A TEXTBOOK
OF
CHEMISTRY

for

Class XI

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With learners for life

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Preface

A Textbook of Chemistry for **Class XI** has been written in strict conformity with the **Science Curriculum Framework** prepared by **Department of Curriculum Research and Development, Ministry of Education, Royal Government of Bhutan.**

A sincere attempt has been made for developing this book to adhere the spirit of 'learning without burden' and presenting science as a live and growing body of knowledge with many open areas of investigation, rather than a finished product.

The book also follows a pedagogy that is hands-on and inquiry based. The examples have been taken from things that are directly related to a child's experience.

Some of the salient features of this book are:

- Simple and easily understandable language has been used throughout.
- Informal interactive style, which the students will find appealing and easy to understand.
- SI units have been invariably used throughout the book.
- Each chapter contains **Miscellaneous Solved Questions**. In this section, we are providing the solutions of some typical questions.
- **Quick Scan**. A detailed summary of the Chapter has been provided under this heading. This can be very beneficial to the students for last minute revision of the Chapter without hassle.
- **Text Plus.** At times, questions appear in the competitive examinations which are not strictly part of the syllabus. This section addresses this difficulty of the students.
- **Exercises.** This section provides very short answer type questions, short answer type questions, long answer type questions. A large number of problems have been framed for the practice of the students. Answers to very short answer questions and short answer questions have been provided.
- **Competition File.** This section has been further divided into *subjective problems, numerical problems, objective questions* and *some additional questions* taken from various entrance examinations. Solutions to all the subjective and numerical problems have been given while answers to all the objective questions have been provided.

Every effort has been made to keep this book error free. All suggestions and constructive feedbacks are welcome and we shall try our best to accommodate them in subsequent editions.

– Authors

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Syllabus

Strand: Material and their Properties

1. Classifying materials: Atom structure and bonding

(i) Atomic structure

(a) Nuclear structure

- Describe a proton, a neutron and an electron in terms of relative charge and relative mass.
- Describe the structure of the nucleus of an atom and the arrangement of protons and neutrons in the nucleus.
- State that the atomic number of an element is the number of protons in the nucleus and the mass number is the number of protons plus the number of neutrons.
- Calculate the number of protons, neutrons and electrons in an atom using given atomic number and mass number.
- Explain an isotope is in terms of atoms of the same element with different numbers of neutrons in the nucleus.
- State that ^{12}C is used as the standard measurement of relative masses.
- Define the term relative atomic mass based on the ^{12}C isotope.
- Calculate the relative atomic mass of an element when the relative abundances of its isotopes is given.
- Calculate relative molecular mass and relative formula mass from relative atomic masses.

(b) Electron structure

- State the definitions of first ionisation energy and successive ionisation energies.
- Explain that the values of ionisation energies are influenced by nuclear charge, electron shielding and the distance of the outermost electrons from the nucleus.
- Predict, from successive ionisation energies, the number of electrons in each shell of an atom and the group to which the element belongs.
- State the number of electrons that fill the first four quantum shells.
- Explain that an orbital is a region that holds up to two electrons which have opposite spins.
- Describe the shapes of *s*-orbital, *p*-orbital and *d*-orbital.
- State the number of orbitals making up *s*-subshell, *p*-subshell and *d*-subshell and the number of electrons that occupy *s*-subshell, *p*-subshell and *d*-subshell.
- Describe the relative energies of *s*-orbital, *p*-orbital, and *d*-orbitals for the quantum levels 1, 2, 3 and the 4*s*- and 4*p*-orbitals.
- Deduce the electron configurations of the atoms of elements up to atomic number 36.
- Classify elements as *s*-block, *p*-block or *d*-block elements.

(ii) Bonding

(a) Ionic bonding

- Explain that ionic bonding results from the electrostatic attraction between oppositely charged ions.
- Draw dot and cross diagrams to show the electron arrangement of ions in ionic bonding.
- Predict the charge on the ions of an element from its group number in the Periodic Table.
- State the formulae for a range of ions including the nitrate ion, nitrite ion, carbonate ion, sulphate ion, sulphite ion, phosphate ion and ammonium ion.

(b) Covalent bonding and dative covalent bonding (coordinate bonding).

- Describe the nature of the covalent bond.
- Draw dot and cross diagrams to describe single covalent bonding (e.g. Cl_2, HCl, H_2O, CH_4), multiple covalent bonding (e.g. O_2, N_2, CO_2), dative covalent (coordinate) bonding (e.g. H_3O^+, NH_4^+, H_2SO_4, HNO_3, oxyacids of chlorine), molecules and ions (e.g. NO_3^-, SO_4^{2-}, CO_3^{2-}).

(c) The shapes of molecules and ions

- Explain the factors that determine the shapes of molecules including hybridisation of orbitals.
- Explain the shapes and bond angles in molecules and ions with up to six electron pairs (including lone pairs) surrounding a central atom, e.g. BF_3 (trigonal planar), CH_4 and NH_4^+ (tetrahedral), SF_6 (octahedral), NH_3 (pyramidal), H_2O (non linear), CO_2 (linear).
- Predict the shapes of molecules and their bond angles for other molecules and ions.

(d) Polar molecules

- Define term electronegativity and explain that the atoms of some elements are more electronegative than others.
- Use the concept of electronegativity to explain that some molecules, e.g. HCl, CH_3Cl, have polar bonds and are permanent dipole.

(e) Intermolecular forces

- Describe the origin of intermolecular forces, e.g. van der Waals forces (based on induced dipoles, e.g. N_2, H_2, O_2), dipole-dipole forces (based on permanent dipoles, e.g. HCl and CH_3Cl).
- Describe hydrogen bonding in molecules such as H_2O, NH_3, HF.
- Explain, using hydrogen bonding, the anomalous properties of the hydrides of the second period, e.g. NH_3, H_2O and HF.

(f) Metallic bonding

- Describe the structure of metals in terms of the attraction of positive metal ions to a delocalised 'sea' of electrons.

2. Materials and change: Organic Chemistry

(i) Introduction to Organic Chemistry–naming organic compounds

- State the difference among the terms empirical formula, molecular formula, structural formula, homologous series and functional group.
- Represent an organic compound in terms of empirical formula, molecular formula and structural formula.
- Apply the IUPAC rules to the nomenclature of simple organic compounds.

(ii) Alkanes

(a) Structure, bonding, isomerism and nomenclature

- Write the general formula for alkanes (C_nH_{2n+2}) and the correct formulae for any aliphatic alkane.
- Describe the tetrahedral shape of shape around each carbon atom in an alkane molecule using sp^3 hybridisation.
- Explain that the principle type of isomerism in alkanes is structural isomerism and draw and name structural isomers for alkanes with the same chemical formula, e.g. C_6H_{14}.

(b) Substitution reactions of alkanes

- Describe the reactions of alkanes with chlorine.
- Explain the mechanism of free radical substitution for the reaction of alkanes with chlorine (initiation, propagation and termination).

(iii) Alkenes

(a) Structure, bonding and isomerism

- Explain the general formula of alkenes (C_nH_{2n}) and write correct formulae for any aliphatic alkene.
- Apply the IUPAC rules to the nomenclature of simple alkenes.
- Explain the alkenes are unsaturated hydrocarbons.
- Explain that the $C=C$ is planar and describe the overlap of adjacent *p*-orbitals to form a π-bond using sp^2 hybridisation.
- Explain that the π-bond is an area of high electron density.
- Explain that alkenes exhibit E-Z isomerism because of the restricted rotation about the $C=C$ double bond.
- Draw structures of E and Z isomers for simple alkenes.

(b) Addition reactions of alkenes

- Describe the reactions of alkenes with Br_2, H_2SO_4 and HCl.
- Explain the mechanism of electrophilic addition for the reaction of alkenes with Br_2, H_2SO_4 and HCl.
- Explain that bromine can be used as a test for unsaturation.
- Predict, using Markovnikov's rule, the products of addition of HCl to unsymmetrical alkenes.
- Explain the pattern of addition of HCl to unsymmetrical alkenes referring to the relative stabilities of primary, secondary and tertiary carbocation intermediates.
- State the reaction conditions and equation for the industrial production of ethanol from ethene.
- Describe how margarine is manufactured by catalytic hydrogenation of unsaturated vegetable oil.

(c) Polymerisation

- Describe the addition polymerisation of alkenes for examples like the formation of poly (ethene), poly (propene), polytetrafluoroethene (PTFE), polyvinylchloride (PVC), polystyrene and natural and synthetic rubber.
- State uses of polymers, e.g. poly (ethene), poly (propene), polytetrafluoroethene (PTFE), and polyvinylchloride (PVC).
- Identify the repeating unit, the monomer unit, using the structure of the polymer.

(iv) Alkynes

(a) Structure, bonding and isomerism

- State the general formula of alkynes (C_nH_{2n-2}) and write correct formulae for any alkyne.
- Apply the IUPAC rules to the nomenclature of simple alkynes.
- Explain that alkynes are unsaturated hydrocarbons.
- Explain that the shape of ethyne is linear and describe the overlap of adjacent *p*-orbitals to form a 2π-bond by *sp*-hybridisation.

(b) Source of Ethyne

- Describe the preparation of ethyne from natural gas.
- State the uses of ethyne in oxy-acetylene torches and the manufacture of a variety of organic compounds.

(c) Addition reactions of alkynes

- Describe the reactions of alkynes with H_2, Br_2 and HCl.
- Explain the mechanism of electrophilic addition for the reaction of alkynes with H_2, Br_2, and HCl.
- Compare and contrast the reactions of alkanes, alkenes and alkynes.

(v) Alcohols

(a) Nomenclature and classification

- Apply the IUPAC rules to the nomenclature of simple alcohols.
- Classify alcohols as primary alcohol, secondary alcohol or tertiary alcohol and name them accordingly.

(b) Reactions of alcohols

- Describe the oxidation of primary alcohols to form either aldehydes or carboxylic acids depending on the reaction conditions.
- Describe the oxidation of secondary alcohols to form ketones.
- Explain the tertiary alcohols are resistant to oxidation.
- Describe the elimination of water (H_2O) from alcohols in the presence of an acid catalyst.

(vi) Halogenoalkanes

(a) Structure and isomersim

- Apply the IUPAC rules to the nomenclature of simple halogenoalkanes.
- Classify halogenoalkanes as primary halogenoalkane, secondary halogenoalkane and tertiary halogenoalkane and name them accordingly.

(b) Substitution reactions of halogenoalkanes

- Describe the reactions of halogenoalkanes with OH^-, CN^- and NH_3.
- Explain the mechanism of nucleophilic substitution for the reaction of halogenoalkanes with OH^-, CN^- and NH_3.
- Outline the importance of the reaction with CN^- in organic synthesis as a means to add a carbon atom to an organic compound.
- Explain the rates of hydrolysis of halogenoalkanes in terms of the relative bond enthalpies of carbon-halogen bonds (e.g. C–F, C–Cl, C–Br, C–I).

(c) Elimination reactions of halogenoalkanes

- Explain that simultaneous elimination and displacement occurs in the reaction of a halogenoalkanes (e.g. 2-bromopropane with potassium hydroxide) and the role of reagent as a base and a nucleophile (including mechanisms).

(vii) Arenes

(a) Structure and bonding

- Explain the structure of benzene and compare the Kekulé and delocalised models for benzene in terms of *p*-orbital overlap forming π-bonds.
- Use the evidence (e.g. bond lengths, enthalpy of hydrogenation and resistance to reaction compared to alkenes) to explain how this supports the delocalised model for the structure of benzene.
- Explain that delocalisaton gives stability to the benzene molecule.

(b) Electrophilic substitution of arenes

- Describe the reactions of arenes with concentrated nitric acid in the presence of sulphuric acid.
- Explain the mechanism of electrophilic substitution for the reaction of arenes with concentrated nitric acid in the presence of concentrated sulphuric acid.
- Explain the mechanism of electrophilic substitution for the reaction of arenes with a halogen in the presence of a halogen carrier.
- Explain the mechanism of electrophilic substitution for the halogenation reactions of arenes limited to monosubstitution of the arene only.
- Describe Friedel-Crafts alkylation and acylation reactions.
- Explain the importance of Friedel-Crafts in organic synthesis, for example, industrial production of ethylbenzene and manufacture of polystyrene.
- Explain the mechanism for the alkylation and acylation reactions of arenes using $AlCl_3$ as a catalyst.

(c) Phenols

- Describe the industrial preparation of phenol from petroleum oil.
- Describe the preparation of phenol from sodium benzenesulphonate, chlorobenzene (Dow's process) and from the hydrolysis of diazonium salts.
- Explain why phenol is more reactive than benzene and, therefore, more susceptible to electrophilic substitution.
- Explain the substitution patterns (*ortho* and *para*) for phenol.
- Describe the reactions of phenol with dilute and concentrated nitric acid and Kolbe's reaction to form salicylic acid (2-hydroxybenzoic acid).

(viii) Green Chemistry – caring for our changing planet

(a) The Greenhouse Effect and global climate change

- Explain natural Greenhouse Effect.
- Name and state the origins of the key naturally occurring trace gases, e.g. water vapour, carbon dioxide, methane, nitrous oxide and ozone which cause the natural Greenhouse Effect.
- Explain enhanced Greenhouse Effect (Global Warming).
- Outline the key chemical processes by which human activity has increased the concentration of Greenhouse Gases in the atmosphere.

- Explain the effects of the global warming on the environment both in Bhutan and across the world.
- Describe actions that humans can take to lessen the harmful effects of global climate change both locally and globally.

(b) The Ozone layer

- Explain the chemistry of origin of the Ozone layer in the upper layers of the atmosphere.
- Explain the role of the Ozone layer in protecting the Earth's surface from harmful UV radiation.
- State the uses of halogenoalkanes including the use of Chlorofluorohydrocarbons (CFCs) as aerosols, refrigerants and in air conditioning.
- Explain that CFCs damages to the Ozone layer and the actions taken by humans to reduce the use of CFCs and explain the role of 'green chemistry' in developing biodegradable alternatives to CFCs.
- State the HFCs are used as replacements for CFCs and explain its implications.

3. Pattern in Chemistry

(i) Patterns in the Periodic Table

(a) Periodicity

- Classify an element as *s*-block, *p*-block or *d*-block based on its position in the Periodic Table.
- Describe the trends in atomic radius, first ionisation energy, melting and boiling points of the elements in the second period (Li-Ne) and third period (Na-Ar).
- Explain the physical properties of the highest oxides of the elements Na-S in terms of their structure and bonding.
- Describe the reactions of the oxides Na_2O, MgO, Al_2O_3, SiO_2, P_4O_{10} and SO_2 and SO_3 with water.
- Explain the harmful effects of SO_2 and SO_3 in acid rain.
- Describe the pH changes of the resulting solutions of the oxides with water across the period.

(b) Oxidation numbers

- Apply the rules for assigning oxidation numbers to atoms in elements, compounds and ions.
- Explain oxidation and reduction in terms of electron transfer and changes in oxidation number.
- Write chemical formulae using oxidation numbers.

(c) Group 2 – The Alkaline earth metals

- Describe the trends in atomic radius, first ionisation energy and melting points of the elements in group 2.
- Describe the reactions of the elements in group 2 with oxygen, chlorine and water.
- Explain the trends in reactivity of group 2 elements.
- Describe the reactions of the oxides of group 2 elements with water and dilute acids and their hydroxides with dilute acid.
- Describe the trends in the thermal decomposition of group 2 carbonates and nitrates.
- Describe the trends in solubility of the hydroxides and sulphates of group 2.
- Describe the uses of a variety of compounds of group 2 e.g. the use of calcium hydroxide in agriculture, magnesium hydroxide as an antacid, barium sulphate in medicine and calcium carbonate in making cement.

(d) Group 17 – The Halogens

- Describe the trends in electronegativity and boiling points of the halogens.
- Describe the reactions of potassium halides with concentrated sulphuric acid.

- Describe the reactions of halide ions with silver ions and describe the trends in solubility of the silver halides in diluted and concentrated ammonia as a test for halide ions in solution.
- Describe the disproportionation reactions of chlorine, bromine and iodine with water, cold and hot alkali and outline the uses of the solutions formed.
- State the uses of chlorine, e.g. its use in water treatments and its harmful effects (e.g. the toxic hazards of chlorine gas).
- Make predictions about fluorine and astatine and their compounds based on the trends in the physical and chemical properties of the halogens.

(iii) Chemical kinetics

(a) Factors which influence the rate of reaction

- State the factors that affect the rate of reaction, e.g. concentration, temperature, pressure, surface area of a solid and catalysts.
- Explain the changes in rate from the effects of concentration, pressure, temperature, surface area using collision theory.
- Explain qualitatively the Maxwell Boltzmann distribution of molecular energies and its relationship to activation energy.
- Explain qualitatively the effect of temperature changes on the rate of reaction using the Maxwell Boltzmann model of the distribution of molecular energies.
- Explain using enthalpy level profile diagrams that a catalyst speeds up a chemical reaction by allowing it to proceed via lower activation energy.
- Explain catalytic behaviour in terms of the Maxwell Boltzmann model of the distribution of molecular energies.
- Explain the benefits of using catalysts, e.g. catalysts in reducing energy demands, enzymes generating specific products; Ziegler-Natta catalyst in the production of polyethene and platinum or palladium or rhodium.

(iv) Equilibria

(a) Chemical equilibria

- Give examples of chemical reactions that are reversible.
- Explain the dynamic nature of a reaction in equilibrium as applied to states of matter, solutions and chemical reactions.
- Apply Le Chatelier's principle to predict the effects of changes in concentration, pressure and temperature on the position of equilibrium in homogenous reactions.
- Explain that a catalyst speeds up the attainment of an equilibrium but not its position.
- Deduce expressions for homogeneous and heterogeneous reactions for the equilibrium constant K_c and K_p from equilibrium concentrations or equilibrium partial pressures.
- Calculate the values of K_c and K_p and state the units of K_c and K_p.
- Explain the effects of the changing temperature on the value of K_c and K_p for exothermic and endothermic reactions.
- State that the value of K_c or K_p is unaffected by changes in concentration, pressure or by the presence of a catalyst.
- Apply the concepts of equilibria, kinetics and economics to industrial processes like the Haber Process to explain that particular reactions conditions are adopted.

(b) Phase equilibria

- Explain the term vapour pressure and its measurement and that it is affected by temperature.
- Describe the relationship between vapour pressure and boiling point.
- Explain the meaning of the term ideal solution.
- Describe influence on the vapour pressure of an ideal solution by its composition.
- Convert boiling point and composition curves into vapour pressure and composition curves.
- Classify two component mixtures as ideal or showing positive or negative deviation from an ideal solution.
- Explain positive and negative deviations from an ideal solution in terms of intermolecular forces.
- State Raoult's law and express it mathematically.
- Demonstrate that vapour pressure and composition curves can be constructed from a knowledge of Raoult's law and Dalton's law of partial pressures.
- Draw a vapour pressure and composition and a boiling point and composition diagram for an ideal solution showing the compositions of the liquid and vapour.
- Explain the term phase diagram.
- Explain the principles for fractional distillation for ideal solutions.
- Draw phase diagrams for non-ideal mixtures showing gross positive and negative deviation.
- Explain the term azeotropic mixture (for constant boiling mixtures).
- Explain that mixtures showing gross positive and negative deviations cannot be separated by fractional distillation.
- State Raoult's law for dilute solutions of non-volatile solutes.

Assessment

Assessment in science involves detailed process of measuring students' achievement in terms of knowledge, skills, and attitude. The progress of learning is inferred through analysis of information collected. The accuracy and objectivity of assessment determines its validity. The modality and components of assessment should be clearly conveyed to the students. The teacher's expectations should be made clear to students and appropriate learning outcomes should be set. The teachers can play an important role in the students' achievement by effectively monitoring their learning, and giving them constructive feedback on how they can improve, and provide the necessary scaffolding for the needy learners as identified through reliable assessment techniques and tools.

PURPOSE OF ASSESSMENT

Assessment is used to:

- **Inform and guide teaching and learning:** A good assessment plan helps to gather evidences of students' learning that inform teachers' instructional decisions. It provides teachers with information about the performance of students. In addition to helping teachers formulate the next teaching steps, a good classroom assessment plan provides a road map for students. Therefore, students should have access to the assessment so they can use it to inform and guide their learning.
- **Help students set learning goals:** Students need frequent opportunities to reflect on what they have learnt and how their learning can be improved. Accordingly, students can set their goals. Generally, when students are actively involved in assessing their own next learning steps and creating goals to accomplish them, they make major advances in directing their learning.
- **Assign report card grades:** Grades provide parents, employers, other schools, governments, post-secondary institutions and others with summary information about students' learning and performances.
- **Motivate students:** Students are motivated and confident learners when they experience progress and achievement. The evidences gathered can usher poor performers to perform better through remedial measures.

