_6H_5-C_2H_5} + 2NaBr$$

3) Fittig reaction : In the absence of alkyl halides, aryl halides in ether solution react with sodium to give biaryl compounds in which two benzene rings are bonded together.

$$C_6H_5Br + 2Na + BrC_6H_5 \rightarrow C_6H_5 - C_6H_5 \text{Biphenyl}$$

4) Reduction : When reduced with nickel-aluminium alloy in the presence of sodium hydroxide, aryl halides give the corresponding arenes.

$$C_6H_5Cl + 2[H] \xrightarrow[NaOH]{Ni-Al} C_6H_6 + HCl$$

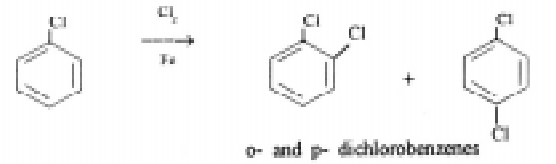
5) Formation of Grignard reagents : Aryl bromides and iodides form Grignard reagents when refluxed with magnesium powder in dry ether. Aryl chlorides do so in presence of tetrahydrofuran (THF) instead of ether.

$$C_6H_5Cl + Mg \xrightarrow{THF} C_6H_5MgCl$$

6) Reactions involving the aromatic ring: Electrophilic aromatic substitution reactions

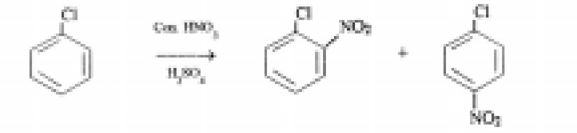
Aryl halides undergo the typical electrophilic aromatic substitution reactions like halogenation, nitration, sulphonation and alkylation. Here the halogen of the aryl halide directs the electrophilic reagents to ortho and para positions. The electrophilic substitution reactions of aryl halides are illustrated by taking the example of chlorobenzene.

i. Chlorination



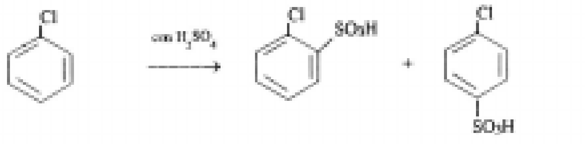
o- and p- dichlorobenzenes

ii. Nitration



o- and p-nitrochlorobenzes

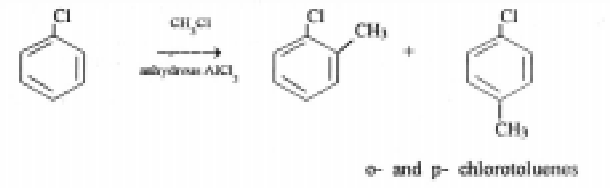
iiii. Sulphonation



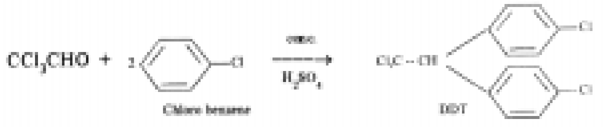
o- and p- chlorobenzenesulphonic acids

www.tntextbooks.in

iv. Alkylation



v. Formation of DDT : Chlorobenzene reacts with trichloroacetaldehyde (chloral) in the presence of concentrated sulphuric acid to give p-p'-dichloro diphenyltrichloroethane (DDT). It is an effective insecticide.



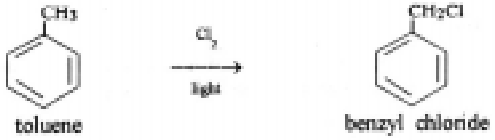
20.10 Uses of aryl halides :

Chlorobenzene is used for the preparation of phenol and nitrochlorobenzenes which are erequired for the manufacture of azo and sulphur dyes; DDT and BHC (benzenehexachloride) which are insecticides.

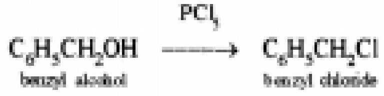
Side-chain halogenated compounds or aralkyl halides

A typical example of this class of compounds is benzyl chloride which can be prepared as follows:

1. Side chain halogenation is favoured by high temperature and light. It occurs in the absence of halogen carriers. For example, benzyl chloride is prepared by chlorination of boiling toluene in light.