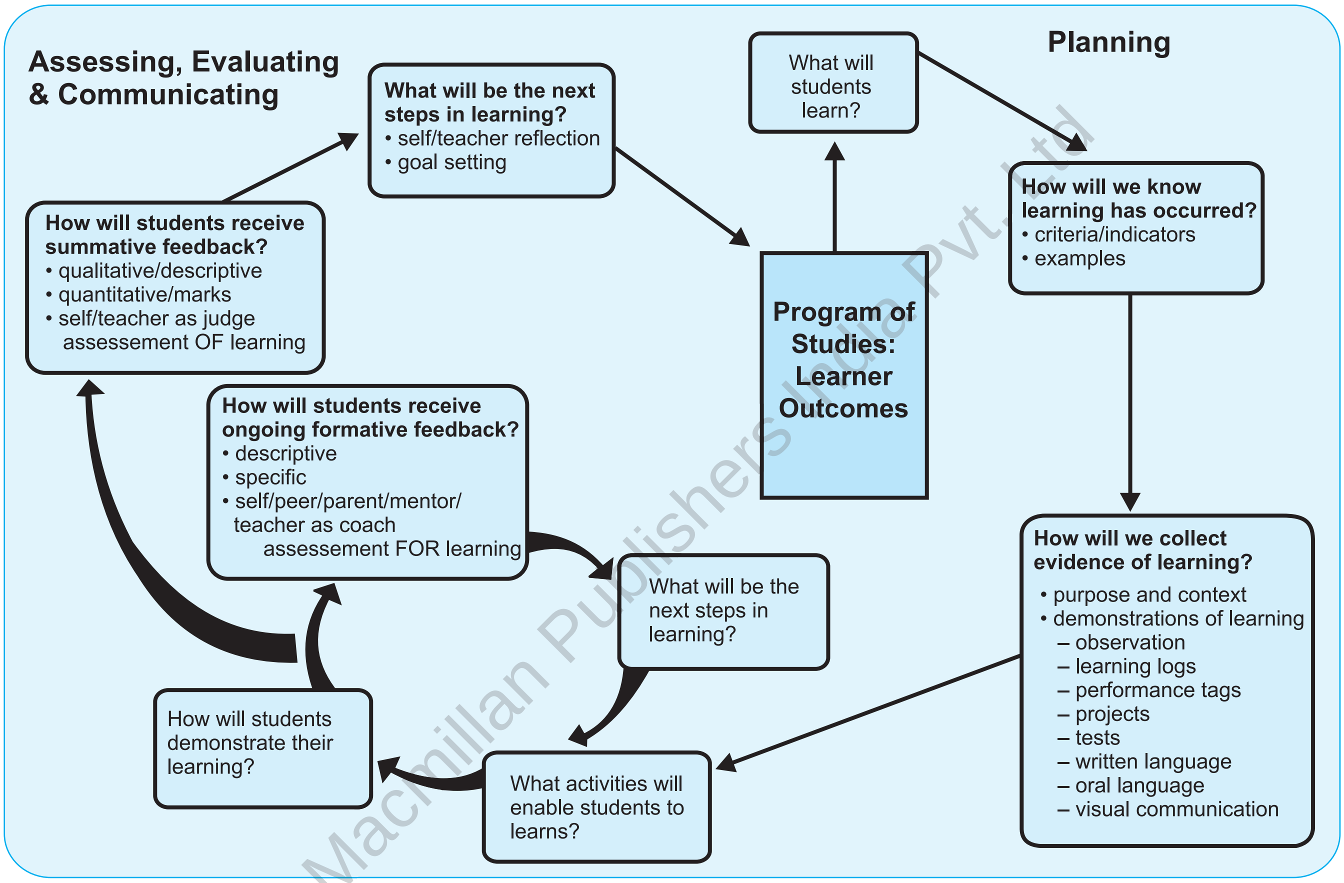
The achievements and performances of the learners in chemistry are assessed on the following three domains:

- **Scientific knowledge:** Basic knowledge and understanding of formation of substances with varying properties; hydrocarbons and their uses; reactivity series of metals that influence their properties; patterns in the periodic table with focus on group 1 and group 0 elements; chemical reactions, their kinetics and energy transfer; Biogeochemical cycles, and the impact of toxic chemicals on the environment and the community.
- **Working scientifically:** Basic understanding of the nature of science, and how science works. Demonstration of logical and abstract thinking and comprehension of complex situations. Explore how technological advances are related to the scientific ideas underpinning them. Compare, contrast, synthesize, question and critique the different sources of information, and communicate their ideas clearly and precisely in a variety of ways, including the use of ICT.
- **Scientific values and attitudes:** Consider the power and limitations of science in addressing social, industrial, ethical and environmental issues, and how different groups in the community and beyond may have different views about the role of science. They make informed judgments on statements and debates that have a scientific basis, and use their learning in science for planning positive action for the welfare of themselves, others in their community and the environment.

The Assessment Process

Effective classroom assessment in Science:

- assesses specific outcomes in the program of studies.
- the intended outcomes and assessment criteria are shared with students prior to the assessment activity.
- assesses before, during and after instruction.
- employs a variety of assessment strategies to provide evidence of students' learning.
- provides frequent and descriptive feedback to students.
- ensures students can describe their progress and achievement, and articulate what comes next in their learning.
- informs teachers and provides insight that can be used to modify instruction.



Scheme of Assessment in Chemistry

The following schemes of assessment are used to assess students' performance:

1. *Continuous Formative Assessment (CFA)*

   Formative assessment is used to provide feedback to teachers and students, so that teaching and learning can be improved through the provision of regular feedback and remedial learning opportunities. It also enables teachers to understand what teaching methods and materials work best.

   CFA facilitates teachers to diagnose the learning needs of learners and recognize the individual differences in learning. Through the constructive feedback, students are able to understand their strengths and weaknesses. It also empowers them to be self-reflective learners, who monitor and evaluate their own progress.

   CFA should happen daily throughout the teaching-learning processes of the academic year. It is NOT graded, as it is only to give continuous feedbacks to the students.

2. *Continuous Summative Assessment (CSA)*

Continuous Summative Assessment is another form of continuous assessment (CA). It helps in determining the student's performance and the effectiveness of instructional decisions of teachers. The evidences from this assessment help students to improve learning, and mandate teachers to incorporate varied teaching strategies and resources to ensure quality teaching and learning in the science classes. This assessment also empowers students to be self-reflective learners, who monitor and evaluate their own progress.

In CSA, the students' performances and achievements are graded. This ensures active participations of learners in the teaching and learning processes.

3. *Summative Assessment (SA)*

Summative assessment (SA) is conducted at the end of the first term and at the end of the year to determine the level of learning outcomes achieved by students. The information gathered is used by teachers to grade students for promotion, and to report to parents and other stakeholders.

The identified techniques for SA are term examinations - first term and annual examinations. The questions for the term examinations should cover all the three domains of science learning objectives, using the principles of Bloom's taxonomy.

Assessment Matrix

Types of assessment	CFA			CSA			SA	
Definition	It is a continuous process of assessing student's problems and learning needs and to identify the remedial measures to improve student's learning. It also enables teachers to understand what teaching methods and materials work best.			It is a continuous process of grading student's performances and achievements. Teachers provide feedbacks for improvement. It also enables teachers to understand what teaching methods and materials work best.			Assesses student's cumulative performances and achievements at the end of each term.	
Domains	Scientific knowledge (SK)	Working scientifically (WS)	Scientific values and attitudes (SV)	Scientific knowledge (SK)	Working scientifically (WS)	Scientific values and attitudes (SV)	SK, WS & SV	SK, WS & SV
Techniques	Quiz and debate, class presentation, homework, class work, immediate interaction with students.	Immediate interaction with students, class work, home work, experiments, exhibition, case studies.	Observation of student's conduct, in group work, field trip, excursion, etc.	Class test	Practical work	Project work	Term exam.	Term exam.
Assessment Tools	Q&A, checklist and anecdotal records.	Checklist and anecdotal records.	Checklist and anecdotal records.	Paper pencil test	Rubrics (Practical work)	Rubrics (Project work)	Paper pencil test	Paper pencil test
Frequency interval (when and how)	Checklists and anecdotal records must be maintained for each topic throughout the academic year.			HW-for every chapter, Chapter end test – for every chapter.	Twice in each term	Project work – [One PW for Cl 11 and 12 but assessed in each year]	Once in a term.	Once in a year.
Format in Progress Report				SK	WS	SV	Mid-Term	Annual Exam
Weightings				T1 = 2.5 T2 = 2.5	T1 = 15 T2 = 15	T1 = 2.5 T2 = 2.5	T1 = 20	T2 = 40
NB:	1. Same mode of assessment will be followed in Mid Term and Trial examinations for Class 12. 2. The mark for the Project Work of Class 12 is the sum total of Cl 11 and 12, which is out of 10 (5+5). 3. The Cl 12 Practical Examination (20) is assessed externally.							

Assessment Techniques and Tools

The following techniques and tools are used in assessing students' performances with objectivity.

(a) Observation Checklist

Observing students as they solve problems, model skills to others, think aloud during a sequence of activities, or interact with peers in different learning situations provides insight into student's learning and growth. The teacher finds out under what conditions success is most likely, what individual students do when they encounter difficulty, how interaction with others affects their learning and concentration, and what students need to learn next. Observations may be informal or highly structured, and incidental or scheduled over different a period in different learning contexts.

Observation checklists are tools that allow teachers to record information quickly about how students perform in relation to specific outcomes from the program of studies. Observation checklists, written in a yes/no format can be used to assist in observing student performance relative to specific criteria. They may be directed toward observations of an individual or group. These tools can also include spaces for brief comments, which provide additional information not captured in the checklist.

Tips for using Observation Checklists

(i) Determine specific outcomes to observe and assess.

(ii) Decide what to look for. Write down criteria or evidence that indicates the student is demonstrating the outcome.

(iii) Ensure students know and understand what the criteria are.

(iv) Target your observation by selecting four to five students per lesson and one or two specific outcomes to observe. Date all observations.

(v) Collect observations over a number of lessons during a reporting period and look for patterns of performance.

(vi) Share observations with students, both individually and in a group. Make the observations specific and describe how this demonstrates or promotes thinking and learning.

(vii) Use the information gathered from observation to enhance or modify future instruction.

Sample Checklist

Name	Topic: Chemical Kinetics									Teacher's comments
	Scientific knowledge			Working scientifically			Scientific values			
	States the factors affecting rate of chemical reaction	Explains enthalpy profile diagrams of chemical reaction involving catalyst.	Explain the applications of the concept of kinetics in industrial processes.	Follows correct experimental procedures.	Chooses appropriate equipment and chemical for the experiment.	Demonstrates ability to control variables.	Appreciates the benefits of using catalyst in daily life activities	Shows curiosity to learn science by engaging in group activities.	Demonstrates concern for oneself, others and the environment.	
Rinchen										
Ugyen										
Pramod										
Choden										

(b) Anecdotal Notes

Anecdotal notes are used to record specific observations of individual student **behaviours, skills, and attitudes** in relation to the outcomes of the science teaching and learning process. Such notes provide cumulative information on students' learning and direction for further instruction. Anecdotal notes are often written as ongoing observations during the lessons, but may also be written in response to a product or performance of the students. They are generally brief, objective, and focused on specific outcomes. The notes taken during or immediately following an activity are generally the most accurate. Anecdotal notes for a particular student can be periodically shared with the student, or be shared at the student's request.

The purpose of anecdotal notes is to:

- provide information regarding a student's development over a period of time.
- provide ongoing records about individual instructional needs.
- capture observations of significant behaviours that might otherwise be lost.

Tips for maintaining Anecdotal Notes

(i) Keep a notebook or binder with a separate page for each student. Write the date and the student's name on each page of the notebook.
(ii) Following the observations, notes are recorded on the page reserved for that student in the notebook.
(iii) The pages may be divided into three columns: Date, Observation and Action Plan.
(iv) Keep notes brief and focused (usually no more than a few sentences or phrases).
(v) Note the context and any comments or questions for follow-up.
(vi) Keep comments objective. Make specific comments about student strengths, especially after several observations have been recorded and a pattern has been observed.

(c) Project Work

Project work is one of the best ways to practice the application of scientific conceptual ideas and skills. The very purpose of including project work is to provide opportunity to explore and extend their scientific knowledge and skills beyond the classroom. Students learn to organize, plan and piece together many separate ideas and information into a coherent whole. Through project work, students learn various scientific techniques and skills, including data collection, analysis, experimentation, interpretation, evaluation and drawing conclusion; and it fosters positive attitude towards science and environment.

The science curriculum mandates students to carryout project work to help them to:

(i) develop scientific skills of planning, designing and making scientific artefacts, carrying out investigations, observation, analysis, synthesis, interpretation, organization and recording of information.
(ii) enhance deeper understanding of social and natural environment.
(iii) develop student's ability to work in group and independently.
(iv) provide opportunity to explore beyond the classroom in enhancing their scientific knowledge and skills, which will contribute towards the development of positive attitudes and values towards science and environment.
(v) understand how science works and the nature of scientific knowledge.
(vi) develop oral and written communication skills.

Teachers can facilitate students to carry out the project work by considering the following suggested guidelines.

- Allow students to select their own project ideas and topics.
- Encourage students to be scientifically creative and productive.

- Provide a clear set of guidelines for developing and completing projects.
- Help students to locate sources of information, including workers in science-related fields who might advise them about their projects.
- Allow students the option of presenting their finished projects to the class.
- Inform students about the general areas on which assessment may be made. For example, scientific content or concepts, originality of ideas, procedures, and the presentation.
- Advice students to contact their teacher for further assistance or consultations, for, students must be closely guided by the teacher starting from the selection of the topic, doing investigations, data collection, and analysis to writing report in a formal style.

At the end of the project work, every student must prepare a project work report, about 2000 to 2500 words, in the formal format, suggested in the following section. The product of the project work must be inclusive of write ups, illustrations, models, or collection of real objects.

Each student is assigned a Project Work for the academic year. The project work is assessed out of 28 points, which should be converted to 5 marks for the whole year. Students can share their project work findings, either in the form of class presentation or display.

Following are some of the useful steps that students may follow.

1. *Select a topic for the science project*

The first step in doing science project is selecting a topic or subject of your interest. Teachers guide students in identification and selection of the topic. The concerned teacher has to approve the topic prior to the commencement of the project work.

2. *Gather background information*

Gather information about your topic from books, magazine, Internet, people and companies. As you gather information, keep notes from where you got the information as reference list.

3. *Write your hypothesis*

Based on your gathered information, design a hypothesis, which is an educated guess in the form of a statement, about what types of things affect the system you are working with. Identifying variables is necessary before one can make a hypothesis. For example, the rate of a chemical reaction is affected by the size of particles of reactants. Develop a research question supported by a few questions to test your hypothesis. For example, how does the particle size affect the rate of a chemical reaction? Sub-questions may include, what is the reaction rate when granulated forms of reactants are used? What happens to the reaction rates when powdered reactants are used?

4. *Identify variables*

The hypothesis and the research questions should guide you to identify the variables. When you think you know what variables may be involved, think about ways to change one at a time. If you change more than one at a time, you will not know what variable is causing your observation. Sometimes, variables are linked and work together to cause something. At first, try to choose variables that you think act independently of each other.

5. *Design an experiment or observation method*

Having made the hypothesis, design an experiment to test the hypothesis and devise the method of observation. Make a systematic list of what you will do or observe to answer each question. This list is known as experimental or observational procedure. For observations or an experiment to give answers, one must have a 'control'. A control is a neutral 'reference point' for comparison that allows you to see what changing or dependent variable does by comparing it to not changing anything. Without a control, you cannot be sure what variable causes your observations.

6. *Write a list of material*

Make a list of materials useful to carry out your experiment or observations.

7. *Write experiment results*

Experiments are often done in series. A series of experiments can be done by changing one variable at a time. A series of experiments are made up of separate experimental "runs". During each run, you make a measurement of how much the variable affected the system under the study. For each run, a different amount of change in the variable is used. This produces a different degree or amount of responses in the system. You measure these responses and record data in a table form. The data from the experiments and observations are considered as a "raw data" since it has not been processed or interpreted yet. When raw data is processed mathematically, for example, it becomes result.

8. *Write a summary of the results*

Summarize what happened. This can be in the form of a table of processed numerical data, or graphs. It could also be a written statement of what occurred during experiments. It is from calculations using recorded data that tables and graphs are made. Studying tables and graphs, one can see trends or patterns that tell you how different variables cause to change the observations. Based on these trends, you can draw conclusions about the system under the study. These conclusions help to confirm or deny your original hypothesis. Often, mathematical equations can be made from graphs. These equations can help you to predict how a change will affect the system without the need to do additional experiments. Advanced levels of experimental science rely heavily on graphical and mathematical analysis of data. At this level, science becomes even more interesting and powerful.

The **Format for Project Work** write-up (report) should include the following aspects:

- The title of the project work.
- Acknowledgement: Show courtesy to thank the people and organizations for the help received.
- Table of content.
- Introduction: What is the topic about, and why was the topic chosen? hypothesis, research question.
- Background information: Scientific concepts, principles, laws and information on the topic.
- Methodology: Methods of data collection – sampling, tools used, etc; data sorting.
- Data analysis: Data tabulation, data processing, findings, etc. presented in a logical order with illustrations, photographs, and drawings where appropriate and necessary to support the findings.
- Conclusion: Reflection of the findings, learner's experiences and opinions regarding the project.
- Bibliography: List of the sources of the information.

9. *Draw conclusions*

Using the trends in your experimental data and your experimental observations, try to answer your original questions. Is your hypothesis correct? Now is the time to pull together what happened in the form of conclusion, and assess the experiments you did. Describe, how variables have affected the observations, and synthesize a general statement. For example, the rate of chemical reaction increases with increase in surface area of reactants.

10. *Write a report on the project*

Having completed all the steps of experiment and investigation with appropriate results and conclusion drawn, the last thing is to write a report. The report should start with an introduction on the topic related to your hypothesis, purpose of the study, literature review, methods used, findings, and conclude with conclusions. Do not forget to acknowledge the support provided by all individuals and organizations. Write a bibliography to show your references in any form. Such information includes the form of document, name of writer, publisher, and the year of publication.

The teacher uses the 'Rubric for the Project Work' given below to assess the student's project work. Random viva voce is necessary to guide and support students' work during the course of project work.

Criteria for the Project Work

Name	Criteria						Bibliography (4)	Total scores (28)
	Problem and hypothesis (4)	Background research on the hypothesis (4)	Experimental design / materials / procedure (4)	Investigation (4)	Analysis (4)	Format and editing (4)		
Nima								
Dawa								
……..								

(Name & Signature of HOD)	**(Name & Signature of Subject Teacher)**

Rubrics for the Project Work

Name: .... R. No: ..../ .... Class section: ..../ ....

Criteria	Scoring				Total Score (28)	Remarks
	4	3	2	1		
Problem and Hypothesis	• Problem is new, meaningful and well researched. • Hypothesis is clearly stated in the "IF...THEN" format.	• Problem is not new but meaningful. • Hypothesis is clearly stated.	• Problem is stated but neither new nor meaningful. • Hypothesis is not clearly stated.	• Problem is not stated and • Hypothesis is unclear.		Cl 11 Term 1
Background research on the hypothesis	• Research is thorough and specific. • All the ideas are clearly explained.	• Research is thorough but not specific. • Most ideas are explained.	• Research is not thorough and not specific. • Few ideas are explained.	• Research not thorough and • Ideas are not explained.		
Experimental design / materials / procedure	• Procedure is detailed and sequential. • All materials are listed. • Safety issues have been addressed.	• Procedure is detailed but not sequential. • Most materials are listed. • Safety issues have been addressed.	• Procedure is not detailed and not sequential. • Few materials are listed. • Few safety issues have been addressed.	• A few steps of procedure are listed. • Materials list is absent. • Safety issues are not addressed.		Cl 11 Term 2
(Name & Signature of HOD)		**(Name & Signature of Subject Teacher)**		**Total score for Cl 11**		

Criteria	Scoring				Total Score (28)	Remarks
	4	3	2	1		
Investigation	• Variables have been identified, controls are appropriate and explained. • Sample size is appropriate and explained. • Data collected from at least 4 sources.	• Variables have been identified and controls are appropriate but not explained. • Sample size is appropriate. • Data collected from at least 3 sources	• Variables have somewhat been identified, controls are somewhat known. • Sample size is not appropriate. • Data collected from at least 2 sources.	• Missing two or more of the variables or the controls. • Sample size is not considered. • Data collected from only 1 source.		Cl 12 Term 1
Analysis & conclusion	• Appropriate tool used for analysis. • Explanation is made for how or why the hypothesis was supported or rejected. • Conclusion is supported by the data. • Reflection is stated clearly.	• Appropriate tool used for analysis. • Conclusions are supported by the data. • Not enough explanation is made for how or why the hypothesis was supported or rejected. • Reflection is stated.	• No appropriate tool used for analysis. • Not enough explanation is made for how or why the hypothesis was supported or rejected. • Conclusion is not appropriate. • Reflection is not clear.	• No appropriate tool used for analysis. • Not enough explanation is made for acceptance and rejection of hypothesis. • Conclusion is absent. • Reflection is not stated.		
Format and editing	• Correct format followed throughout. • Report is free of errors in grammar, spelling or punctuation.	• Only one aspect of format is incorrectly done. • Report contains a few errors in grammar, spelling, and punctuation.	• Only two aspects of format are incorrectly done. • Report contains some errors in grammar, spelling, punctuation	• Three or more aspects of format are missing. • Report contains many errors in grammar, spelling, and punctuation.		Cl 12 Term 2
Bibliography	• Five or more references are cited in APA format and referenced throughout the paper and presentation.	• Three or four references are cited and referenced throughout the paper and presentation.	• One or two references are cited and referenced throughout the paper and presentation.	• No references made.		
				Total score for Cl 12		
(Name & Signature of HOD)		**(Name & Signature of Subject Teacher)**		**Grand Total (10)**		This is the mark for PW in Cl 12.

(d) *Practical Work*

Learning by doing is fundamental to science education. Practical work is one of the means that helps students to develop their understanding of science, appreciate that science is evidence driven and acquire hands-on skills that are essential to science learning and in their future lives. The practical work as defined by SCORE (2009a) is '*a "hands-on" learning experience which prompts thinking about the world in which we live*'.Therefore, the purposes of doing practical in science classes are to:

(i) help students to gain or reinforce the understanding of scientific knowledge.

(ii) develop students' understanding of the methods by which the scientific knowledge has been constructed.

(iii) increase a student's competence to engage in scientific processes such as in manipulating and/or observing real objects and materials with due consideration for safety, reliability, etc.

(iv) develop technical and scientific skills that improve science learning through understanding and application.

(v) develop manipulative skills, knowledge of standard techniques, and the understanding of data handling.

(vi) Inculcate excitement of discovery, consolidation of theory, and the general understanding of how science works.

Practical work is integral to the aspects of thinking and working scientifically in science, and must be built in as a full learning experience for students. Students are engaged in a range of practical activities to enable them to develop their understanding through interacting with apparatus, objects and observations.

The assessment of students' scientific skills and their understanding about the scientific processes through practical work is crucial in the process of science learning. To ensure the validity, assessment needs to sample a range of activities in different contexts; and reliability is ensured through the appropriate moderation procedures so that fairness in assessment is maintained.

The new science curriculum envisages that students are given the opportunity to undertake work in which they make their own decisions. They should be assessed on their ability to plan, observe, record, analyze, communicate and evaluate their works.

To ensure that the assessment in the practical is evidence-based and objective, rubrics is used. The rubrics are scored out of 16, which must be reduced to 5% each for the two terms.