2. It can also be prepared by the action of phosphorus pentachloride on benzyl alcohol.



$$\underset{\text{benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow{PCl_5} \underset{\text{benzyl chloride}}{C_6H_5CH_2Cl}$$

www.tntextbooks.in

Properties

i) Reduction of aralkyl halides

Reduction of benzyl chloride with Zn-Cu couple gives toluene.

$$C_6H_5CH_2Cl \xrightarrow{\text{Zn-Cu}} C_6H_5CH_3$$

ii) Oxidation

Benzyl chloride on oxidation with alkaline potassium permanganate gives benzoic acid.

On mild oxidation with $Cu(NO_3)_2$ gives benzaldehyde.

$$C_6H_5CH_2Cl \xrightarrow{[O]} C_6H_5 - CHO$$

20.11 Grignard reagents

Organic Compounds in which alkyl or aryl groups are directly attached to a metal are called organometallic compounds. Many metals form organometallic compounds. For example,

CH_3Li	C_2H_5MgI
$(C_2H_5)_2Zn$	$Pb(C_2H_5)_4$

Organomagnesium halides are called Grignard reagents. They are named after the French Chemist, Victor Grignard, who discovered them and developed them as synthetic reagents.

General formula and nomenclature : Their general formula can be written as RMgX where R=alkyl or aryl group and X=Cl, Br or I. Examples, CH_3MgBr and CH_3CH_2MgBr.

Nomenclature : Grignard reagents are named by simply adding the name of the metal to that of the organic group bonded to the metal. For example,

CH_3MgI	methylmagnesium iodide
CH_3CH_2MgBr	ethylmagnesium bromide
CH_3Li	methyllithium
$(CH_3CH_2)_4Pb$	tetraethyllead

www.tntextbooks.in

20.11.1 Preparation of methylmagnesium iodide

Methylmagnesium iodide is prepared by the action of methyl iodide on magnesium suspended in dry ether. All the reagents used should be pure and dry. Dry magnesium ribbon is washed with ether to remove grease and then with dilute acid to remove any oxide and then dried. The ether is kept absolutely dry by distilling over metallic sodium to make it free from ethanol. Methyl iodide is dried over anyhydrous calcium chloride and then distilled over phosphorus pentoxide.

Clean dry magnesium is placed in dry ether in a flask fitted with reflex condenser. Pure dry methyl iodide is added gradually. When the reaction starts, the ether becomes cloudy and also begins to boil. It is necessary to cool the mixture. If the reaction does not start, one or two crystals of iodine are dropped into the flask. When the reaction is complete, a clear solution of methyl magnesium iodide is obtained. this is used as such in all the reactions.

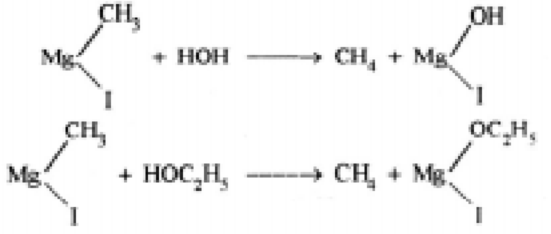
$$CH_3I + Mg \xrightarrow[\text{ether}]{\text{dry}} CH_3MgI$$

20.12 Synthetic uses of methylmagnesium iodide

Grignard regents are generally one of the most reactive compounds. These are used for the synthesis of a variety of organic compounds. The following reactions illustrate the synthetic uses of methylmagnesium iodide.

1. **Preparation of alkanes**

Methylmagnesium iodide undergoes double decomposition with water and alcohol to produce alkanes.

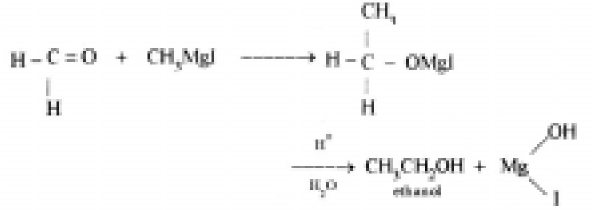


$$Mg\begin{matrix} CH_3 \\ I \end{matrix} + HOH \longrightarrow CH_4 + Mg\begin{matrix} OH \\ I \end{matrix}$$

$$Mg\begin{matrix} CH_3 \\ I \end{matrix} + HOC_2H_5 \longrightarrow CH_4 + Mg\begin{matrix} OC_2H_5 \\ I \end{matrix}$$