Criteria for the Practical Work

Name	Criteria				Practical records (4)	Total Score (20)
	Scientific operation & report format (4)	Results & data representation (4)	Analysis & discussion (4)	Conclusions (4)		
Sonam						
Wangmo						

Rubrics for the Practical Work

Criteria	Scoring				Total Score (20)
	4 (Very good)	3 (Good)	2 (Fair)	1 (Poor)	
Scientific operation	• Purpose is clear purposeful. • All the procedures are followed systematically. • Full attention is given to relevant safety for oneself and others.	• Purpose is clear purposeful. • All the procedures are followed but not done systematically. • Work is carried out with some attention to relevant safety procedures.	• Purpose is inaccurate, general or extraneous. • A few procedures are skipped. • Safety procedures were frequently ignored.	• Purpose is vague or inaccurate. • Procedures are not followed. • Safety procedures are ignored completely.	
Results & data representation	• Representation of the data/results in tables and graphs with correct units of measurement. • Transformations in the results/data are evident. • Graphs and tables are scaled correctly, with appropriate titles and labels.	• Representation of the data/results in tables and graphs with some error in units of measurement. • Transformations in some of the results/data are evident. • Graphs and tables are scaled correctly with appropriate titles but no labels.	• Representation of the data/results in tables and graphs numerous error in units of measurement. • Transformations in most of the results/data are not evident. • Graphs and tables are scaled correctly, but without appropriate titles and labels.	• Representation of the data/results in tables and graphs are not relevant. • Transformations in the results/data are not evident. • Some attempts are evident to produce graphs from the data/results.	
Analysis & discussion	• All the tools used for analysis are appropriate. • A comprehensive discussion, containing a comparative analysis is evident. • The experimental findings are significant to the purpose of the experiment.	• Most of the tools used for analysis are appropriate. • A comprehensive discussion, containing some comparative analysis is evident. • The experimental findings do not have strong significance to the purpose of the experiment.	• Only a few tools are used for analysis. • A comprehensive discussion, containing a few comparative analysis is evident. • The experimental findings have weak significance to the purpose of the experiment.	• No appropriate tools are used for analysis. • Comprehensive discussion is absent. • The experimental findings have no significance to the purpose of the experiment.	
Conclusions	• Conclusions are drawn from the findings and are significant to objectives of the experiment. • Limitations of experiment are identified, and ways to improve are evident.	• Conclusions are drawn from the findings but less significant to objectives of the experiment. • Limitations of experiment are identified.	• Conclusions are not drawn from the findings and have no significance to objectives of the experiment. • Some limitations of experiment are identified.	• No valid conclusions drawn from the findings. • Limitations of experiment are not identified.	
Practical records	• All the components of the practical work are evident • Practical records are clean and free of grammar & spelling errors.	• A few of the components of the practical work are absent. • Records are clean and contains minor grammar & spelling errors.	• A few components of the practical work are present and not sequenced. • Records are clean and contains numerous grammar & spellings errors.	• Most of the components of the practical work are absent. • Records are untidy and full of grammar & spelling errors.	
				TOTAL SCORE	

Chapter-wise Weighting and Time allocation

Chapters	Chapter title	Maximum time required (mins)	Weighting (%)
Chapter 1	Atomic Structure	525	8%
Chapter 2	Periodic Table	575	9%
Chapter 3	Chemical Bonding	625	10%
Chapter 4	Oxidation Numbers	200	3%
Chapter 5	Group 2 Alkaline Earth Metals	225	4%
Chapter 6	Group 17 The Halogens	225	4%
Chapter 7	Chemical Kinetics	500	8%
Chapter 8	Chemical Equilibria	575	9%
Chapter 9	Phase Equilibria	600	10%
Chapter 10	Introduction to Organic Chemistry	575	9%
Chapter 11	Hydrocarbons: Alkanes, Alkenes, Alkynes	625	10%
Chapter 12	Haloalkanes	250	4%
Chapter 13	Alcohols	200	3%
Chapter 14	Aromatic Compounds (Benzene and Phenol)	400	6%
Chapter 15	Green Chemistry	150	2%
	Total	6250	100%

The total time required to complete the topics is 6250 minutes or 125 periods of 50 minutes in a period.

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15. GREEN CHEMISTRY 548–562

Introduction to Chemistry

SCOPE AND APPLICATIONS OF CHEMISTRY

Chemistry is present in every aspect of life. Chemistry explains how food changes as we cook it and how it rots. With the knowledge of chemistry, we know how to preserve food, or how our body uses the food that we eat and how different ingredients interact to make food. Our body is made up of chemical compounds, which are combinations of elements. A major part of our body is water which is a combination of hydrogen and oxygen.

Chemistry explains how the process of cleaning works. We use our knowledge of chemistry when we have to decide which cleaner is the best for dishes, laundry, ourself and our home. The use of bleaches, disinfectants, and ordinary soaps and surfactants is dependent on the chemical principles. It is important to understand basic chemistry to know how vitamins, supplements and drugs can help us to lead a healthy life. Importance of chemistry lies in developing and testing new medical treatments and medicines.

Chemistry is at the heart of environmental issues. Chemical reactions occur when we breathe or eat. All matter is made up of chemicals, so the importance of chemistry is that it is the study of everything. We need to think what makes one chemical as a nutrient and the other chemical a pollutant. We need to think which processes produce the things that we require without harming the environment. Forensic science which is the comprehensive scientific analysis of material evidence, uses the principles of chemistry to help in crime investigation. Lately, the chemistry of semiconductors and nanotubes has been used in telecommunication, information technology and space missions.

The famous green revolution to increase agricultural produce so as to feed everybody on the earth was possible with the development of inorganic fertilizers. Farmers have been using these fertilizers in their fields to restore the fertility of the soil. Pesticides, again chemicals are extensively used to protect the crops from pests, rats and mice. Genetically modified seeds are being developed to enhance production of cereals, vegetables and fruits and earn profits through export to other countries. Refrigeration techniques have made it possible to increase the shelf life of meat, poultry products, fruits and vegetables and have facilitated transport of these products to distant places in refrigerated vehicles.

Branches of Chemistry

Originally, chemistry used to be studied as inorganic chemistry, organic chemistry and physical chemistry. But, with the explosion of information on different topics, the number of branches of the subject for instruction at graduate level and research has increased. We shall describe here some of the important branches of chemistry:

Inorganic Chemistry: It is the study of properties and reactions of inorganic and organometallic compounds. The extraction of various metals and non-metals from their ores is studied under this branch.

Organic Chemistry: It is the study of structure, properties, composition, mechanisms and reactions of compounds of carbon. An organic compound is defined on the basis of carbon skeleton present in it.

Physical Chemistry: It is the study of physical properties of chemical systems and processes of interest to physical chemists. Important areas include chemical thermodynamics, chemical kinetics, chemical equilibrium, electrochemistry, spectroscopy and surface properties.

Besides the above main branches, we have biochemistry, analytical chemistry, polymer chemistry, materials chemistry, etc.

Methodology: Interactive teaching methods may be employed which include lectures, mentoring work, independent study of the students, laboratory exercises, seminars, paper presentations and consultations. Use of models of organic and inorganic molecules is recommended. Experiments based on a particular topic in theory may be carried out just after the topic has been completed. Visit to industrial units manufacturing cement, glass, rubber, plastics and iron. Aluminium and copper extracting units are encouraged.

Misdeeds of Chemists: Generations in Japan have suffered the devastation caused by the destructive effects of atom bombs dropped on Hiroshima and Nagasaki. Looming large is the threat of weapons of mass destruction like nuclear, chemical and biological weapons. Terrorists are using RDX and other explosives to spread fear in the humans around the globe. Nuclear reactors which will remain the only future mode of power supply (as fossil fuels are fast dwindling) leave us with the problem of nuclear waste management.

1

CHAPTER

Atomic Structure

LEARNING OBJECTIVES

- Nuclear structure
    - Describe a proton, a neutron and an electron in terms of relative charge and relative mass.
    - Describe the structure of the nucleus of an atom and the arrangement of protons and neutrons in the nucleus.
    - State that the atomic number of an element is the number of protons in the nucleus and the mass number is the number of protons plus the number of neutrons.
    - Calculate the number of protons, neutrons and electrons in an atom using given atomic number and mass number.
    - Explain an isotope in terms of atoms of the same element with different numbers of neutrons in the nucleus.
    - State that ^{12}C is used as the standard measurement of relative masses.
    - Define the term relative atomic mass based on the ^{12}C isotope.
    - Calculate the relative atomic mass of an element when the relative abundances of its isotopes is given.
    - Calculate relative molecular mass and relative formula mass from relative atomic masses.
- Electron structure
    - State the definitions of first ionisation energy and successive ionisation energies.
    - Explain that the values of ionisation energies are influenced by nuclear charge, electron shielding and the distance of the outermost electrons from the nucleus.
    - Predict, from successive ionisation energies, the number of electrons in each shell of an atom and the group to which the element belongs.
    - State the number of electrons that fill the first four quantum shells.
    - Explain that an orbital is a region that holds up to two electrons which have opposite spins.
    - Describe the shapes of *s*-orbital, *p*-orbital and *d*-orbital.
    - State the number of orbitals making up *s*-subshell, *p*-subshell and *d*-subshell and the number of electrons that occupy *s*-subshell, *p*-subshell and *d*-subshell.
    - Describe the relative energies of *s*-orbitals, *p*-orbitals, and *d*-orbitals for the quantum levels 1, 2, 3 and the 4*s*- and 4*p*-orbitals.
    - Deduce the electron configurations of the atoms of elements up to atomic number 36.
    - Classify elements as *s*-block, *p*-block or *d*-block elements.

1.1 INTRODUCTION

The laws of chemical combination led Dalton to give his views on atom. He regarded atom as the ultimate particle of matter which cannot be further sub-divided. But later investigations proved that atom is not the ultimate particle of matter. It was found that atom can be further broken into *electrons, protons* and *neutrons*. Electron is a negatively charged particle with a negligible mass. Protons and neutrons are positively charged and neutral particles respectively with almost equal masses. Protons and neutrons are present together in a space called **nucleus** which forms the central part of the atom with electrons revolving around it in certain orbits. The size of the nucleus is very small compared to the size of the atom and the rest of the space is occupied by electrons.

A clue to the electrical nature of the atom and its constituents was provided by early experiments in which glass and ebonite rods rubbed with silk and fur respectively produced electricity of positive and negative charges respectively.

Becquerel, in 1900, during his studies on the phenomenon of radioactivity also came to the same conclusion. He discovered that radioactive substance emits continuously α, β and γ particles. The α-particles were later identified as helium nuclei and β-particles as electrons.

The concept that atom is not the ultimate particle of matter was reported first by Faraday in his electrolysis experiments. During electrolysis the ions of the substance moved towards the oppositely charged electrodes and were deposited there. Systematic discovery of various constituents of matter is explained below:

1.2 DISCOVERY OF ELECTRONS

Julius Plucker, in 1859, observed that gases which otherwise do not conduct electricity, do so when a high voltage is applied to the electrodes fitted in the cylinder containing a gas at low pressure. The apparatus used is called *discharge tube* (Fig. 1.1). It is a 60 cm long glass tube with electrodes sealed at both ends. There is a provision for evacuating and thus reducing the pressure of the gas. On passing a high voltage current, some rays are produced by the cathode and move towards the anode. These were called *cathode rays* which were later identified as electrons. J.J. Thomson studied the properties of these rays which are explained below:

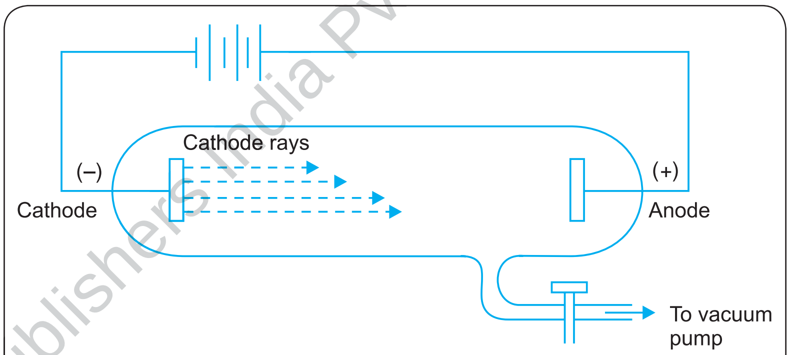


Fig. 1.1: *Production of cathode rays*

1.2.1 Properties of Cathode Rays

(*i*) **Cathode rays travel in a straight line.** These rays cast a shadow of the object which comes in their path (Fig. 1.2). This is a property of light which travels in a straight line. Thus, cathode rays also travel in a straight line and they do so with the velocity of light, *i.e.* 3×10^8 metre per second.

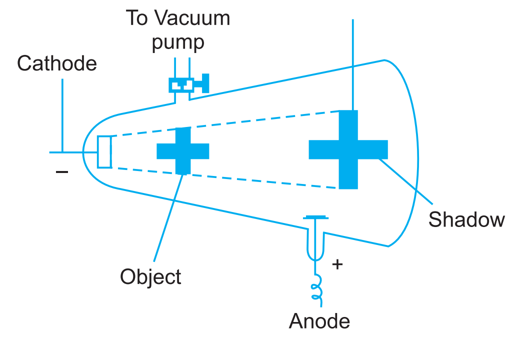


Fig. 1.2: *Cathode rays travel in a straight line*

(*ii*) **They consist of material particles.** If a light paddle wheel is placed in the path of the rays, the wheel begins to rotate (Fig. 1.3). This proves that cathode rays are constituted of material particles.

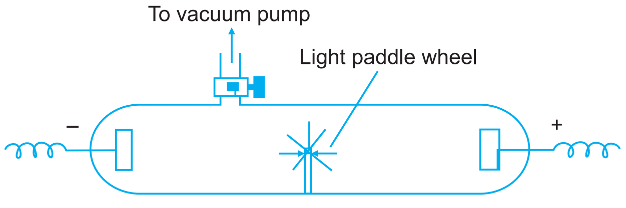


Fig. 1.3: *Particle nature of cathode rays*

(*iii*) **They are negatively charged.** When an electric or magnetic field is applied across the cathode rays, they are deflected towards the positively charged field (Fig. 1.4). This proves that cathode rays are negatively charged.

(*iv*) They ionise gases through which they pass. Due to high kinetic energy possessed by the cathode rays, they knock out electrons from the gas molecules and ionise them. Other properties of cathode rays are — they cause heating effect when they strike a surface, they produce fluorescence on substances like zinc sulphide, produce X-rays when they strike against metals like tungsten and they affect a photographic plate.

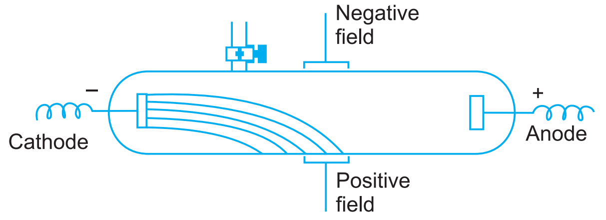


Fig. 1.4: *Effect of electric field on cathode rays*

1.3 CHARGE ON ELECTRON (*e*/*m* RATIO)

The ratio of charge to mass (e/m ratio) was determined by Thomson by studying the deflection of rays under the influence of electric and magnetic fields using an apparatus shown in Fig. 1.5.

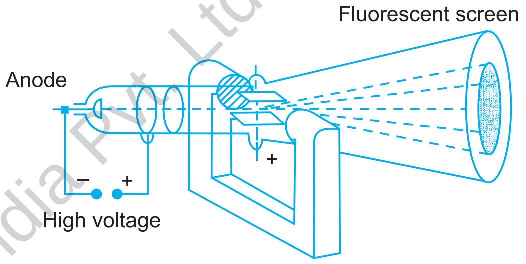


Fig. 1.5: *Determination of e/m ratio*

The ratio e/m was independent of the nature of the gas taken and the nature of the cathode. Its value was found out to be $1.76 \times 10^8 \text{C g}^{-1}$ of the particles and these were identified to be electrons.

Millikan determined the charge of the electrons as 1.6×10^{-19} coulomb. Thus, the value of mass of the electron can be calculated.

$$m = \frac{e}{e/m} = \frac{1.6 \times 10^{-19}\,\text{C}}{1.76 \times 10^{8}\,\text{Cg}^{-1}} = 9.1 \times 10^{-28}\,\text{g.}$$

Millikan's determination of value of e involves spraying of droplets of oil between two charged plates (Fig. 1.6). Oil drops lose electrons and become positively charged.

They are under the influence of gravitational field because of which they fall down. They are also under the influence of electric field because of which they rise upwards. By adjustment of the electric field, they can be made to suspend in air. Value of e can thus be calculated out. The movement of the oil drops can be viewed through a side window.

It was pointed out that since e/m ratio is constant irrespective of the nature of the gas and the material of the electrode, these cathode rays or electrons are fundamental particles of all elements. The relative charge of the electron is taken as –1.

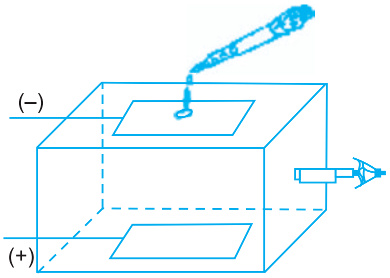


Fig. 1.6: *Millikan's experiment*

1.4 DISCOVERY OF PROTONS

It was noticed by Goldstein that during the passage of electricity through a gas, positively charged particles are emanated from the anode and they moved towards the cathode (Fig. 1.7).

Goldstein studied the properties of these rays and inferred that these are the *nuclei* of the atoms, after electrons have been removed from them.

The presence of positively charged particles was also indicated by the emission of α-rays from radioactive substances.

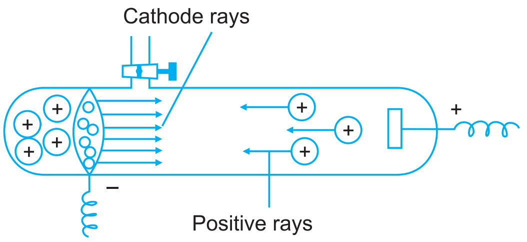


Fig. 1.7: *Production of positive rays*

Origin of Anode Rays. These rays are produced as a result of the knock out of the electrons from the gaseous atoms by the bombardment of high speed electrons of the cathode rays on them. Thus, anode rays are not emitted from the anode but are produced in the space between the anode and the cathode.

Properties of Anode Rays. Anode rays were found to possess the following properties:

(*i*) They travel in straight lines. However, their speed is much less than that of the cathode rays.

(*ii*) They are made up of material particles.

(*iii*) They are positively charged, as indicated by the direction of deflection of these rays in the electric and magnetic fields. That is why they are called *positive rays*.

(*iv*) Unlike cathode rays, the ratio of charge/mass (*i.e. e/m*) is found to be different for the particles constituting anode rays when different gases are taken inside the discharge tube. In other words, the value of *e/m* is determined by the nature of the gas taken inside the discharge tube.

(*v*) The value of the charge (*e*) on the particles constituting the anode rays is also found to depend upon the nature of the gas taken inside the discharge tube. However, the charge on these particles is found to be a whole number multiple of the charge present on the electron. In other words, these positively charged particles may carry one, two or three units of positive charge, depending upon the number of electrons knocked out.

(*vi*) The mass (*m*) of the particles constituting the anode rays is also found to be different for different gases taken in the discharge tube. However, its value is found to be nearly equal to that of the atom of the gas.

These particles were termed as *protons*. Hence, *a proton may be defined as that fundamental particle which carries one unit positive charge and has a mass nearly equal to that of the hydrogen atom*.

1.5 DISCOVERY OF NEUTRON

In 1932, Sir James Chadwick discovered that when beryllium or boron element is bombarded by α-particles, some new particles are emitted, which carry no electrical charge but have mass almost equal to that of a proton. These particles are called *neutrons*.

Neutron is regarded as the third fundamental particle of an atom, present in the nuclei of atoms of all the elements, except normal hydrogen.

1.6 THOMSON MODEL OF ATOM

After discovering the negatively charged particles called electrons, Thomson suggested a structure for atom. According to him, atom is a sphere of positive charge, with electrons embedded in it, as shown in Fig. 1.8. This model is also popularly known as **plum-pudding** model.

But this model was soon replaced by other models based on studies that followed.

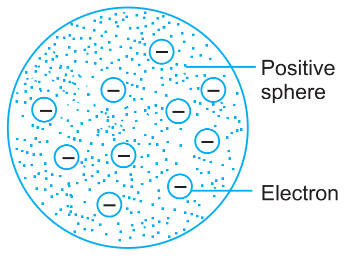


Fig. 1.8: *Thomson model of atom*

1.7 RUTHERFORD'S EXPERIMENT AND MODEL

In 1911, Lord Rutherford and his co-workers performed experiment of far-reaching importance, known as alpha particles scattering experiment. They worked with α-particles emitted from a sample of a radioactive substance. It may be noted that *α-particles are, in fact, helium atoms with two electrons removed. Thus, each α-particle carries two units of positive charge (i.e. +2 charge) and has a mass equal to about 4 times that of a hydrogen atom. It is represented by helium nucleus* ($_2He^4$).

Rutherford bombarded alpha (α) particles emitted from a radioactive source (*e.g.*, polonium or radium) on a piece of thin gold foil (0.00004 cm thick) (See Fig. 1.9).

The observations made from these experiments are given below:

(*i*) Most of the α-particles (nearly 90%) passed through the gold foil undeflected and produced bright spots on the screen.

(*ii*) Some of them got deflected through small angles.

(*iii*) Very few, *i.e.* about 1 in 100,000 did not pass through the foil at all but suffered large deflections (more than 90°) or even bounced back in the direction from which they came.

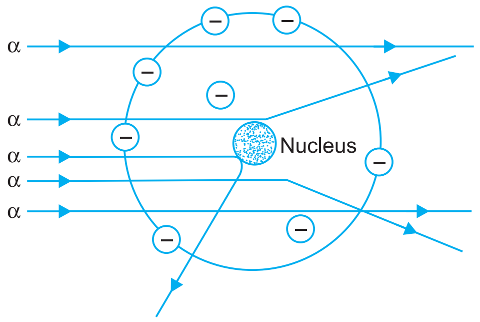
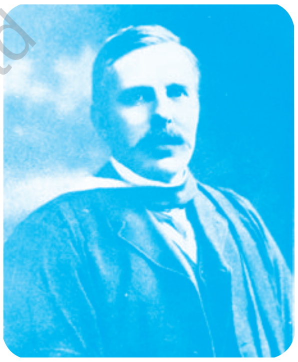


Fig. 1.9: *Scattering of alpha particles by the atom of a metal foil (e.g., gold foil)*

According to Thomson model, atom is regarded as a sphere of positive charge in which negative electrons are embedded. Lord Rutherford argued that if Thomson's view was correct, then all the α-particles would have been deflected and none of these could have passed the metallic gold foil. So, on the basis of above experiment, Rutherford rejected Thomson's model of atom and put forward his own well known hypothesis of *Nuclear Atom*. The main features of Rutherford's hypothesis are given below:



Rutherford

1. Since most of the α-particles pass through the gold foil (thin metallic sheet) undeflected, it shows that *the atom consists predominantly of empty space*.
2. As a few of the α-particles, which have an appreciable mass and are positively charged, get deflected through wider angles or even backwards, so there must be present in each atom, *a heavy positively charged body*. For such large scattering to occur, the α-particles will have to come close to or even collide with a massive positively charged body.
3. As the number of α-particles which undergo such strong deflections is very small, it shows that the volume occupied by this positively charged body is only a small fraction of the volume of the atom.
4. The positive charge on the nucleus is different for different atoms.
5. The electrons are not stationary but revolving around the nucleus at high speed in circular paths called *orbits*. The nuclear model of atom was compared to solar system in which the planets revolve around the sun.

1.7.1 Failure of Rutherford's Atomic Model

The nuclear atom of Rutherford was a big step in the exposure of the nature of atom but the behaviour of electrons in the atom remained unexplained. Neils Bohr pointed out that Rutherford's planet-like picture for electrons was defective and unsatisfactory as it did not ensure a stable atom.

James Clark Maxwell had shown a few years earlier that *whenever electric charge is subjected to acceleration, it emits radiations and loses energy*. Bohr therefore, argued that if an electron (a charged particle) moves round the nucleus in an orbit, as in Rutherford's model, it should be subjected to acceleration due to continuous change in its direction of motion. The electron should, therefore, continuously change its direction of motion. The electron should continuously emit radiation (electro-magnetic) and lose energy. As a result of this, its orbit should become smaller and smaller (Fig. 1.10), and finally it should fall into the nucleus.

Thus, atom should collapse in a fraction of second. But it does not happen in actual practice. Thus, Rutherford's atomic model is invalid.

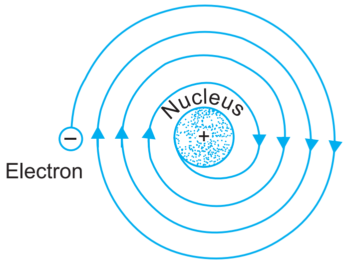


Fig. 1.10: *Path indicating the fall of an electron due to continuous loss of energy. (Failure of Rutherford's atomic model)*

1.7.2 Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon such as diffraction and interference can be explained by the wave nature of electromagnetic radiation. However, following are some of the observations which could not be explained with the help of even the electromagnetic theory of 19th century physics (known as classical physics):

(i) the nature of emission of radiation from hot bodies (black body radiation)
(ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)
(iii) variation of heat capacity of solids as a function of temperature
(iv) line spectra of atoms with special reference to hydrogen.

The explanation for the phenomenon of the black body radiation was given by Max Planck in 1900. This phenomenon is given below:

When solids are heated they emit radiation over a wide range of wavelengths. For example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. In terms of frequency, it means that the frequency of emitted radiation goes from a lower frequency to a higher frequency as the temperature increases. The red colour lies in the lower frequency region while blue colour belongs to the higher frequency region of the electromagnetic spectrum. The ideal body, which emits and absorbs radiations of all frequencies, is called a black body and the radiation emitted by such a body is called black body radiation. The exact frequency distribution of the emitted radiation (i.e., intensity versus frequency curve of the radiation) from a black body depends only on its temperature. At a given temperature, intensity of radiation emitted increases with decrease of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further decrease of wavelength to its frequency (ν) and is expressed by equation

$$E = h\nu \quad = h \times \frac{C}{\lambda}$$

The proportionality constant, '*h*' is known as Planck's constant and has the value 6.626 x 10^{-34} J s. "C" velocity of light, 'λ' wavelength of radiation.

With this theory, Planck was able to explain the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures.

1.8 BOHR'S MODEL OF THE ATOM


Bohr

To overcome the shortcomings of Rutherford's theory, Neils Henrik David Bohr, a Danish physicist put forward his model of atom in 1913. He retained Rutherford's model of a very small positively charged nucleus at the centre. He also accepted the view that all the protons and neutrons (and, hence, most of the mass of the atom) are contained in the nucleus. He also agreed that the negatively charged electrons are revolving round the nucleus in the same fashion as the planets are revolving round the sun. But to account for the drawbacks in Rutherford's model of an atom and to explain the stability of atoms, Neils Bohr put forward a new theory of atomic structure known as **Bohr's theory**. He applied **Planck's Quantum theory** to explain why electrons keep on revolving round the nucleus without losing energy. The important postulates of Bohr's theory are:

1. An atom consists of a dense nucleus surrounded by electrons moving in circular orbits.
2. The electrons continue revolving in their respective orbits without losing energy. This is because energy in fractions of a quantum cannot be lost.

   According to this postulate, *the energy of an electron remains constant as long as it stays in the same orbit*. This led to the idea that *each orbit is associated with a definite energy, i.e. with a definite whole number of quantas of* *energy*. The orbits, therefore, are also known as energy levels or energy shells. Further, these orbits are also called *stationary states*. Bohr gave numbers 1, 2, 3, 4, etc., (starting from the nucleus to these energy levels, see Fig. 1.11). These are now termed as **principal quantum numbers**. The various energy levels are also designated by letters K, L, M, N, etc.

3. The farther the energy level from the nucleus the greater is the energy associated with it. As long as the electron remains in a particular energy level, it neither emits nor absorbs energy.
4. The allowed orbits of electronic motion are those in which the angular momentum* of the electron is an integral whole number multiple of the quantity ($h/2\pi$), h being *Planck's constant*. This postulate constitutes the *quantization* of the angular momentum.

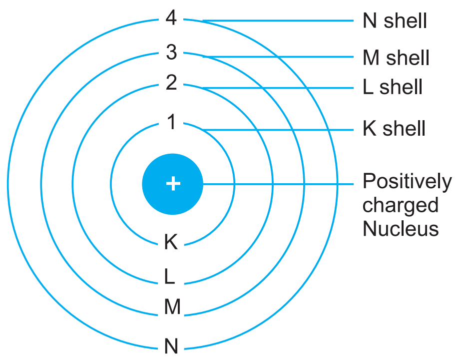
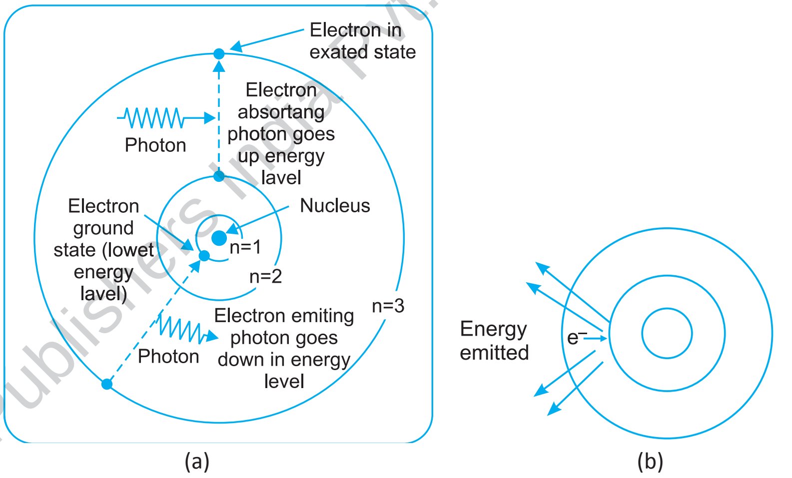


Fig. 1.11: *Orbit-like representation of various energy levels*

Thus, $mvr = \dfrac{nh}{2\pi}$, where n = 1, 2, 3, ..., n.

5. Energy is emitted or absorbed by an atom only when an electron moves from one level to another. The amount of energy emitted or absorbed is given by the difference of the energies associated with the two energy levels concerned. Thus, the energy of an electron cannot change continuously. It changes only abruptly as the electron *jumps* from one energy level to another. The same idea has been expressed by the statement that *for a change of electronic energy, the electron has to jump and not 'flow' from one energy level to another.*



(a) (b)

Fig. 1.12: *Energy changes in electron jumps*

When the electron jumps from a higher energy level to a lower energy level, the energy is emitted [Fig. 1.12(*a*)]. On the other hand, energy is absorbed when the electron jumps from a lower energy level to some higher energy level [Fig. 1.12(*b*)]. This energy is emitted or absorbed in *quantas* and is equal to the difference between energies of two energy levels or $\Delta E = E_2 - E_1$.

Drawback of Bohr's Atomic Model

1. Bohr's model was unable to explain the line spectra of multi-electron atom. It explains the line spectra of hydrogen containing single electron.
2. Bohr's model could not explain splitting of spectral lines in magnetic field (Zeeman effect) and in electric field (Stark effect).

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* Just as a body undergoing translatory motion has a linear momentum (= mass × linear velocity), one revolving in a circle has an angular momentum equal to the product of its moment of inertia and angular velocity. The moment of inertia = mr^2, where m is the mass and r is the radius of the circle transversed by it and angular velocity = v/r, where v is the linear velocity and r is the radius. Thus, angular momentum of a body rotating in a circle = $mr^2 \times v/r = mvr$.

3. According to Bohr, electron revolve around the nucleus in circular paths in one plane, which is a flat model of atom. But atom is a three dimensional structure and not flat.
4. Bohr's model could not explain de Broglie concept of dual nature of matter and Heisenberg's uncertainty principle.

1.8.1 Atomic Number and Mass Number

Since the atom as a whole is electrically neutral, therefore, the number of positively charged particles, *i.e.* protons present in the atom must be equal to the number of negatively charged particles, *i.e.* electrons present in it. This number is called *atomic number*. Hence,

Atomic number of an element = Total number of protons present in the nucleus
= Total number of electrons present in the atom.

Atomic number is also known as *proton number* because the charge on the nucleus depends upon the number of protons.

Further, since the electrons have negligible mass, the entire mass of the atom is mainly due to protons and neutrons only. Since these particles are present in the nucleus, therefore, they are collectively called **nucleons**. Further, as each of these particles has one unit mass on the atomic mass scale, therefore, the sum of the number of protons and neutrons will be nearly equal to the mass of the atom. This is called **mass number**. Hence,

Mass number of an element = No. of protons + No. of neutrons

The mass number of an element is nearly equal to the atomic mass of that element. However, the main difference between the two is that mass number is always a whole number whereas atomic mass is usually not a whole number.

1.9 DUAL NATURE OF MATTER

Light is said to have a dual character. Such studies on light were made by Einstein in 1905. Louis de Broglie, in 1924 extended the idea of photons to material particles such as electron and he proposed that matter also has a dual character—wave and particle nature.

The wavelength of the wave associated with any material particle was calculated by analogy with photon.

In case of photon, if it is assumed to have wave character, its energy is given by

$$E = hv \qquad \text{... } (i)$$

(According to the Planck's quantum theory)

Where v is the frequency of the wave and 'h' is Planck's constant.

If the photon is supposed to have particle character, its energy is given by

$$E = mc^2 \qquad \text{... } (ii)$$

(According to Einstein's equation)

where 'm' is the mass of photon, 'c' is the velocity of light.

By equating (i) and (ii)

$$hv = mc^2 \qquad \text{But} \qquad v = c/\lambda$$

$$h \times \frac{c}{\lambda} = mc^2$$

(or) $$\lambda = h/mc$$

The above equation is applicable to any material particle if the mass and velocity of photon is replaced by the mass and velocity of material particle. Thus for any material particle like electron,

$\lambda = h/mv$ or $\lambda = h/P$ where $mv = p$ is the momentum of the particle.

The above equation is called de Broglie equation and λ is called de Boglie wavelength. According to this equation, de Broglie wavelength of a particle is inversely proportional to its momentum.

Louis de Broglie
(1892–1987)

Heisenberg’s Uncertainty Principle

In 1927, Werner Heisenberg, a German physicist, gave a principle about the uncertainty in simultaneous measurement of position and momentum of small particles.

Heisenberg’s uncertainty principle states that:

It is impossible to measure simultaneously the position and momentum of a small particle with absolute accuracy or certainty. The product of the uncertainty in the position (Δx*) and the uncertainty in the momentum (*Δp*) is always constant and is equal to or greater than* $h/4\pi$*, where h is the Planck’s Constant, i.e.,*

$$\Delta x \; \Delta p \geq \frac{h}{4\pi}$$

Significance of Heisenberg Uncertainty Principle

Heisenberg’s uncertainty principle holds good for all objects but it is significant only for microscopic particles. The energy of the photon is insufficient to change the position and velocity of bigger bodies when it collides with them.

For a particle of mass 1 mg, we have

$$\Delta x \,.\, \Delta v = h/4\pi m$$

$$\Delta x \,.\, \Delta v = 6.626 \times 10^{-34}/4 \times 3.1416 \times (10^{6})$$

$$\Delta x \,.\, \Delta v = 10^{-28}\ \text{m}^2\text{s}^{-1}$$

The product Δx and Δv is extremely small. For a particle of mass greater than 1 mg, the product will be still smaller. Hence these values are negligible.

For a microscopic particle like an electron, we have

$$\Delta x \,.\, \Delta v = 6.626 \times 10^{-34}/4 \times 3.1416 \times (9.11 \times 10^{-31})$$

$$\Delta x \,.\, \Delta v = 10^{-4}\ \text{m}^2\text{s}^{-1}$$

If uncertainty in position is 10^{-4}, uncertainty in velocity will be 0.1 m/s.

Bohr’s concept of fixed circular path with definite position and momentum of electron have been replaced by stating that the electron has the probability of having a given position and momentum.

Electron cannot exist in the nucleus

This is because the diameter of the atomic nucleus is of the order 10^{-15} m. If the electron were to exist within the nucleus, the maximum uncertainty in its position would have been 10^{-15} m. Taking the mass of electron as 9.1×10^{-31} kg, the minimum uncertainty in velocity can be calculated by applying Heisenberg’s uncertainty principle as follow:

$$\Delta x \,.\, \Delta p = h/4\pi$$

$$\Delta x \,.\, (m \times \Delta v) = h/4\pi$$

$$\Delta v = h/4\pi \times \Delta x \times m$$

$$\Delta v = 6.626 \times 10^{-34}/4 \times 3.1416 \times 10^{-15} \times 9.1 \times 10^{-31}$$

$$\Delta v = 5.77 \times 10^{10}\ \text{m/s}$$

This value is much higher than the velocity of light (3×10^{8}) and hence is not possible.

Quantum or Wave Mechanical Model of Atom

The important features of this model are summarised below:

(*i*) Energy of electrons in atom is quantized, they can have only specific value.

$$E_n = -\frac{1312}{n^2}\ \text{kJ mole}^{-1} \text{ for hydrogen}$$

The existence of quantized electronic energy levels is a result of the wave-like properties of atom.

(*ii*) This model provides the most probable region is the atom where there is maximum probability of finding electrons. These regions are termed as atomic orbitals.

(*iii*) This model provides three constants *n*, *l* and *m* which are known as *quantum number*. These numbers specify the position, energy and orientation of the electrons in an atom.

(*iv*) This model provides information about the exact shapes of various atomic orbitals.

(*v*) An atom is described by a wave function, ψ. In each orbital, the electron has a definite energy. An orbital cannot have more than two electrons.

(*vi*) The probability of finding the electron at a point within an atom is proportional to the square of wave function that is ψ^2 at that point. ψ^2 is known as electron density.

1.10 NUCLEAR STRUCTURE

Knowing the atomic number and mass number of an element, the number of electrons, protons and neutrons in the atom of the element can be calculated. Hence, the composition of the nucleus can be known.

For example, if Z represents the atomic number of an element and A represents its mass number, then

No. of electrons = No. of protons
= Atomic number (Z)

and No. of protons + No. of neutrons = Mass number (A)

∴ No. of neutrons = Mass number (A) – Atomic number (Z)

For example, for sodium

Atomic number (Z) = 11
Mass number (A) = 23
No. of protons = No. of electrons
= Z = 11

and No. of neutrons = A – Z = 23 – 11 = 12

Thus, the nucleus of sodium atom contains 11 protons and 12 neutrons.

The atomic number (Z) and mass number (A) of an element X are usually represented alongwith the symbol as $^{A}_{Z}X$.

e.g. $^{23}_{11}Na$, $^{35}_{17}Cl$, $^{40}_{20}Ca$, etc.

Arrangement of protons, neutrons and electrons is shown in Fig. 1.13.

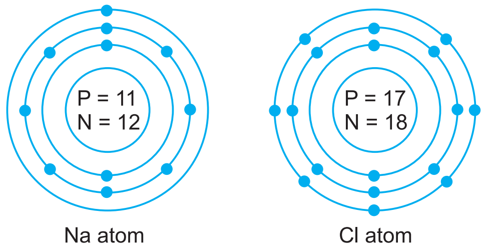


Fig. 1.13: *Arrangement of protons, neutrons and electrons in the atoms. Protons (P) and neutrons (N) are packed in the nucleus. Electrons represented as ● are distributed in the shells*

Sometimes atoms of the same element are not identical in all respects. Similarly, sometimes atoms of different elements show some kind of similarity. Such type of particles are discussed below:

1. **Isotopes.** In some cases, atoms of the same element are found to contain the same number of protons but different number of neutrons. As a result, they have the same atomic number but different mass numbers.

   Such atoms of the same element having same atomic number but different mass numbers are called ***isotopes***.

   For example, there are three isotopes of hydrogen having mass numbers, 1, 2 and 3 respectively and each of them having atomic number equal to 1. They are represented as $^{1}_{1}H$, $^{2}_{1}H$ and $^{3}_{1}H$ and named as protium, deuterium (D) and tritium (T) respectively. Ordinary hydrogen is protium. Isotopes of other elements do not have special names. They are represented by simply indicating the values of A on the symbol. For example, isotopes of chlorine are written as ^{35}Cl and ^{37}Cl. It may be mentioned that isotopes possess the same chemical properties.

2. **Isobars.** Some atoms of different elements are found to have same mass number.

   Such atoms of different elements which have same mass numbers but different atomic numbers are called ***isobars,*** *e.g.,* $^{40}_{18}$Ar, $^{40}_{19}$K and $^{40}_{20}$Ca.

3. **Isotones.** It may be noted that isotopes differ in the number of neutrons only whereas isobars differ in the number of neutrons as well as the number of protons. However, some atoms of different elements are found to have the same number of neutrons.

   Such atoms of different elements which contain the same number of neutrons are called ***isotones****, e.g.,* $^{14}_{6}$C, $^{15}_{7}$N and $^{16}_{8}$O.

4. **Isosters.** *These are the molecules of different substances which contain the same number of atoms and the same total number of electrons which leads to similarity in their physical properties. This phenomenon is called* ***isosterism.*** For example, carbon dioxide, CO_2 and nitrous oxide, N_2O are isosters.

Example 1. *Find out the atomic number, mass number, number of protons, electrons and neutrons present in the element with the notation* $^{235}_{92}U$.

Solution. Atomic number (Z) = 92

Mass number (A) = 235

But we know that

No. of protons = No. of electrons

= Atomic number (Z)

∴ No. of protons = 92

and No. of electrons = 92

Further, No. of neutrons = Mass number – Atomic number

= A – Z = 235 – 92

= 143

Example 2. *The nuclear radius is of the order of* 10^{-13} *m while the atomic radius is of the order* 10^{-8} *cm. Assuming that the nucleus and the atom are spherical, what fraction of the atomic volume is occupied by the nucleus?*

Solution. The volume of a sphere = $4\pi r^3/3$, where r is the radius of the sphere.

∴ Volume of the nucleus = $4\pi r^3/3$

$= 4\pi(10^{-13})^3/3 \text{ cm}^3$

Similarly, volume of the atom = $4\pi r^3/3$

$= 4\pi(10^{-8})^3/3 \text{ cm}^3$

∴ Fraction of the volume of atom occupied by the nucleus

$$= \frac{4\pi(10^{-13})^3/3\,\text{cm}^3}{4\pi(10^{-8})^3/3\,\text{cm}^3}$$

$$= 10^{-15}$$

It may, thus, be noted that the volume of the nucleus is very very small compared to that of the atom.

1.11 RELATIVE ATOMIC MASSES

After knowing that the matter is composed of atoms, scientists were eager and interested to know how to determine the mass of an atom. As an atom is too small to be seen or isolated, it is impossible to determine the actual mass of a single atom by weighing it. An alternate suggestion was put forward that by weighing a large sample of the element, mass of an atom could be calculated, but there was no method to count the number of atoms. Finally, it was Avogadro's hypothesis which helped in solving the problem. Avogadro stated that *equal volumes of different gases under similar conditions of temperature and pressure contain equal number of molecules.* Thus, if equal volumes of two different gases are taken under similar conditions of temperature and pressure and then weighed, the ratio of their masses will be equal to the ratio of the masses of their molecules, since they contain equal number of molecules.

For example, let us take equal volumes of hydrogen and oxygen, their masses are in the ratio of 1 : 16. This means that a molecule of oxygen is 16 times heavier than a molecule of hydrogen. Moreover, as one molecule of hydrogen contains two atoms of hydrogen and one molecule of oxygen contains two atoms of oxygen, an atom of oxygen is 16 times heavier than an atom of hydrogen. Although the actual masses of the atoms could not be determined but their relative masses could be found out. *Thus, it follows that if the atomic mass of hydrogen is taken as one, the relative atomic mass of oxygen is 16* (More accurately it comes out to be 15.88).

Initially, the atomic masses of all the elements were obtained by comparing with the mass of hydrogen taken as 1 (since it was the lightest element). But by taking hydrogen as standard, masses of most of the other elements come out to be in fractions.

The atomic masses of the elements have been found out accurately during the recent years by using **mass spectrometer** (Fig. 1.14). It has been found that in a number of cases, atoms of the same elements possess different masses. These are called **isotopes**. So in such cases, the atomic mass of the element is taken as the average value. For example, ordinary chlorine is a mixture of two isotopes with atomic masses 35 amu and 37 amu and they are present in the ratio of 3 : 1.

Now, carbon with atomic mass 12 amu is taken as standard for comparing weights. On this basis, the relative mass of hydrogen comes out to be 1.008 amu and that of oxygen as 15.9994 amu (or 16). Thus, the atomic mass of an element may be defined as follows:

The atomic mass of an element is the number of times an atom of an element is heavier than an atom of C-12.

It should be noted that the atomic masses as obtained above are the relative atomic masses and not the actual masses of the atoms. These masses on the atomic mass scale are expressed in terms of **atomic mass units** (u).