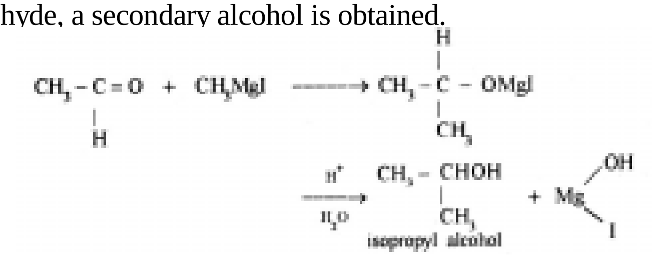
2. **Preparation of primary alcohols**

Formaldehyde reacts with methylmagnesium iodide to give addition product which on hydrolysis yield primary alcohol.



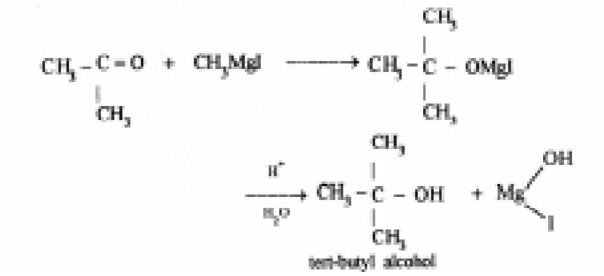
3. Preparation of secondary alcohols

When methylmagnesium iodide is treated with any aldehyde other than formaldehyde, a secondary alcohol is obtained.



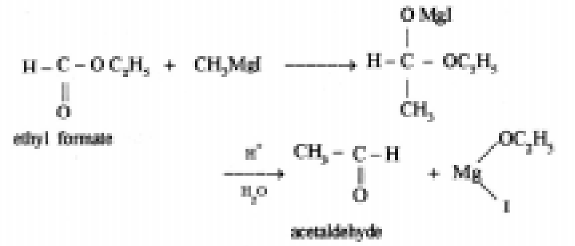
4. Preparation of tertiary alcohols

Methylmagnesium iodide reacts with ketones to give an addition compound which on hydrolysis yield tertiary alcohols.

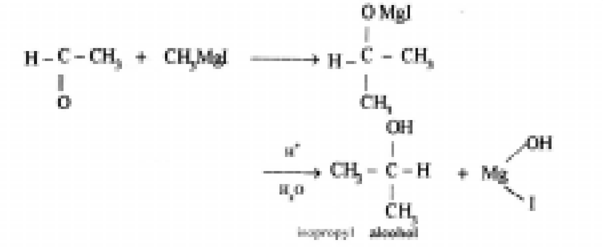


5. Preparation of aldehydes

An aldehyde is prepared by treating one molecule of methylmagnesium iodide with one molecule of ethyl formate.

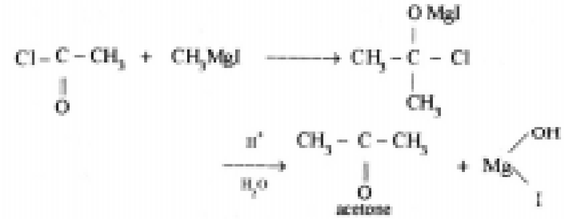


A secondary alcohol is obtained if methylmagnesium iodide is in excess. Aldehyde produced reacts further to give secondary alcohol.



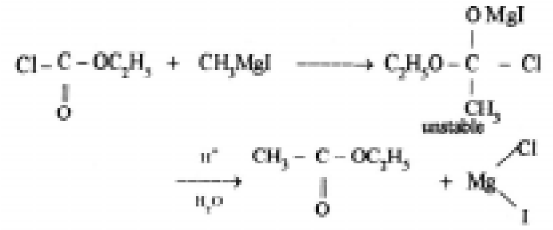
6. Preparation of ketones

Methylmagnesium iodide reacts with acid chlorides to form ketones.