One atomic mass unit (amu) is equal to $^{1}/_{12}$ *th of the mass of an atom of carbon.* Hence, the average atomic mass of chlorine would be as below:

$$\frac{35 \times 3 + 37 \times 1}{3 + 1} = 35.5 \text{ u}$$

Bromine occurs as two isotopes with mass number 79 and 81 in the ratio of 1:1. Hence, its average atomic mass would be

$$\frac{79 + 81}{2} = 80 \text{ u}$$

So it is clear that word average, must be incorporated in the definition. Thus, the atomic mass of an element may more accurately be defined as below:

The atomic mass of an element is the average relative mass of its atoms as compared with an atom of carbon taken as carbon-12. (C-12)

In the end, it may be pointed out that naturally occurring carbon contains **3 isotopes of carbon** with atomic masses 12, 13 and 14 amu. It is the carbon-12 isotope which is taken as a reference on the atomic mass scale.

1.11.1 Working of a Mass Spectrometer

A mass spectrometer is an important analytical instrument which scientists can use to identify the amount and type of different chemicals in a substance.

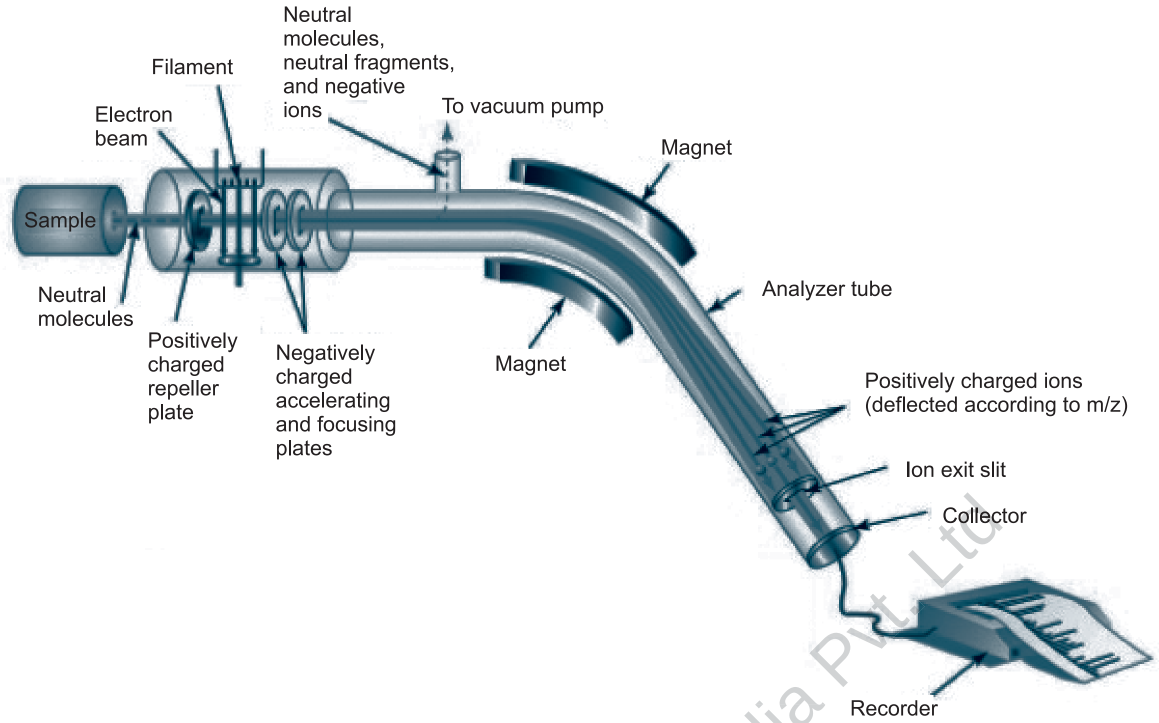


Fig. 1.14: *Working of a mass spectrometer*

There are four stages in a mass spectrometer which we need to consider. These are — **ionisation, acceleration, deflection, and detection.**

Ionisation

The sample needs to be vapourised first, before being passed into the ionisation chamber. Here, an electrically heated metal coil gives off a stream of electrons. The atoms or molecules in the sample are bombarded by this stream of electrons, and in some cases, the collision **will knock an electron from the particle, resulting in a positively charged ion.** Most of the ions formed have one positive charge, as it is difficult to remove a second electron from an already positive ion.

Acceleration

The positively charged ions are repelled from the ionisation chamber (which is positively charged), and pass through negatively charged slits which focus and accelerate this into a beam.

Deflection

The stream of positively charged ions are then deflected by a magnetic field. The amount of deflection of the ions depends on

- the **mass of the ion** (lighter ions will be deflected more than heavier ones)
- the **charge of the ion** (ions with a greater charge than +1 are deflected more)

We can consider these properties as a mass/charge ratio (m/z), where the mass of the ion is divided by its positive charge.

Detection

By varying the strength of the magnetic field, the different ion streams (after deflection) can be focused on the ion detector, in order of increasing mass/charge ratio (as the lightest ions would need to be deflected the least). When an ion hits the detector, the charge is neutralised, and this generates an electrical current. This current is proportional to the abundance of the ion. These are sent to a computer for analysis. A mass spectrum is generated, which shows the different *m/z* values of ions present, and their relative abundance.

Atomic masses of some common elements are given in Table 1.1 (taking C – 12 = 12.000)

Table 1.1: Atomic Masses

Element	Symbol	Atomic Number	Atomic Mass (u)
Hydrogen	H	1	1.008
Helium	He	2	4.00
Lithium	Li	3	6.94
Beryllium	Be	4	9.01
Boron	B	5	10.8
Carbon	C	6	12.0
Nitrogen	N	7	14.0
Oxygen	O	8	16.0
Fluorine	F	9	19.0
Neon	Ne	10	20.2
Sodium	Na	11	23.0
Magnesium	Mg	12	24.3
Aluminium	Al	13	27.0
Silicon	Si	14	28.1
Phosphorus	P	15	31.0
Sulphur	S	16	32.1
Chlorine	Cl	17	35.5
Argon	Ar	18	39.9
Potassium	K	19	39.1
Calcium	Ca	20	40.1
Scandium	Sc	21	45.0
Titanium	Ti	22	47.9
Vanadium	V	23	50.9
Chromium	Cr	24	52.3
Manganese	Mn	25	54.9
Iron	Fe	26	55.8
Cobalt	Co	27	58.9
Nickel	Ni	28	58.7
Copper	Cu	29	63.5
Zinc	Zn	30	65.4

Table 1.1 *Contd.*

Element	Symbol	Atomic Number	Atomic Mass (u)
Gallium	Ga	31	69.7
Germanium	Ge	32	72.6
Arsenic	As	33	74.9
Selenium	Se	34	79.0
Bromine	Br	35	79.9
Krypton	Kr	36	83.8
Rubidium	Rb	37	85.5
Strontium	Sr	38	87.6
Yttrium	Y	39	88.9
Zirconium	Zr	40	91.2
Niobium	Nb	41	92.9
Molybdenum	Mo	42	95.9
Technetium	Tc	43	98.9
Ruthenium	Ru	44	101.1
Rhodium	Rh	45	102.9
Palladium	Pd	46	106.4
Silver	Ag	47	107.9
Cadmium	Cd	48	112.4
Indium	In	49	114.8
Tin	Sn	50	118.7
Antimony	Sb	51	121.8
Tellurium	Te	52	127.6
Iodine	I	53	126.9
Xenon	Xe	54	131.3
Caesium	Cs	55	132.9
Barium	Ba	56	137.3
Lanthanum	La	57	138.9
Cerium	Ce	58	140.1
Praseodymium	Pr	59	140.9
Neodymium	Nd	60	144.2
Promethium	Pm	61	(145)
Samarium	Sm	62	150.4
Europium	Eu	63	152.0
Gadolinium	Gd	64	157.3
Terbium	Tb	65	158.9
Dysprosium	Dy	66	162.5
Holmium	Ho	67	164.9
Erbium	Er	68	167.3
Thulium	Tm	69	168.9

Table 1.1 *Contd.*

Element	Symbol	Atomic Number	Atomic Mass (u)
Ytterbium	Yb	70	173.0
Lutetium	Lu	71	175.0
Hafnium	Hf	72	178.5
Tantalum	Ta	73	180.9
Tungsten	W	74	183.8
Rhenium	Re	75	186.2
Osmium	Os	76	190.2
Iridium	Ir	77	192.2
Platinum	Pt	78	195.1
Gold	Au	79	197.0
Mercury	Hg	80	200.6
Thallium	Tl	81	204.4
Lead	Pb	82	207.2
Bismuth	Bi	83	209.0
Polonium	Po	84	(209)
Astatine	At	85	(210)
Radon	Rn	86	(222)
Francium	Fr	87	(223)
Radium	Ra	88	226
Actinium	Ac	89	(227)
Thorium	Th	90	232.0
Protactinium	Pa	91	231.0
Uranium	U	92	238.0
Neptunium	Np	93	237.0
Plutonium	Pu	94	(242)
Americium	Am	95	(243)
Curium	Cm	96	(247)
Berkelium	Bk	97	(247)
Californium	Cf	98	(251)
Einsteinium	Es	99	(252)
Fermium	Fm	100	(257)
Mendelevium	Md	101	(258)
Nobelium	No	102	(259)
Lawrencium	Lw (Lr)	103	(260)

Note: Atomic masses of radioactive species are given in parentheses.

Gram-Atomic Mass: *The atomic mass of an element expressed in grams is called gram-atomic mass*. This amount of the element is also known as one gram atom. For example,

Atomic mass of oxygen = 16 u
(or one gram atom of oxygen) = 16 g.

Calculation of relative molecular mass and relative formula mass: First of all, let us be clear about the two terms, relative molecular mass and relative formula mass. Relative molecular mass refers to the relative mass of a molecule of a substance compared to the mass of carbon atom taken as 12. Relative formula mass is the mass of one formula unit of an ionic substance compared to the mass of carbon atom taken as 12. Thus molecular mass refers to a covalent molecule while formula mass refers to an ionic substance.

Relative molecular mass (or simply molecular mass) is obtained by adding the relative atomic masses of all the atoms present in one molecule of the substance. Likewise, relative formula mass is obtained by adding the relative atomic masses of atoms present in one formula unit of the substance. This is illustrated with the help of the following examples.

Relative molecular mass of glucose ($C_6H_{12}O_6$)

$$\begin{aligned}(6 \times 12) + (12 \times 1) + (6 \times 16) &= 72 + 12 + 96 \\ &= 180 \text{ u}\end{aligned}$$

Relative formula mass of sodium sulphate (Na_2SO_4)

$$\begin{aligned}\text{Formula unit} &= Na_2SO_4 \\ \text{Formula mass} &= (2 \times 23) + (1 \times 32) + (4 \times 16) = 46 + 32 + 64 \\ &= 142 \text{ u}\end{aligned}$$

1.11.2 Concept of Atomic Orbital

An orbital may be defined as the region in space around the nucleus where the probability of finding an electron is maximum.

Differences between an orbit and an orbital

Fig. 1.15 illustrates a comparison between the picture of an orbit and an orbital and Table 1.2 gives the differences between them.

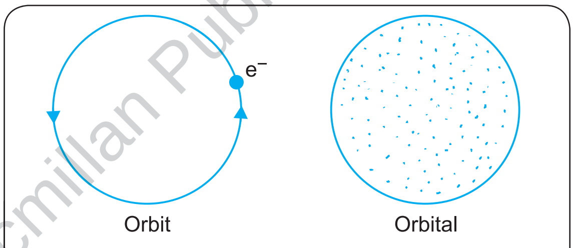


Fig. 1.15: *Illustration of an orbit and an orbital*

Table 1.2: Differences between Orbit and Orbital

Orbit	Orbital
1. An orbit is the fixed path of an electron around the nucleus (given by Bohr's concept).	1. It is the space around the nucleus where the probability of finding electrons is maximum.
2. It represents the planar motion of an electron.	2. It represents the three dimensional motion of an electron around the nucleus.
3. An orbit can accommodate electrons according to $2n^2$, where n represents the principal quantum number.	3. An orbital can accommodate only two electrons.
4. An orbit is circular.	4. An orbital can have different shapes depending upon the energy and angular momentum of the electron e.g., *s*- and *p*-orbitals have different shapes. *s*-orbital is spherical while *p*-orbital is dumbbell shaped.

1.12 QUANTUM NUMBERS

Main energy shells are considered to be further split into sub-energy level orbitals. Therefore, to describe each electron in an atom, we use four numbers. These four numbers which are required to specify the position and energy of the electron in an atom are called quantum numbers. These are:

(*i*) Principal quantum number (n).
(*ii*) Azimuthal quantum number (l).
(*iii*) Magnetic quantum number (m).
(*iv*) Spin quantum number (s).

1. **Principal quantum number (n).** It is represented by n. It may have any integral value except zero, *i.e.* $n = 1, 2, 3, 4$, etc.

   The value of n indicates the main energy shell the electron belongs to:

   If $n = 1$, electron belongs to K-shell.
   If $n = 2$, electron belongs to L-shell.
   If $n = 3$, electron belongs to M-shell and so on.

   The energy of the principal quantum number increases with increase in the value of n. The following information is conveyed by the principal quantum number:

   (*i*) It gives the distance of the electron from the nucleus and thus determines the size of the electron cloud.
   (*ii*) It determines the energy of the electron in simple cases (one electron species) and gives approximate energies in other cases.
   (*iii*) The maximum number of electrons that can be present in any principal shell is given by $2n^2$, where n is the number of the principal shell.

2. **Azimuthal or subsidiary or angular momentum quantum number (l).** The principal quantum number is further subdivided into a number of azimuthal quantum numbers. It is denoted by the letter l. All the electrons present in a particular principal shell don't have the same energy. These energies are different and depend upon the angular momentum of the electron. Within one principal shell, we have a number of secondary shells. Azimuthal quantum number conveys the following information to us:

   (*i*) The number of subshells present in a particular principal shell and their energies.
   (*ii*) The shapes of subshells are also given by azimuthal quantum number.
   (*iii*) Orbital angular momentum which is equal to $\frac{h}{2\pi}\sqrt{l(l+1)}$ helps to explain fine lines of spectrum. Due to the presence of large number of subshells, the number of transitions become large.

   For a given value of n (a principal quantum number), the azimuthal quantum number have values from zero to $(n - 1)$.

   For the first shell $n = 1$, $l = 1 - 1$ or $l = 0$
   For the second shell $n = 2$, $l = 0$ and $l = 1$
   For the third shell $n = 3$, $l = 0$, $l = 1$ and $l = 2$.

   That means a main shell has as many subshells as its principal quantum number.

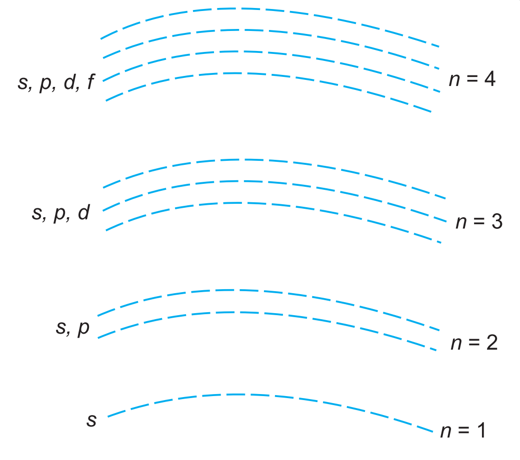


Fig. 1.16: *Spectral lines*

The values 0, 1, 2, 3, etc., for l have a definite significance.

$l = 0$ refers to *s*-orbital having spherical shape.

$l = 1$ refers to *p*-orbital having a dumb-bell shape.

$l = 2$ refers to *d*-orbital having a double dumb-bell shape.

$l = 3$ refers to *f*-orbital having a still more complex shape.

These letters *s*, *p*, *d* and *f* are derived from the first letter of the words sharp, principal, diffused and fundamental respectively.

These terms used in connection with the different spectral lines that are obtained are shown in Fig. 1.16.

Energies of subshell increase as we move from *s* to *f* orbital. Their energies are in the order:

$$s < p < d < f.$$

The energies of subshells of various principal shells are shown in Fig. 1.17. The number of electrons in a particular subshell are given in the bracket. e^- denotes electron.

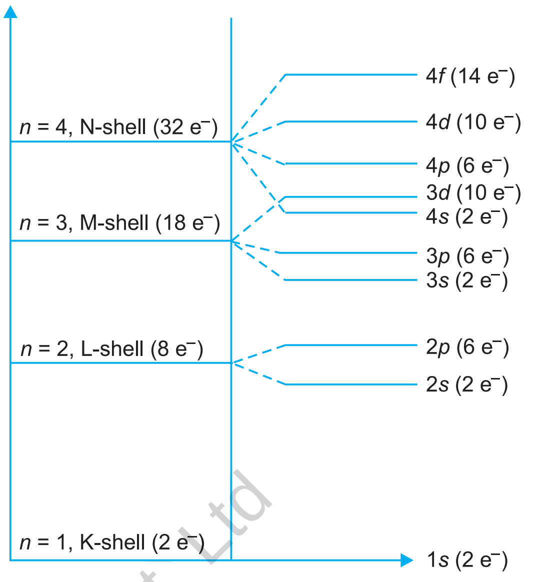


Fig. 1.17: *Energy level of subshells*

3. **Magnetic quantum number (m).** When electrons revolve around the nucleus, they also revolve around their own axis. And this angular momentum of electron creates a magnetic field. This small magnetic field can interact with an external magnetic field. Under the influence of the external magnetic field, the electrons orient themselves in certain preferred regions of space around the nucleus. These are called **orbitals**. The magnetic quantum number m determines the preferred orientations of the orbitals in space. The values of m are integral and dependent upon the value of l. For a given value of l, m can have all values from $-l$ through zero to $+l$ so that values of m are $(2l + 1)$. For example, when

   $l = 0$, $l = 1$, $l = 2$

   $m = 0$, $m = -1, 0, +1$, $m = -2, -1, 0, +1, +2$

   Thus, it is evident if $l = 0$, m has only one value which is 0, *i.e.* *s* subshell contains one orbital called *s*-orbital. And the only possible geometry which has one orientation is sphere. Hence, *s*-orbital is spherical.

   If $l = 1$, m has three values $-1, 0, +1$, *i.e.* *p* subshell contains three orbitals.

   If $l = 2$, m has 5 values $-2, -1, 0, +1, +2$, *i.e.* *d* subshell contains five orbitals or there are five *d*-orbitals.

   For $l = 3$, $m = -3, -2, -1, 0, +1, +2, +3$, *i.e.* *f* subshell contains seven orbitals or there are seven *f*-orbitals.

4. **Spin quantum number (s).** As electron besides moving in an orbit spins about its own axis. It may spin in the clockwise direction or anticlockwise direction. Arbitrarily, we say that when it is spinning in the clockwise direction, it has $+\frac{1}{2}$ spin quantum number and when it is spinning in the anticlockwise direction, we say it has $-\frac{1}{2}$ spin quantum number (Fig. 1.18).

   This quantum number explains the magnetic behaviour of a substance. Corresponding to a particular value of m, there are always two values of spin quantum numbers $+\frac{1}{2}$ and $-\frac{1}{2}$ which have to be mentioned in

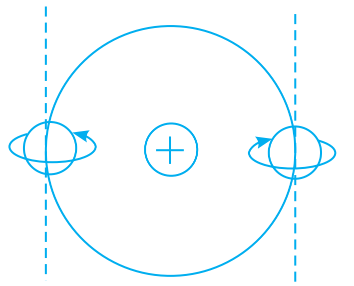


Fig. 1.18: *Spinning of electrons*

order to describe completely an electron. In an orbital, if two electrons are present, they must have the opposite spins. If the spins of all the electrons present in various subshells, are cancelled, the substance will show no magnetic behaviour (diamagnetic). On the other hand, if there are unpaired electrons in various subshells of an atom, we expect paramagnetism. A large number of unpaired electrons produce strong magnetic effects. Substances with such configurations are ferromagnetic. Spin quantum number is represented by the letter *s*.

1.13 SHAPES OF ORBITALS

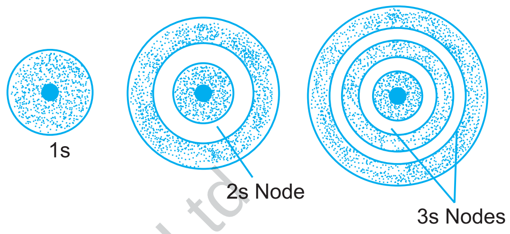


Fig. 1.19: *Shapes of 1s, 2s- and 3s-orbitals*

Shape of *s*-orbitals. The *s*-orbitals are spherically symmetrical about the nucleus, *i.e.* the probability of finding *s* electron is same in all directions from the nucleus. The size of the orbital depends on the value of principal quantum number. For every value of principal quantum number, there is one spherically symmetrical orbital. The 1*s*-orbital is smaller than 2*s*-orbital and 2*s*-orbital is smaller than 3*s*, but all are spherical in shape as shown in Fig. 1.19.

Although the *s*-orbitals belonging to different shells are spherically symmetrical, yet they differ in certain respects as explained below:

(*i*) The probability of 1*s* electron is found to be maximum near the nucleus and decreases as the distance from the nucleus increases. In case of 2*s* electrons, the probability is again maximum near the nucleus and then decreases to zero and increases again and then decreases as the distance from the nucleus increases. The intermediate region (a spherical shell) where the probability is zero is called a **nodal surface** or simply **node**. Thus, 2*s*-orbital differs from 1*s*-orbital in having one node within it. Similarly, 3*s* have two nodes. In general, any *ns*-orbital has (n – 1) nodes.

(*ii*) The size and energy of the *s*-orbital increases as the principal quantum number n increases, *i.e.* the size and energy of *s*-orbital increases in the order 1*s* < 2*s* < 3*s*...

Shapes of *p*-orbitals. There are three *p*-orbitals, commonly referred to as p_x, p_y, p_z. These three *p*-orbitals, possess equivalent energy and, therefore, have same relation with the nucleus. They, however, differ in their directional distribution of the charge. These three *p*-orbitals are situated at right angle to one another and are directed along x, y and z axes (Fig. 1.20).

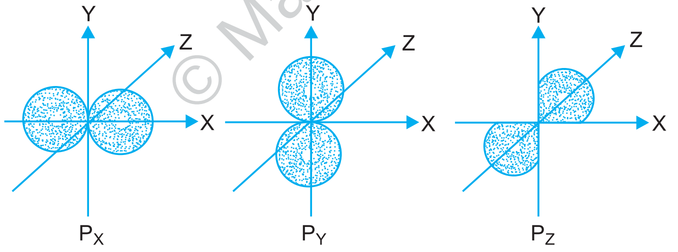


Fig. 1.20: *Different orientations of p-orbitals*

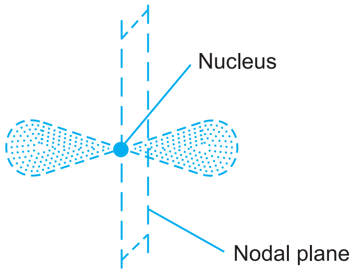


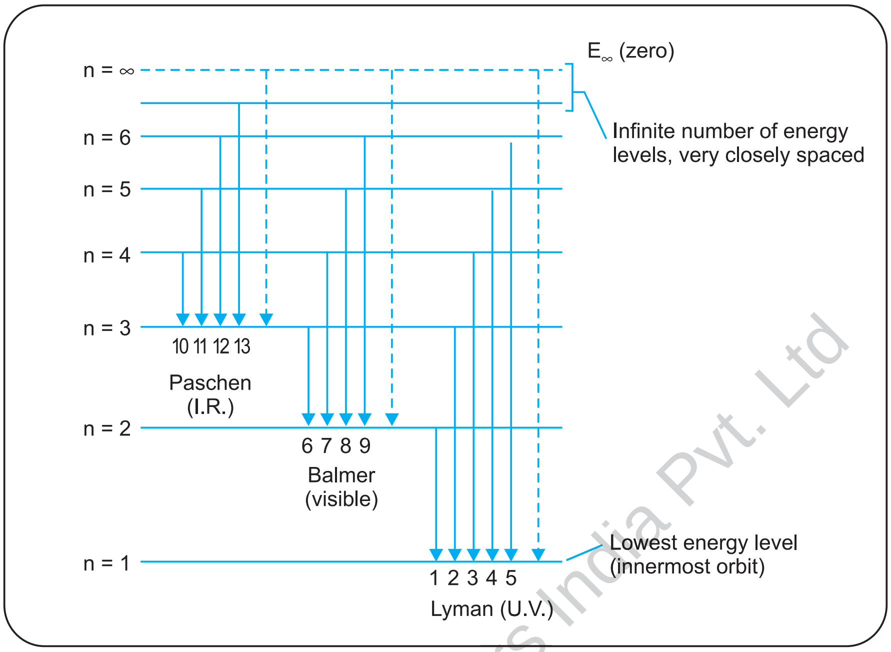
Fig. 1.21: *Nodal plane*

Each of the *p*-orbitals has the shape of a dumbbell. Each of the dumbbell is called lobe. The two lobes of each orbital are separated by a plane of zero electron density called Nodal plane (Fig. 1.21).

1.14 ENERGY LEVEL DIAGRAM ENERGY DISTRIBUTION AND ORBITALS

A diagram representing relative energies of various orbitals in an atom is called an *energy level diagram*. Regarding energy distribution the following two cases arise:

(*i*) Hydrogen and hydrogen like ion



- *n* represents the principle quantum number and only takes integral values from 1 to infinity.
- The ground state refers to the lowest energy level *n* = 1 in which the atom is the most stable. The electron normally occupies this level unless given sufficient energy to move up to a higher level. An atom is said to be in an excited state when its electrons are found in the higher energy levels. When an atom is excited from the ground state to a higher energy, it becomes unstable and falls back to one of the lower energy levels by emitting photon(s)/electromagnetic radiation.

  For hydrogen – like species such as He^+, Li^{2+} and Be^{3+}, the following formula can be applied:

$$E_n = -\frac{1312}{n^2} \times z^2 \text{ kJ mol}^{-1}$$

  where *z* is the atomic number and $n = 1, 2, 3, \ldots$

- The highest energy level $n = \infty$ corresponds to an energy state whereby the electron is no longer bound to the atom, (the electron has escaped from the atom.) By convention, it is usually assigned an energy value of 0 eV.
- The lower the energy level, the more negative the energy value associated with that level. Thus, the lower energy states correspond to more stable states.
- The energy difference between any two adjacent levels gets smaller as *n* increases, which results in the higher energy levels getting very close and crowded together just below $n = \infty$.

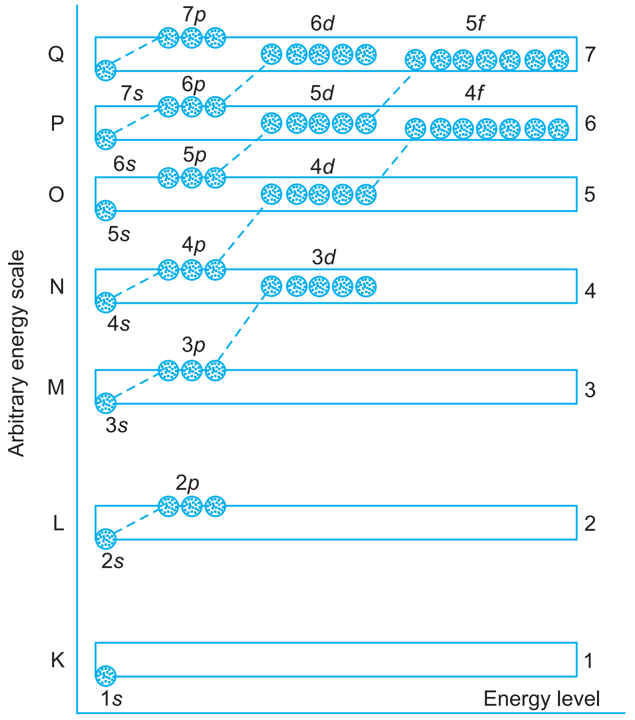


Fig. 1.22: *Energy level diagram for multi-electron atoms*

- The ionization energy of an atom is the energy required to remove the electron completely from the atom. (transition from ground state $n = 0$ to infinity $n = \infty$). For hydrogen, the ionization energy = 13.6eV.
- When an excited electron returns to a lower level, it loses an exact amount of energy by emitting a photon. The Lyman (ultraviolet) series of spectral lines corresponds to electron transitions from higher energy levels to level $n = 1$. Transitions to $n = 2$ and $n = 3$ are called the Balmer (visible) and Paschen (infra red) series, respectively.

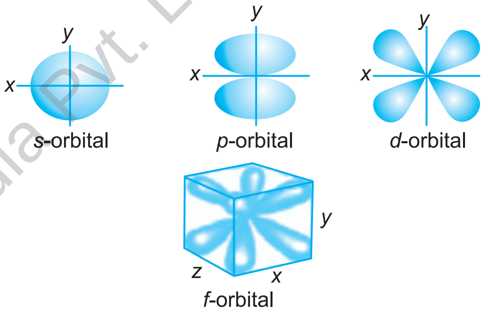
(*ii*) Multi-electrons atoms

The energy level diagram for multi-electron atoms is as shown in Fig. 1.22.

From this diagram, the following points can be noted:

- In multi-electron atoms, the electrons in different subshells belonging to the same shell, have different energies.

  This is due to the fact that in case of multi-electron atoms the energies of the orbitals do not depend only upon the value of the principal quantum number n but also upon the azimuthal quantum number l. For the same value of n, the lower the value of l, the lower will be the energy. Thus, a 2*s* electron ($n = 2$, $l = 0$) has lower energy than a 2*p* electron ($n = 2$, $l = 1$).
- The energies of *s*- and *p*-orbitals for the same principal quantum number n, are close together. The energies corresponding to *d*- and *f*-orbitals are much higher.
- Energy of 3*d*-orbital is in between those of 4*s*- and 4*p*-orbitals and there are many other such crossovers as shown in Fig. 1.22.
- Another feature of the energy-level diagram is that it may be divided into quite well-defined energy zones called *electron shells*. An electron shell may contain groups of orbitals which may have different values of principal quantum number n. For instance, groups of 4*s*, 3*d*- and 4*p*-orbitals form one electron shell.



Shape of Orbitals

1.15 FILLING OF ORBITALS

The filling of electrons into various orbitals is governed by the following rules:

1. **Aufbau principle.** According to this principle, *the electrons are filled to the orbitals one by one in order of increasing energies*. The orbitals have been arranged in order of their energies. The lowest energy is that of 1*s*-orbital. The electrons start filling the orbitals of lower energy levels first and continues to orbitals of higher energies. This order is shown diagrammatically in Fig. 1.23.

   The order of filling is

   1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*, 6*d*, 7*p*, etc.

2. **($n + l$) rule.** According to this rule, the energy of an orbital depends upon the ($n + l$) value. Higher the value, higher will be the energy of the orbital. However, if two orbitals have the same value of ($n + l$), the orbital with a lower value of n has the lower energy. Let us consider the case of 3*p*- and 4*s*-orbitals and 3*d*- and 4*p*-orbitals.

Orbital	n	l	($n + l$)
3*p*	3	1	4
4*s*	4	0	4
3*d*	3	2	5
4*p*	4	1	5

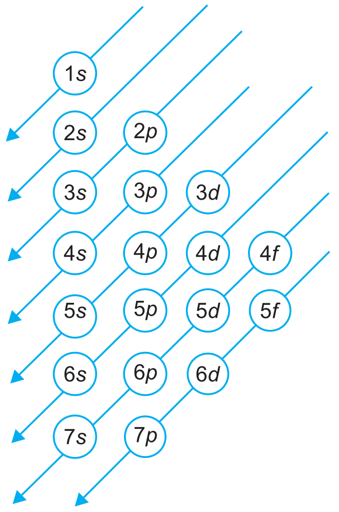


Fig. 1.23: *Order of filling of orbitals*

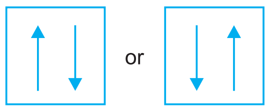


Fig. 1.24: *Opposite spins*

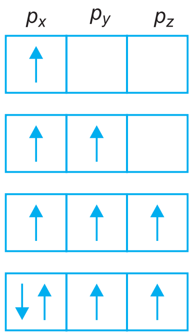


Fig. 1.25: *Sequence of filling of electrons in 2p-orbitals*

Out of 3*p*- and 4*s*-orbitals, 3*p* has the lower energy because of lower value of *n*. Similarly, out of 3*d* and 4*p*, 3*d* has the lower value of energy.

3. **Pauli's exclusion principle.** According to this principle, an orbital can have a maximum of two electrons with opposite spins. So both the electrons in the same orbital are not permitted to have clockwise spin or anticlockwise spin. The spins of the electrons in an orbital are shown in Fig. 1.24.
4. **Hund's rule of maximum multiplicity.** According to this rule, when electrons are being filled in the orbitals they will occupy separate orbitals of the same energy if these are available. For example, the three 2*p*-orbitals p_x, p_y and p_z are of equal energy. While filling three electrons in these orbitals, separate orbitals will be occupied by each electron because no extra energy is needed. However, if the fourth electron is to be filled further, it will pair with one of the three electrons, because next orbital 3*s* is associated with higher energy. So one orbital will have paired electrons. The electrons avoid crowding or pairing as long as possible.

   Fig. 1.25 shows the sequence of filling of four electrons in 2*p*-orbitals.

1.16 ELECTRONIC CONFIGURATION OF ELEMENTS

Electronic configuration of some of the elements are given below. Here, the rules followed are the same as have been explained earlier.

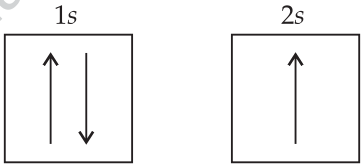
Hydrogen (At. no. = 1). This is the smallest and simplest element. It has only one electron filled in the orbital of lowest energy, *i.e.* 1*s*.

Its configuration will be written as $1s^1$.

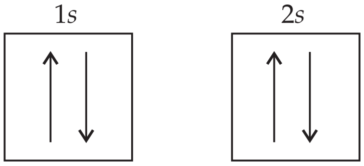
Helium (At. no. = 2). It has two electrons. Both the electrons are filled in 1*s*-orbital because 2*s* has a higher energy. The two electrons in the same orbital have opposite spins.

Its configuration will be written as $1s^2$.

Lithium (At. no. = 3). It has got three electrons. According to the rules, the configuration will be $1s^2\ 2s^1$.

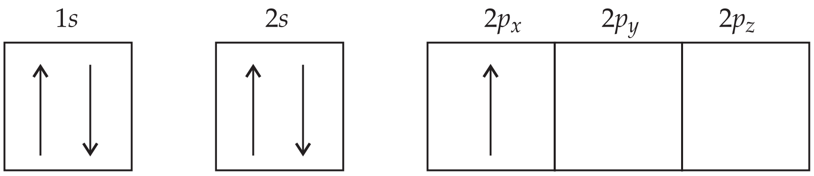


Beryllium (At. no. = 4). The four electrons will be paired in two orbitals.

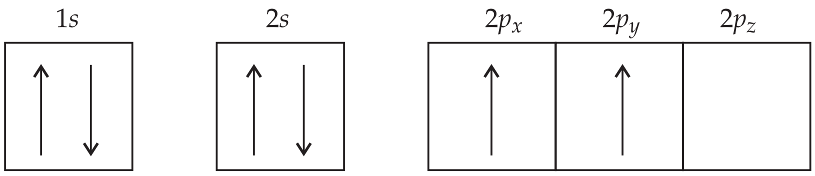


It has the configuration $1s^2\ 2s^2$.

Boron (At. no. = 5). Its configuration is as follows:



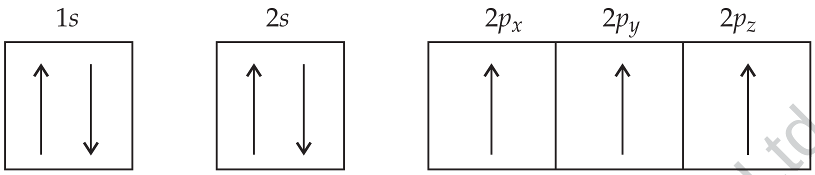
Carbon (At. no. = 6). Its configuration is as follows:



or $1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}$

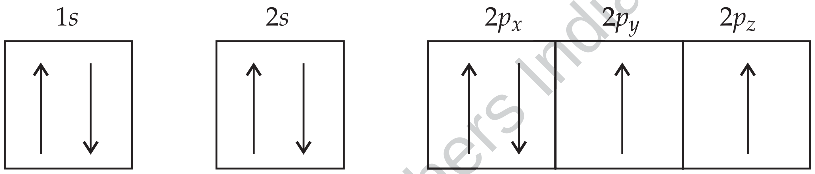
However, in excited state in compound formation one electron from 2*s* level is excited to $2p_z$ level.

Nitrogen (At. no. = 7). Here the no. of electrons is 7.



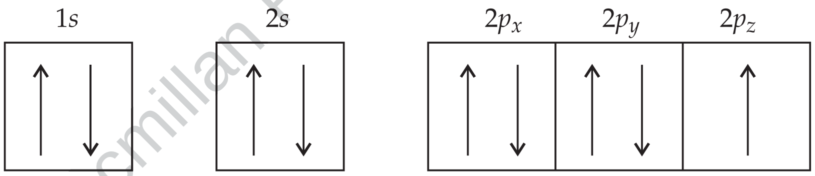
or $1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$

Oxygen (At. no. = 8). The eight electrons are filled as under:



or $1s^2\ 2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$

Fluorine (At. no. = 9). Its configuration is as given below:



or $1s^2\ 2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 2}\ 2p_z^{\ 1}$

Similarly, we can write the configurations of other elements also. Electronic configurations of elements from at. no. 1 to 36, *i.e.* from hydrogen to krypton are given in Table 1.3.

Table 1.4 gives the electronic configurations of the elements from at. no. 37 to 103. The configuration of the last orbit is given while that of the inner orbits has been mentioned in the form of frame of the inert gases like Kr, Xe, Rn. It becomes cumbersome to give the complete electronic configuration of the bigger atoms.

If we have a close look at the configuration of elements, we come across striking features. After calcium, the next element scandium has one electron in 3*d*-orbital because after 4*s*-orbital comes 3*d*-orbital in order of energy. And the capacity of 3*d*-orbital is 10 electrons. So, ten elements are constituted when 3*d*-orbitals are progressively filled. After 3*d*-orbital is completely filled, 4*p*-orbital starts filling up giving elements from Ga to Kr. Same pattern is repeated when we go to elements of higher atomic number. Elements after uranium are unstable and have short half-life periods. They are called **transuranic elements**.

Table 1.3: Electronic Configuration of Elements

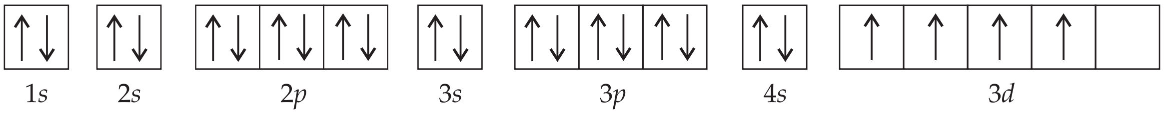
Atomic No.	Element	K 1 s	L 2 s p	M 3 s p d	N 4 s p d f
1	H	$1s^1$			
2	He	$1s^2$			
3	Li	$1s^2$	$2s^1$		
4	Be	$1s^2$	$2s^2$		
5	B	$1s^2$	$2s^2\ 2p^1$		
6	C	$1s^2$	$2s^2\ 2p^2$		
7	N	$1s^2$	$2s^2\ 2p^3$		
8	O	$1s^2$	$2s^2\ 2p^4$		
9	F	$1s^2$	$2s^2\ 2p^5$		
10	Ne	$1s^2$	$2s^2\ 2p^6$		
11	Na	$1s^2$	$2s^2\ 2p^6$	$3s^1$	
12	Mg	$1s^2$	$2s^2\ 2p^6$	$3s^2$	
13	Al	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^1$	
14	Si	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^2$	
15	P	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^3$	
16	S	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^4$	
17	Cl	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^5$	
18	Ar	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6$	
19	K	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6$	$4s^1$
20	Ca	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6$	$4s^2$
21	Sc	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^1$	$4s^2$
22	Ti	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^2$	$4s^2$
23	V	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^3$	$4s^2$
24	Cr	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^5$	$4s^1$
25	Mn	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^5$	$4s^2$
26	Fe	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^6$	$4s^2$
27	Co	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^7$	$4s^2$
28	Ni	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^8$	$4s^2$
29	Cu	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10}$	$4s^1$
30	Zn	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10}$	$4s^2$
31	Ga	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10}$	$4s^2\ 4p^1$
32	Ge	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10}$	$4s^2\ 4p^2$
33	As	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10}$	$4s^2\ 4p^3$
34	Se	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10}$	$4s^2\ 4p^4$
35	Br	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10}$	$4s^2\ 4p^5$
36	Kr	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6\ 3d^{10}$	$4s^2\ 4p^6$

Table 1.4: Electronic Configuration of Elements

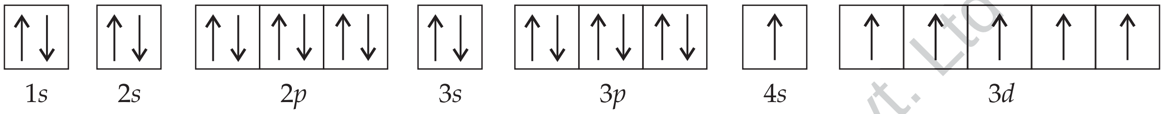
At. No.	Element	Configuration	At. No.	Element	Configuration
37	Rb	Kr $5s^{1}$	71	Lu	— $4f^{14}\ 5d^{1}\ 6s^{2}$
38	Sr	— $5s^{2}$	72	Hf	— $4f^{14}\ 5d^{2}\ 6s^{2}$
39	Y	— $4d^{1}\ 5s^{2}$	73	Ta	— $4f^{14}\ 5d^{3}\ 6s^{2}$
40	Zr	— $4d^{2}\ 5s^{2}$	74	W	— $4f^{14}\ 5d^{4}\ 6s^{2}$
41	Nb	— $4d^{4}\ 5s^{1}$	75	Re	— $4f^{14}\ 5d^{5}\ 6s^{2}$
42	Mo	— $4d^{5}\ 5s^{1}$	73	Ta	— $4f^{14}\ 5d^{3}\ 6s^{2}$
43	Tc	— $4d^{5}\ 5s^{2}$	74	W	— $4f^{14}\ 5d^{4}\ 6s^{2}$
44	Ru	— $4d^{7}\ 5s^{1}$	75	Re	— $4f^{14}\ 5d^{5}\ 6s^{2}$
45	Rh	— $4d^{8}\ 5s^{1}$	76	Os	— $4f^{14}\ 5d^{6}\ 6s^{2}$
46	Pd	— $4d^{10}$	77	Ir	— $4f^{14}\ 5d^{7}\ 6s^{2}$
47	Ag	— $4d^{10}\ 5s^{1}$	78	Pt	— $4f^{14}\ 5d^{8}\ 6s^{2}$
48	Cd	— $4d^{10}\ 5s^{2}$	79	Au	— $4f^{14}\ 5d^{10}\ 6s^{1}$
49	In	— $4d^{10}\ 5s^{2}\ 5p^{1}$	80	Hg	— $4f^{14}\ 5d^{10}\ 6s^{2}$
50	Sn	— $4d^{10}\ 5s^{2}\ 5p^{1}$	81	Tl	— $4f^{14}\ 5d^{10}\ 6s^{2}\ 6p^{1}$
51	Sb	— $4d^{10}\ 5s^{2}\ 5p^{2}$	82	Pb	— $4f^{14}\ 5d^{10}\ 6s^{2}\ 6p^{2}$
52	Te	— $4d^{10}\ 5s^{2}\ 5p^{3}$	83	Bi	— $4f^{14}\ 5d^{10}\ 6s^{1}\ 6p^{3}$
53	I	— $4d^{10}\ 5s^{2}\ 5p^{4}$	84	Po	— $4f^{14}\ 5d^{10}\ 6s^{2}\ 6p^{4}$
54	Xe	— $4d^{10}\ 5s^{2}\ 5p^{6}$	85	At	— $4f^{14}\ 5d^{10}\ 6s^{2}\ 6p^{5}$
55	Cs	Xe $6s^{1}$	86	Rn	— $4f^{14}\ 5d^{10}\ 6s^{2}\ 6p^{5}$
56	Ba	— $6s^{2}$	87	Fr	Rn $7s^{1}$
57	La	— $5d^{1}\ 6s^{2}$	88	Ra	— $7s^{2}$
58	Ce	— $4f^{2}\ 6s^{2}$	89	Ac	— $6d^{1}\ 7s^{2}$
59	Pr	— $4f^{3}\ 6s^{2}$	90	Th	— $6d^{2}\ 7s^{2}$
60	Nd	— $4f^{4}\ 6s^{2}$	91	Pa	— $5f^{2}\ 6d^{1}\ 7s^{1}$
61	Pm	— $4f^{5}\ 6s^{2}$	92	U	— $5f^{3}\ 6d^{1}\ 7s^{2}$
62	Sm	— $4f^{6}\ 6s^{2}$	93	Np	— $5f^{4}\ 6d^{1}\ 7s^{2}$
63	Eu	— $4f^{7}\ 6s^{2}$	94	Pu	— $5f^{6}\ 7s^{2}$
64	Gd	— $4f^{7}\ 5d^{1}\ 6s^{2}$	95	Am	— $5f^{7}\ 7s^{2}$
65	Tb	— $4f^{9}\ 6s^{2}$	96	Cm	— $5f^{7}\ 6d^{1}\ 7s^{2}$
66	Dy	— $4f^{10}\ 6s^{2}$	97	Bk	— $5f^{9}\ 7s^{2}$
67	Ho	— $4f^{11}\ 6s^{2}$	98	Cf	— $5f^{10}\ 7s^{2}$
68	Er	— $4f^{12}\ 6s^{2}$	99	Es	— $5f^{11}\ 7s^{2}$
69	Tm	— $4f^{13}\ 6s^{2}$	100	Fm	— $5f^{12}\ 7s^{2}$
70	Yb	— $4f^{14}\ 6s^{2}$	101	Md	— $5f^{13}\ 7s^{2}$
71	Lu	— $4f^{14}\ 5d^{1}\ 6s^{2}$	102	No	— $5f^{14}\ 7s^{2}$
72	Hf	— $4f^{14}\ 5d^{2}\ 6s^{2}$	103	Lr	— $5f^{14}\ 6d^{1}\ 7s^{2}$

1.17 SOME EXCEPTIONAL ELECTRONIC CONFIGURATIONS

Generally, the filling of electrons in the orbitals takes place according to Aufbau rule, Pauli's exclusion principle and Hund's rule of maximum multiplicity. But sometimes, we observe situations, where these rules are violated. This happens in case where the configuration after contravening these rules is going to have a symmetry. Symmetrical configurations are more stable than other configurations. Half-filled and completely-filled configurations are some examples of the symmetrical configurations. Consider the electronic configuration of chromium (At. no. 24). According to normal rules, it should have the following configuration

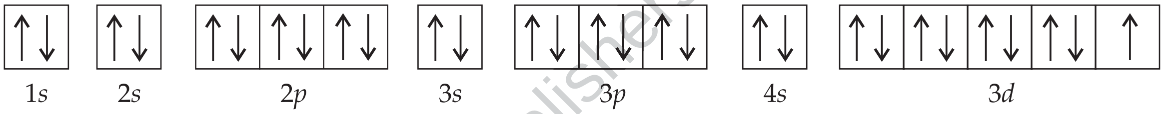


But it is found to have the following configuration

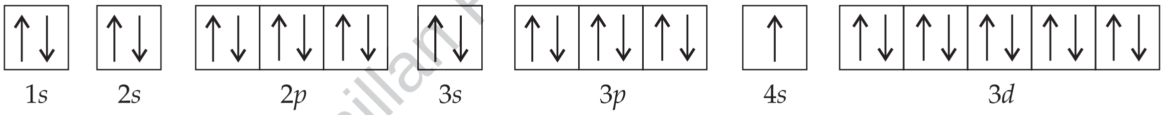


This is because there is not much difference between the energies of 4*s*-orbitals and 3*d*-orbitals. Hence, one electron from 4*s* shifts to 3*d*-orbitals to give a half-filled symmetrical and, hence, more stable configuration. Here all the 3*d*-orbitals are half-filled.