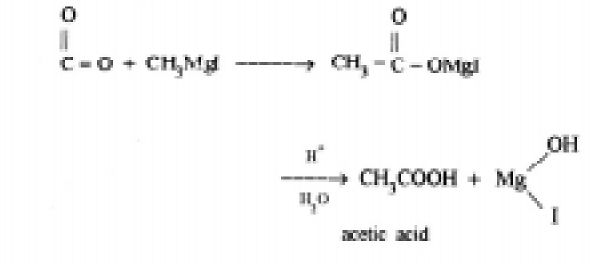
7. Preparation of esters

Methylmagnesium iodide reacts with ethyl chloroformate to form higher esters



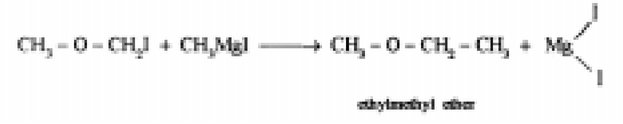
8. Preparation of acids

Methylmagnesium iodide reacts with solid carbon dioxide to give addition product which on hydrolysis in the presence of acid yields carboxylic acid.



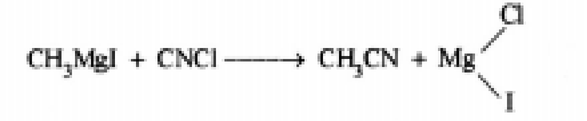
9. Preparation of ethers

When a monohalogen derivative of an ether is treated with methylmagnesium iodide, ether homologue is obtained.



10. Preparation of alkyl cyanide

Methylmagnesium iodide reacts with cyanogen chloride to form an alkyl cyanide or alkyl nitrile.

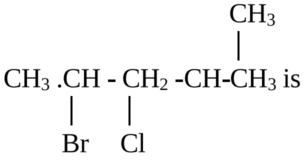


methyl cyanide or acetonitrile

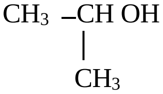
Questions

A. Choose the correct answer

1. The IUPAC name of



$CH_3.\underset{Br}{CH} - \underset{Cl}{CH_2} - \overset{CH_3}{CH}-CH_3$ is

   a. 2-Bromo-3-chloro-4-methylpentane
   b. 2-Methyl-3-chloro-4-bromopentane
   c. 2-Bromo-3-chloro-3-isopropyl propane
   d. 2,4-Dimethyl-4-Bromo-3-chloro butane.
2. For reacting with HCl, the alcohol which does not require $ZnCl_2$ is
   a. $CH_3\,CH_2\,OH$ b. $CH_3 - CH_2\,CH_2\,OH$
   c.  $\underset{CH_3}{CH_3 - CH}\,OH$ d. $C\,(CH_3)_3\,C\text{-}OH$.
3. For converting alcohols into alkyl halides, the best reagent is
   a. PCl_3 b. PCl_5 c. $SOCl_2$ d. None of the above
4. The olefin, which is not important for Markovni Koff's addition of HCl, is
   a. Propene b. But-1-ene c. 2-Methyl-propene d. Ethylene
5. The S_N1 reaction of alkyl halides is not affected by the nature of the
   a. alkyl group b. the halogen c. medium d. nucleophile

www.tntextbooks.in

B. Fill in the blanks

1. Markonikoff's rule is followed for the addition of HCl to.....................
2. In Swarts reaction metallic fluorides are added to.................
3. Hoffman's rule is applicable to elimination ....
4. Chloropicrin is prepared by adding nitric acid to........................

C. Write in one or two sentence

1. What are Lewis acids?
2. What is an electrophilic addition?
3. What is Hunsdiecker reaction?
4. What is Finkelstein reaction?
5. What is Swarts reaction?

D. Explain briefly on the following

1. Discuss S_N^1 mechanism
2. Discuss S_N^2 mechanism
3. Discuss E1 elimination
4. Discuss E2 elimination
5. What are the uses of alkyl halides?
6. What are the general reactions of aryl halides.
7. What are aralkyl halides ? How are they prepared?
8. What are Grignard reagents? Discuss its synthetic uses.
9. Discuss the general methods of preparation of alkyl halides.

SUMMARY

- Organic halogen compounds are classified into alkyl, aryl and aralkylhalides.
- Alkyl halides are very good synthetic compounds from which various compounds are synthesised.
- In Aryl halides chloro group is ortho and meta directing.
- If a halogenoalkane is reacted with magnesium metal in dry ethoxyethane, a Grignard reagent is the product - these act as nucteophiles and are commonly used to form new carbon-carbon bonds.

REFERENCES

1. Organic Chemistry IL Finar ELBS
2. Organic Chemistry by Morrison and Boyd.