Similarly, copper (At. no. 29) is expected to exhibit the configuration



In fact, it exhibits the configuration



In the later configuration, all the 3*d* orbitals are completely filled. Hence, this is symmetrical and, hence, more stable configuration. This is achieved by shifting one electron from 4*s*-orbital to 3*d*-orbital as there is very little difference between the energies of the two orbitals. Some other exceptional electronic configurations that we encounter are:

Molybdenum (Atomic number = 42)

Expected configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^4\ 5s^2$

Actual configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^5\ 5s^1$

Palladium (Atomic number = 46)

Expected configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^8\ 5s^2$

Actual configuration: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^0$

Thus, generally only one electron jumps from lower energy orbital to higher energy orbital, *e.g.* from 4*s* to 3*d*. However, in case of palladium, two electrons are involved (the only case with a difference).

The reason for the tendency of the subshells to be completely filled or exactly half-filled is that it leads to greater stability.

Cause of greater stability of exactly half-filled and completely filled configurations. The greater stability of these configurations can be explained in terms of the following factors:

(*i*) **Symmetry.** The half-filled and completely filled configurations are more symmetrical and symmetry leads to greater stability.

(*ii*) **Exchange of energy.** The electrons present in the different orbitals of the same subshell can exchange their positions. Each such exchange leads to a greater stability. As the number of exchanges that can take place is maximum in the exactly half-filled and completely filled arrangements (*i.e.*, more in d^5 than in d^4 and more in d^{10} than in d^9), therefore exchange energy is maximum and hence the stability is maximum.

Some important points in writing electronic configurations. While writing the electronic configurations, the following points may also be noted:

(*i*) Unless otherwise mentioned, electronic configuration always means the electronic configuration in the ground state.

(*ii*) Although the orbitals of lower energy are filled first but the electronic configurations are written in the order of principal quantum numbers.

(*iii*) To avoid the writing of electronic configurations in a lengthy way, usually the symbols $[\text{He}]^2$, $[\text{Ne}]^{10}$, $[\text{Ar}]^{18}$, etc., are used as the first part of the configuration. Such a symbol stands for the electronic configuration of that inert gas and is usually called the core of the inert gas.

Example 1. *Find the number of unpaired electrons present in phosphorus (atomic no. 15) and copper (atomic no. 29) after writing their orbital electronic configuration.*

Solution.

Element	*At. No.*	*Electronic Configuration*	*No. of Unpaired Electrons*
P	15	$1s^2, 2s^2\ 2p^6, 3s^2, 3p_x^1\ 3p_y^1 3p_z^1$	3
Cu	29	$1s^2, 2s^2\ 2p^6, 3s^2\ 3p^6\ 3d^{10}, 4s^1$	1

Example 2. *Write the electronic configurations of the elements with the following atomic numbers: 8, 10, 17, 25 and 38. Also, mention the groups of the periodic table to which they belong.*

Solution.

Atomic No.	*Electronic Configuration*	*Group of Periodic Table*
8	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$	16
10	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	18
17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$	17
25	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	7
38	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^2$	2

Note:

(*i*) If the last shell contains 1 or 2 electrons, then the group number is 1 and 2 respectively.

(*ii*) If the last shell contains 3 or more than 3 electrons then the group number is the total number of electrons in the last shell plus 10.

(*iii*) If electrons are present in $(n-1)d$ orbital in addition to those in the ns orbital, then the group number is equal to the total number of electrons present in the $(n-1)d$ orbital and ns orbital.

Example 3. *A neutral atom of element has 2K, 8L and 5M electrons. Find out the following from the data: (a) Atomic no. (b) Total no. of s-electrons (c) Total no. of p-electrons (d) Valency of the element.*

Solution. The electronic configuration of the element with 2K, 8L and 5M electrons will be

$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$

(*a*) Total no. of electrons $= 2 + 8 + 5 = 15$.

$\therefore$ Atomic no. of electrons $= 15$

(*b*) Total no. of *s*-electrons $= 2 + 2 + 2 = 6$

(*c*) Total no. of *p*-electrons $= 6 + 3 = 9$

(*d*) Since the element has only three half-filled atomic orbitals, therefore, valency of the element = 3.

Example 4. *Give the electronic configuration of the following ions: (i)* Cu^{2+}*, (ii)* Cr^{3+}*, (iii)* Fe^{3+} *and (iv)* H^-.

Solution. During the formation of cations electrons are lost while in the formation of anions, electrons are added to the valence shell. The number of electrons added or lost is equal to the numerical value of the charge present on the ion. Following this general concept, we can write the electronic configurations of all the ions given in the question.

(*i*) $Cu^{2+} = {}_{29}Cu - 2e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1 - 2e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$

(*ii*) $Cr^{3+} = {}_{24}Cr - 3e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1 - 3e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

(*iii*) $Fe^{3+} = {}_{26}Fe - 3e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2 - 3e^-$

$= 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

(*iv*) $H^- = 1H + 1e^-$

$= 1s^1 + 1e^1 = 1s^2$

Note. For writing the electronic configuration of cations, first write the electronic configuration of neutral atom and then remove number of electrons equal to the units of positive charge, starting from the outermost shell. Similarly, the electronic configurations of anions are written.

Example 5. *Discuss the possibility of the atom for existing in the following electronic configurations:*

(i) $1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$ *(ii)* $1s^2\ 2s^2\ 3s^2$ *(iii)* $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1$.

Solution.

(*i*) This electronic configuration is wrong because it violates Aufbau principle which states that an orbital with lower energy, *i.e.* 2*s* in the present case should be completely filled before the electrons go to higher energy subshell, *i.e.* $2p_x$.

(*ii*) This electronic configuration is wrong since after filling 2*s*-orbital, the electrons should go to 2*p*-orbital rather than 3*s*-orbital.

(*iii*) This electronic configuration is not correct since it violates Hund's rule. According to this rule, all the three 2*p*-orbitals must have one electron each before the pairing occurs. But, in the present case, $2p_x$ orbital has two electrons while $2p_z$ orbital is empty.

PROBLEMS FOR PRACTICE

1. Write the electronic configurations and the names of the elements having the atomic numbers 9, 10, 19 and 20.

[**Ans.**	Atomic no.	Electronic configuration	Name
	9	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$	Fluorine
	10	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$	Neon
	19	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	Potassium
	20	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	Calcium]

2. Write the electronic configurations of the following elements: Chlorine and phosphorus.

[**Ans.** Chlorine ($_{17}$Cl) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$; Phosphorus ($_{15}$P) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$]

3. Write down the electronic configuration of an element with atomic number 14. Which group in the periodic table does this element belong to? [**Ans.** Group 14]

4. Correct the following electronic configurations of the elements in the ground state:

(*i*) $1s^2\ 2s^1\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2\ 3p_x^1$ (*ii*) $1s^2\ 2s^2\ 2p_y^2\ 2p_z^1$ (*iii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$

[**Ans.** (*i*) $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2\ 3s^2$; (*ii*) $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$; (*iii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$]

5. Write the electronic configuration of $_9F^{19}$, $_{16}S^{32}$ and $_{18}Ar^{38}$ and then point out the element with: (*i*) maximum charge, (*ii*) minimum number of neutrons, and (*iii*) maximum number of unpaired electrons.

[**Ans.** $_9F^{19} = 1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$; $_{16}S^{32} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$; $_{18}Ar^{38} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

(*i*) Maximum nuclear charge = 18 in $_{18}Ar^{38}$

(*ii*) Minimum no. of neutrons = 10 in $_9F^{19}$

(*iii*) Maximum no. of unpaired electrons = 2 in $_{16}S^{32}$]

6. Give the electronic configurations of the following elements: $_{19}$K and $_{25}$Mn.

[**Ans.** $_{19}K = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$; $_{25}Mn = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$]

7. Give the electronic configurations of the following ions:

(*i*) H^- (*ii*) Na^+ and (*iii*) N^-.

[**Ans.** (*i*) $1s^2$ (*ii*) $1s^2\ 2s^2\ 2p^6$ (*iii*) $1s^2\ 2s^2\ 2p^4$]

8. Name the elements that correspond to each of the following electronic configurations. Write down their atomic numbers also.

   (*i*) $1s^2\ 2s^2\ 2p^2$ and (*ii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$. [**Ans.** (*i*) C (6) (*ii*) Al (13)]

9. What are the atomic numbers of elements whose outermost electrons are represented by

   (*i*) $2p^3$ and (*ii*) $3d^6$? [**Ans.** (*i*) 7 (*ii*) 26]

10. Which of the following configurations represent the element in the ground and which in the excited state? Name the elements in each case:

    (*i*) $1s^2\ 2s^1\ 2p^1$ (*ii*) $1s^2\ 2s^2\ 2p^1$ and (*iii*)$1s^2\ 2s^1\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$

    [**Ans.** (*i*) Be (*ii*) B (*iii*) C. Be and C are in excited state, B is in ground state]

11. What atoms are indicated by the following configurations?

    (*i*) [He] $2s^1$ and (*ii*) [Ar] $4s^2\ 3d^1$] [**Ans.** (*i*) Li (*ii*) Sc]

QUICK SCAN (FOR REVISION)

1. The concept of '**atom**' was put forward by Dalton in 1808.
2. Cathode rays were first discovered by **Julius Plucker**. In the discharge tube, electric current flows only at low pressure. No electric current flows if the gas pressure in the tube is one atmosphere. Similarly, no electric current flows in vacuum.
3. The ratio of charge/mass of electron was determined by **J. J. Thomson (1897)**. Its value is $e/m = 1.76 \times 10^8\ \text{Cg}^{-1}$.
4. The charge on the electron was found by **R.A. Millikan** (1917) with his oil drop experiment. Its value is found to be, $e = 1.60 \times 10^{-19}$ coulombs or 4.8×10^{-10} e.s.u.
5. Mass of electron = 9.11×10^{-31} kg. It is $\frac{1}{1837}$ of that of H-atom.
6. Cathode rays are first produced from the material of the cathode and then from the gas inside the discharge tube.
7. Charge on 1 mole of electrons = 96500 coulombs = 1 Faraday.
8. The ratio *i.e.* charge/mass (e/m) of the particles (electrons) in the cathode rays is same irrespective of the nature of the gas taken inside the tube. Hence, electrons are universal constituents of all matter.
9. Anode rays are not emitted from the anode but are produced from the gaseous atoms present in the tube by the knock out of the electrons due to bombardment by high speed cathode rays on them.
10. The ratio, *i.e.* charge/mass (e/m) of the particles present in the anode rays depends upon the nature of the gas taken inside the tube. The mass of the particle is nearly same as that of the atom of the gas.
11. Proton was discovered by **Goldstein in 1886**.
12. For protons, charge/mass (e/m) = $9.58 \times 10^4\ \text{C g}^{-1}$

    Charge = 1.6×10^{-19} C is same as that of electron

    Mass = 1.67×10^{-24} g

    = 1.67×10^{-27} kg (that of H-atom)
13. Nucleus was discovered by **Rutherford in 1911** by his alpha particles scattering experiment.
14. Radius of nucleus is of the order of 10^{-15} m and is nearly 1/10,000th of that of the atom.
15. Actual mass of neutron = 1.6749×10^{-27} kg.

    Actual mass of proton = 1.6726×10^{-27} kg.

    Thus, neutron is slightly heavier than proton.
16. Neutron was discovered by **Chadwick in 1932** by bombarding Beryllium and Boron with α-particles.
17. Particles present in the nucleus are called **nucleons**.
18. Atomic no. (Z) = No. of protons in the nucleus = No. of electrons in the atom.
19. Mass no. (A) = No. of protons + No. of neutrons.
20. No. of electrons = No. of protons = Atomic number.

    No. of neutrons = Mass no. (A) – Atomic no. (Z).
21. *s*-orbitals have spherical shape while *p*-orbitals have dumb-bell shape.
22. Number of nodes in any orbital = $(n - l - 1)$.

EXERCISES

Very Short Answer Type Questions

1. Which energy level does not have a p-orbital?
2. What are the different isotopes of hydrogen?
3. How many neutrons are present in $^{238}_{92}U$?
4. Write down the actual value of charge and mass of an electron.
5. Which quantum number determines the (*a*) shape (*b*) orientation and (*c*) size of the orbital?
6. Write the expression for the energy of electron of hydrogen atom in the nth level.
7. Which element does not have neutron in it?
8. What is the number of electrons, protons and neutrons in each of the following?

   $^{27}_{13}Al$; $^{37}_{17}Cl$
9. Give the sequence of energies of 3s, 3p and 3d orbitals in: (*i*) a hydrogen atom (*ii*) a multi-electron atom?
10. Which element has only one electron in the d-orbital?
11. What is the maximum number of electrons that can be accommodated in the d-subshell?
12. Draw a diagram to show the general shape of p-orbitals?
13. Which isotope of carbon is used for getting relative atomic mass?
14. Define one atomic mass units.
15. A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57 μm. Calculate the rate of emission of quanta per second.

Short Answer Type Questions

1. Describe the contributions of Rutherford's model in establishing a picture of the atom.
2. Write a short note on Aufbau Principle.
3. What is the maximum number of electrons with clockwise spin that can be accommodated in
   - (*i*) K shell
   - (*ii*) M shell
   - (*iii*) 3d subshell
   - (*iv*) 4f subshell?
4. Draw the shapes of 2s and $2p_x$ orbitals. Indicate nodal plane in case of $2p_x$ orbital.
5. State Aufbau Principle. Write electronic configurations of the elements with atomic numbers 17 and 24.
6. Draw shapes of s- and p-orbitals.
7. Explain, why atoms with half-filled and completely filled orbitals have extra stability.
8. Define Hund's Rule.
9. Draw a labelled diagram of mass spectrometer.
10. Why don't we observe the wave properties of large objects such as cricket ball?

Long Answer Type Questions

1. Draw an energy level diagram for multi-electron atoms.
2. The atom of an element has the symbol $^{a}_{11}X$.
   - (*i*) Write down the number of protons and electrons in it.
   - (*ii*) Write down the approximate value of mass number a. Give reasons.
   - (*iii*) Write down the electronic configuration of the atom in terms of s, p, d, f.
3. Define the following:
   - (*i*) Aufbau Principle
   - (*ii*) Hund's rule of maximum multiplicity
   - (*iii*) $(n + l)$ rule
4. Size of cation is smaller than the neutral atom while the size of the anion is larger than the neutral atom. Explain.
5. How does Bohr's theory explain the shortcomings of Rutherford's model.
6. Explain the working of mass spectrometer.

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. Ist
2. Protium ($_1H^1$), Deuterium ($_1H^2$), Tritium ($_1H^3$)
3. 238 – 92 = 146
4. Charge = 1.60×10^{-19} coulombs,

   mass = 9.11×10^{-31} kg
5. (*a*) Azimuthal (*b*) Magnetic (*c*) Principal
6. $E = -\frac{1312}{n^2}$ kJ mol^{-1}.
7. Hydrogen
8. $e = 13$, $p = 13$, $n = 14$; $e = 17$, $p = 17$, $n = 20$
9. (*i*) $3s = 3p = 3d$ (*ii*) $3s < 3p < 3d$.
10. Scandium (Z = 21)
11. Ten
13. Carbon - 12
14. 7.16×10^{19}

COMPETITION FILE

SUBJECTIVE PROBLEM

Problem 1. *How can you justify the non-existence of electron in the nucleus of an atom?*

Solution. It can be justified on the basis of Heisenberg's uncertainty Principle.

According to this principle, $\Delta x \times \Delta p \geq \frac{h}{4\pi}$

or $\Delta x \times m \times \Delta v \geq \frac{h}{4\pi}$ or $\Delta v \geq \frac{h}{4\pi \times m \times \Delta x}$

Putting the values of mass of electron (m), Δx = radius of the nucleus = 10^{-14} m and Planck's constant (h), we get

$$\Delta v \geq \frac{6.6 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1}}{4 \times 3.142 \times 9.1 \times 10^{-31}\ \text{kg} \times 10^{-14}\ \text{m}}$$

$$\geq 0.058 \times 10^{11}\ \text{ms}^{-1} > 5.8 \times 10^{9}\ \text{ms}^{-1}.$$

Since the uncertainty in velocity is more than that of velocity of light (3×10^8 ms^{-1}), this means that the velocity of the electron is more than that of light, which is not possible. Therefore, the electron cannot be present in the nucleus of the atom.

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. The uncertainty in the position of an electron is zero, the uncertainty in its momentum would be

(*a*) zero (*b*) $\geq \frac{h}{4\pi}$

(*c*) $< \frac{h}{4\pi}$ (*d*) infinite

2. The number of nodal planes in a p_x orbital is

(*a*) one (*b*) two

(*c*) three (*d*) zero

3. Rutherford's experiment which established the nuclear model of the atom, used a beam of

(*a*) β-particles, which impinged on a metal foil and got absorbed.

(*b*) γ-rays, which impinged on a metal foil and ejected electrons.

(*c*) helium atoms, which impinged on a metal foil and got scattered.

(*d*) helium nuclei, which impinged on a metal foil and got scattered.

4. The number of the radial nodes for 3*s*- and 2*p*-orbitals are respectively

(*a*) 2, 0 (*b*) 0, 2

(*c*) 1, 2 (*d*) 2, 1

(B) Fill in the Blanks

Fill in the blank spaces:

1. The modern atomic mass unit is based on the mass of ________.
2. Rutherford experiment of scattering of α-particles showed for the first time that the atom has ________.
3. The nucleus of an atom consists of ________ and ________ only.
4. The statement "No two electrons in an atom can have all the four quantum numbers identical" is known as ________.
5. The number of electrons in an atom is equal to its ________.
6. The electronic configuration of He is $1s^2$ and that of oxygen is ________.
7. Isotopes have same number of ________ and ________ but different number of ________.
8. The number of unpaired electrons in the Fe^{3+} ion is ________.
9. The $2p_x$, $2p_y$ and $2p_z$ orbitals have identical shapes but differ in ________.
10. Two electrons in the same orbital have ________ spin.
11. The outermost electronic configuration of Cr is ________.
12. The mass of H-atom is ________ kg.

(C) True/False Statements

Write T for true and F for false statements:

1. 3*s* and 3*p*-orbitals have same energy.
2. The maximum number of electrons in 4*f*-orbital can be eighteen.
3. All *p*-orbitals of the same shell have different energies.
4. All photons possess the same amount of energy.
5. Electrons, protons and neutrons are capable of having independent existence.

6. In silver atom, 23 electrons have a spin of one type and 24 of the opposite type (Atomic no. of Ag = 47).
7. The electronic configuration of Cr is [Ar] $3d^5\ 4s^1$.
8. An orbital represents the volume in the space with 99% probability of finding an electron.
9. Wavelength and wave number are not same for a wave.
10. The magnetic quantum number may have negative value.

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. Which of the following conclusions could not be derived from Rutherford's α-particle scattering experiment?
   (*a*) Most of the space in the atom is empty.
   (*b*) The radius of the atom is about 10^{-10}m while that of nucleus is 10^{-15}m.
   (*c*) Electrons move in a circular path of fixed energy called orbits.
   (*d*) Electrons and the nucleus are held together by electrostatic forces of attraction.
2. Which of the following options does not represent ground state electronic configuration of an atom?
   (*a*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
   (*b*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$
   (*c*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
   (*d*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
3. Which of the following statement is not correct about the characteristics of cathode rays?
   (*a*) They start from the cathode and move towards the anode.
   (*b*) They travel in straight line in the absence of an external electrical or magnetic field.
   (*c*) Characteristics of cathode rays do not depend upon the material of electrodes in cathode ray tube.
   (*d*) Characteristics of cathode rays depend upon the nature of gas present in the cathode ray tube.
4. Which of the following statements about the electron is incorrect?
   (*a*) It is a negatively charged particle.
   (*b*) The mass of electron is equal to the mass of neutron.
   (*c*) It is a basic constituent of all atoms.
   (*d*) It is a constituent of cathode rays.
5. Which of the following properties of atom could be explained correctly by Thomson Model of atom?
   (*a*) Overall neutrality of atom.
   (*b*) Spectra of hydrogen atom.
   (*c*) Position of electrons, protons and neutrons in atom.
   (*d*) Stability of atom.
6. Two atoms are said to be isobars if
   (*a*) they have same atomic number but different mass number.
   (*b*) they have same number of electrons but different number of neutrons.
   (*c*) they have same number of neutrons but different number of electrons.
   (*d*) sum of the number of protons and neutrons is same but the number of protons is different.
7. Which of the following is responsible to rule out the existence of definite paths or trajectories of electrons?
   (*a*) Pauli's exclusion principle.
   (*b*) Heisenberg's uncertainty principle.
   (*c*) Hund's rule of maximum multiplicity.
   (*d*) Aufbau principle.
8. Total number of orbitals associated with third shell will be
   (*a*) 2 (*b*) 4
   (*c*) 9 (*d*) 3
9. Chlorine exists in two isotopic forms, Cl-37 and Cl-35 but its atomic mass is 35.5. This indicates the ratio of Cl-37 and Cl-35 is approximately
   (*a*) 1 : 2 (*b*) 1 : 1
   (*c*) 1 : 3 (*d*) 3 : 1
10. The pair of ions having same electronic configuration is
    (*a*) Cr^{3+}, Fe^{3+} (*b*) Fe^{3+}, Mn^{2+}
    (*c*) Fe^{3+}, Co^{3+} (*d*) Sc^{3+}, Cr^{3+}
11. For the electrons of oxygen atom, which of the following statements is correct?
    (*a*) Z_{eff} for an electron in a 2*s*-orbital is the same as Z_{eff} for an electron in a 2*p*-orbital.
    (*b*) An electron in the 2*s*-orbital has the same energy as an electron in the 2*p*-orbital.
    (*c*) Z_{eff} for an electron in 1*s*-orbital is the same as Z_{eff} for an electron in a 2*s*-orbital.
    (*d*) The two electrons present in the 2*s*-orbital have spin quantum numbers m_s but of opposite sign.
12. Identify the pairs which are **not** of isotopes?
    (*a*) ${}^{12}_{6}X$, ${}^{13}_{6}Y$ (*b*) ${}^{35}_{17}X$, ${}^{37}_{17}Y$
    (*c*) ${}^{14}_{6}X$, ${}^{14}_{7}Y$ (*d*) ${}^{8}_{4}X$, ${}^{8}_{5}Y$

II. Matching Type Questions

In some of the following questions, one option of left column may be correlated to more than one option in the right column.

1. Match the species given in Column I with the electronic configuration given in Column II:

Column I	Column II
(*i*) Cr	(*a*) [Ar]$3d^8\ 4s^0$
(*ii*) Fe^{2+}	(*b*) [Ar]$3d^{10}\ 4s^1$
(*iii*) Ni^{2+}	(*c*) [Ar]$3d^6\ 4s^0$
(*iv*) Cu	(*d*) [Ar]$3d^5\ 4s^1$
	(*e*) [Ar]$3d^6\ 4s^2$

III. Assertion-Reason Type Question

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below in each question.

1. ***Assertion* (*A*):** All isotopes of a given element show the same type of chemical behaviour.

   ***Reason* (*R*):** The chemical properties of an atom are controlled by the number of electrons in the atom.

   (*i*) Both A and R are true and R is the correct explanation of A.

   (*ii*) Both A and R are true but R is not the correct explanation of A.

   (*iii*) A is true but R is false.

   (*iv*) Both A and R are false.

IV. Short Answer Type Questions

1. Arrange s, *p* and *d* subshells of a shell in the increasing order of effective nuclear charge (Z_{eff}) experienced by the electron present in them.
2. Show the distribution of electrons in oxygen atom (atomic number 8) using orbital diagram.
3. Nickel atom can lose two electrons to form Ni^{2+} ion. The atomic number of nickel is 28. From which orbital will nickel lose two electrons?
4. The arrangement of orbitals on the basis of energy is based upon their (*n*+*l*) value. Lower the value of (*n*+*l*), lower is the energy. For orbitals having same values of (*n*+*l*), the orbital with lower value of *n* will have lower energy.

   (*i*) Based upon the above information, arrange the following orbitals in the increasing order of energy.

   (*a*) 1*s*, 2*s*, 3*s*, 2*p*　　(*b*) 4*s*, 3*s*, 3*p*, 4*d*

   (*c*) 5*p*, 4*d*, 5*d*, 4*f*, 6*s*　　(*d*) 5*f*, 6*d*, 7*s*, 7*p*

   (*ii*) Based upon the above information, solve the questions given below:

   (*a*) Which of the following orbitals has the lowest energy?

   4*d*, 4*f*, 5*s*, 5*p*

   (*b*) Which of the following orbitals has the highest energy?

   5*p*, 5*d*, 5*f*, 6*s*, 6*p*
5. Which of the following will not show deflection from the path on passing through an electric field?
   Proton, cathode rays, electron, neutron.
6. An atom having atomic mass number 13 has 7 neutrons. What is the atomic number of the atom?

ANSWERS

(A) Multiple Choice Questions

1. (*d*)　2. (*a*)　3. (*d*)　4. (*a*)

(B) Fill in the Blanks

1. C-12
2. nucleus
3. protons, neutrons
4. Pauli's exclusion principle
5. atomic number
6. $1s^2\ 2s^2\ 2p^2_x\ 2p^1_y\ 2p^1_z$
7. electrons, protons, neutrons
8. live
9. orientation
10. opposite
11. $3d^5\ 4s^1$
12. 1.673×10^{-27}

(C) True/False Statements

1. F　2. F　3. F　4. F　5. F　6. T　7. T　8. T　9. T　10. T

Some Additional Questions

I. Multiple Choice Questions

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

II. Matching Type Questions

1. (*i*) → (*d*) (*ii*) → (*c*) (*iii*) → (*a*) (*iv*) → (*b*)

III. Assertion-Reason Type Question

1. (*i*)

IV. Short Answer Type Questions

1. $d < p < s$

2. $\underset{1s}{\boxed{\uparrow\downarrow}} \quad \underset{2s}{\boxed{\uparrow\downarrow}} \quad \underset{2p}{\boxed{\uparrow\downarrow}\boxed{\uparrow\ }\boxed{\uparrow\ }}$

3. $4s$

4. (*i*) (*a*) $1s < 2s < 2p < 3s$ (*ii*) (*a*) $5s$ (*b*) $5f$
   (*b*) $3s < 3p < 4s < 4d$
   (*c*) $4d < 5p < 6s < 4f < 5d$
   (*d*) $7s < 5f < 6d < 7p$

5. neutron

6. $A = 13,\ A - Z = 7 \quad \therefore \quad Z = 6$
   atomic number = 6

2

CHAPTER

Periodic Table

LEARNING OBJECTIVES

- Classify an element as *s*-block, *p*-block or *d*-block based on its position in the Periodic Table.
- Describe the trends in atomic radius, first ionization energy, melting and boiling points of the elements in the second period (Li-Ne) and third period (Na-Ar).
- Explain the physical properties of the highest oxides of the elements Na-S in terms of their structure and bonding.
- Describe the reactions of the oxides Na_2O, MgO, Al_2O_3, SiO_2, P_4O_{10}, SO_2 and SO_3 with water.
- Explain the harmful effects of SO_2 and SO_3 in acid rain.
- Describe the pH changes of the resulting solutions of the oxides with water across the period.

2.1 INTRODUCTION

When a large number (117) of elements were discovered, it was felt that they should be arranged in a certain order to make their study easier. We have seen that in a library, thousands of books are arranged in a certain manner — subjectwise, authorwise — so as to locate them easily. For the classification of elements, the best method would be the one which puts together all those elements which resemble in most respects and are different from others. In the earliest attempts at classification, the elements were classified into metals and non-metals, but this rough classification was not of much help.

With the discovery of more and more elements, it became necessary to devise some kinds of classification whereby elements with similar characteristics could be placed together. Such a classification was necessary to study the elements and their compounds systematically. A number of attempts were made by various scientists to arrive at classification of elements and this ultimately led to the formulation of Periodic Table.

Periodic table is a classification of elements in such a way that elements with similar properties are grouped together in the same vertical column. Dissimilar elements are placed in different vertical columns.

The aim of classification is to simplify study of elements and their compounds. Instead of studying a large number of elements individually, it is much more convenient to study them in a few broad groups.

2.2 MENDELEEV'S PERIODIC LAW


Mendeleev

In 1869, Dmitri Mendeleev, a Russian chemist, achieved a remarkable milestone towards the classification of elements. After studying the chemical properties of the elements, he proposed that *the chemical properties of the elements are a periodic function of their atomic weights*. Lother-Meyer had proposed that *physical properties of the elements are a periodic function of their atomic weights*.

Mendeleev integrated the two statements in form of a law called **Mendeleev-Lother-Meyer's Periodic Law** or simply **Mendeleev's Periodic law**. The law states: *The physical and chemical properties of elements are a periodic function of their atomic weights, i.e. when the elements are arranged in order of their increasing atomic weights, elements with similar properties are repeated after a certain regular interval.*

2.3 MENDELEEV'S PERIODIC TABLE

Mendeleev, a Russian chemist undertook the work in a more systematic manner. He observed that when elements are arranged in order of their atomic weights, elements with similar properties appeared at regular intervals. A table of elements in which the elements of similar properties are placed together is called **Periodic Table**.

During his time, many elements were not known. So he left blank spaces for them in his table. He predicted the existence and properties of these elements. This is the biggest proof of the importance of his work. For example, he predicted the existence of gallium with properties similar to those of aluminium. He proposed the name *eka-aluminium* for it. Similarly, he declared the existence of germanium with properties similar to that of silicon. The name *eka-silicon* was suggested by him. These elements were actually discovered in later years and found to possess properties as suggested by Mendeleev. The wonderful work done by Mendeleev paved the way for a proper classification of elements in order to study the elements in a systematic manner. Table 2.1 gives the modified form of Mendeleev's Table.

Characteristics of Mendeleev's Periodic Table: Modified form of the Mendeleev's periodic table consists of the following:

(*i*) *Nine vertical columns are called groups.* These are designated as I, II, III, IV, V, VI, VII, VIII and zero. Except for the groups VIII and Zero, each group is further divided into two sub-groups, designated as A and B. The elements which lie on the left hand side of each group constitute sub-group A while those placed on the right hand side form sub-group B. Group VIII contains nine elements in three sets each containing three elements. Group Zero consists of inert gases. Elements of sub-group A and B in the same group show different properties.

(*ii*) *Seven horizontal rows are called periods.* These are numbered from 1 to 7. **First period** contains only 2 elements and is the shortest period. **Second and third periods** contain 8 elements each. These are also called **short periods**. **Fourth and fifth periods** contain 18 elements each and are called **long periods**. **Sixth period** contains 32 elements. **Seventh period** is, however, incomplete and contains only 24 elements.

Inert gases were not known when the Mendeleev's periodic table was formulated. With the discovery of inert gases, a new group called Zero group was added to the Mendeleev's original periodic table.

2.3.1 Importance of Mendeleev's Periodic Table

1. **Prediction of new elements.** At the time when Mendeleev's periodic table was conceived, only 56 elements were known. Mendeleev left some blank spaces or gaps in his table. These gaps represented unknown elements. Further, Mendeleev predicted the properties of these unknown elements on the basis of their positions. For example, he predicted the properties of gallium and germanium which were unknown at that time. Later, when these elements were discovered, their properties were found to be similar to those predicted by Mendeleev.

Table 2.1: Mendeleev's Periodic Table (Modified Form)

Groups → ↓ Periods	I		II		III		IV		V		VI		VII		VIII	Zero
	A	B	A	B	A	B	A	B	A	B	A	B	A	B		
1	$_{1}$H 1.008															$_{2}$He 4.003
2	$_{3}$Li 6.919		$_{4}$Be 9.012		$_{5}$B 10.81		$_{6}$C 12.011		$_{7}$N 14.007		$_{8}$O 15.999		$_{9}$F 18.998			$_{10}$Ne 20.183
3	$_{11}$Na 22.99		$_{12}$Mg 24.31		$_{13}$Al 26.98		$_{14}$Si 28.09		$_{15}$P 30.974		$_{16}$S 32.06		$_{17}$Cl 35.453			$_{18}$Ar 39.948
4	$_{19}$K 39.102	$_{29}$Cu 63.54	$_{20}$Ca 40.08	$_{30}$Zn 65.37	$_{1}$Ga 69.72	$_{21}$Sc 44.96	$_{32}$Ge 72.59	$_{22}$Ti 47.90	$_{33}$As 74.92	$_{23}$V 50.94	$_{34}$Se 78.96	$_{24}$Cr 52.00	$_{35}$Br 79.909	$_{25}$Mn 54.94	$_{26}$Fe 55.85 $_{27}$Co 58.93 $_{28}$Ni 58.71	$_{36}$Kr 83.30
5	$_{37}$Rb 85.47	$_{47}$Ag 107.87	$_{38}$Sr 87.62	$_{48}$Cd 112.40	$_{49}$In 114.82	$_{39}$Y 88.91	$_{50}$Sn 118.69	$_{40}$Zr 91.22	$_{51}$Sb 121.75	$_{41}$Nb 92.91	$_{52}$Te 127.60	$_{42}$Mo 95.94	$_{53}$I 126.90	$_{43}$Tc 98.91	$_{44}$Ru 101.07 $_{45}$Rh 102.91 $_{46}$Pd 106.4	$_{54}$Xe 131.30
6	$_{55}$Cs 132.90	$_{79}$Au 196.67	$_{56}$Ba 137.37	$_{80}$Hg 200.59	$_{81}$Ti 204.37	$_{57}$La* 138.9	$_{82}$Pb 207.19	$_{72}$Hf 178.49	$_{83}$Bi 208.98	$_{73}$Ta 180.95	$_{84}$Po (209)	$_{74}$W 183.95	$_{85}$At (210)	$_{75}$Re 186.2	$_{76}$Os 190.2 $_{77}$Ir 192.2 $_{78}$Pt 195.09	$_{86}$Rn (222)
7	$_{87}$Fr (223)		$_{88}$Ra (226)			$_{89}$Ac** (227)		$_{104}$Ku (261)		$_{105}$Ha (262)						

LANTHANIDES	$_{58}$Ce 140.12	$_{59}$Pr 140.91	$_{60}$Nd 144.24	$_{61}$Pm (145)	$_{62}$Sm 150.35	$_{63}$Eu 151.96	$_{64}$Gd 157.25	$_{65}$Tb 158.92	$_{66}$Dy 162.50	$_{67}$Ho 164.93	$_{68}$Er 167.26	$_{69}$Tm 168.91	$_{70}$Yb 173.03	$_{71}$Lu 174.97
ACTINIDES	$_{90}$Th 232.04	$_{91}$Pa (231)	$_{92}$U 238.03	$_{93}$Np (237)	$_{94}$Pu (242)	$_{95}$Am (243)	$_{96}$Cm (247)	$_{97}$Bk (247)	$_{98}$Cf (251)	$_{99}$Es (257)	$_{100}$Fm (257)	$_{101}$Md (258)	$_{102}$No (259)	$_{103}$Lr (260)

Note: Atomic numbers of elements are given on the left hand lower corner of their symbols while atomic weights are given under their symbols.

2. **Systematic study of the elements.** The Mendeleev's periodic table made the study of the elements and their compounds simpler since their properties could now be studied as groups or families rather than individuals. Thus, knowing the properties of one element in a group, the properties of the other elements in the group can be easily predicted.
3. **Correction of ambiguous atomic weights.** Mendeleev's periodic table has helped in correcting the doubt regarding atomic weights of some elements. For example, beryllium was assigned an atomic weight of 13.5 taking its equivalent weight as 4.5 and valency as 3. If beryllium has an atomic weight of 13.5, it should have been placed between carbon (atomic weight 12) and nitrogen (atomic weight 14). But no vacant place was available in between C and N. Also, properties of beryllium did not justify such a position. Therefore, valency 2 was assigned to beryllium which gave it an atomic weight of $4.5 \times 2 = 9$ and it was placed at its proper position between lithium (atomic weight 7) and boron (atomic weight 11).

2.3.2 Defects in the Mendeleev's Periodic Table

In spite of many advantages, Mendeleev's periodic table suffers from many serious defects as discussed below:

1. **Anomalous pairs of elements.** Some elements with higher atomic weights precede the elements with lower atomic weights. For example, Ar (at. weight = 39.9) precedes potassium (at. weight = 39.1), Co (at. weight = 58.9) precedes Ni (at. weight = 58.7) and Te (at. weight = 127.6) precedes I (at. weight = 126.9). No justification was provided for this ambiguity by Mendeleev.
2. **Some dissimilar elements are grouped together while some similar elements are placed in different groups.** For example, alkali metals such as Li, Na, K, etc. (group IA), are grouped together with coinage metals such as Cu, Ag and Au (group IB) though their properties are quite different. At the same time, certain chemically similar elements like Cu (group IB) and Hg (group IIB) have been placed in different groups in Mendeleev Table.
3. **Position of elements of group VIII.** No proper place has been allotted to nine elements of group VIII which have been arranged in three triads.
4. **Position of lanthanides and actinides.** The 14 elements following lanthanum from atomic number 58 to 71 (commonly known as **lanthanides**) and the 14 elements following actinium from atomic number 90 to 103 (commonly known as **actinides**) have not been given proper positions in the main frame of the periodic table but have been placed in two separate rows at the bottom of the periodic table.
5. **Position of isotopes.** Isotopes are the atoms of the same element having different atomic weights. Therefore, according to Mendeleev's classification, these should be placed at different places in the periodic table according to their atomic weights. For example, isotopes of hydrogen, *i.e.* protium, deuterium and tritium with atomic weights 1, 2 and 3 respectively should be placed at different places in the periodic table.
6. **Anomalous position of hydrogen.** Hydrogen is placed in group IA whereas it resembles the elements of both the groups IA (alkali metals) and VIIA (halogens). Therefore, the position of hydrogen in the periodic table is anomalous or controversial.

2.4 MODERN PERIODIC LAW

In 1912, Moseley, a young English physicist, worked on the frequencies of X-rays emitted by a metal when bombarded with high speed electrons. He discovered that the square root of the frequency (ν) of the prominent X-rays emitted by a metal was proportional to the atomic number and not to the atomic weight of the atom of that metal, *i.e.*

$$\sqrt{\nu} = a(z - b)$$

where a is the proportionality constant and b is another constant for all the lines in a given series of X-rays.

He thus concluded that atomic number was a better fundamental property of an element than its atomic weight. He therefore suggested that atomic number (Z) should form the basis of classification of the elements. This is the basis of the modern periodic law which states:

Physical and chemical properties of the elements are a periodic function of their atomic numbers, i.e. if the elements are arranged in order of their increasing atomic numbers, the elements with similar properties are repeated after certain regular intervals.

Justification of the Modern Periodic Law: An atom consists of a nucleus surrounded by electrons. Atomic mass is a nuclear property and depends upon the number of protons and neutrons in the nucleus whereas atomic number implies the number of electrons in the extranuclear part outside the nucleus. Nucleus is deep seated in an atom and is also shielded by electrons in the extranuclear part. So atomic mass has little effect on the chemical properties of elements. Electrons, however, are exposed to the environments and, hence, can interact with the reagent. As a result, the physical and chemical properties of the elements depend upon their atomic numbers rather than atomic masses.

2.5 CAUSE OF PERIODICITY

The physical and chemical properties of an element are determined by the number and arrangement of electrons in the orbitals. In other words, *the cause of periodicity in properties of elements lies in the recurrence of similar outer electronic configurations at certain regular intervals. This means that elements having similar electronic configuration of valency shell have similar chemical properties*. The electronic configuration is based upon the filling of the orbitals, *i.e.* governed by **Aufbau principle**. The following factors determine the periodicity:

1. *Completed electronic shells of an atom do not take part in any chemical combination. The electronic arrangement in the outermost level determines the properties and hence the periodicity.*
2. *If the electronic* ***configuration*** *of the outermost shell of a number of elements remain the same, they will have similar* ***properties*** *and will constitute a family.*
3. *While filling of electrons in the orbitals it can be seen that same electronic configuration recur after an interval of 2, 8, 8, 18, 18 and 32 in atomic number. These numbers are called* ***magic numbers****.*

If the elements are arranged in the increasing order of atomic number, it gives rise to the repetition of similar electronic configuration after certain regular periods or intervals. For example, all the alkaline earth metals have two electrons in the *s*-orbital of their valency shells, *i.e.* their valency shell electronic configuration is ns^2 (n = Principal shell).

The electronic configurations of the alkaline earth metals are given below:

$_{4}$Be	$1s^2\ 2s^2$
$_{12}$Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$
$_{20}$Ca	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
$_{38}$Sr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^2$
$_{56}$Ba	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^2$

Similarity in the properties of alkaline earth metals arises due to the similarity in their electronic configuration in the valence shell.

From the above electronic configuration it is clear that it is repeated after certain regular intervals. Similarly, the elements like fluorine, chlorine, bromine and iodine with atomic numbers, 9, 17, 35 and 53 have the following electronic configurations:

$_{9}$F	$1s^2\ 2s^2\ 2p^5$
$_{17}$Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
$_{35}$Br	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$
$_{53}$I	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$

All the halogens resemble in their properties. This is due to the similarity in the electronic configuration in the outermost level. All have their outermost *s*-sublevel complete while *p*-sublevel is one electron short of the maximum number.

Elements like Li, Na, K, Rb, Cs with atomic numbers 3, 11, 19, 37, 55 respectively are called **alkali metals**. All alkali metals have one electron in the *s*-orbital of their valency shell. The resemblance in their properties is due to the similarity in their electronic configuration in the outermost level.

Hence, the cause of the periodicity of the properties of the elements is illustrated.

2.6 LONG OR EXTENDED FORM OF PERIODIC TABLE

The long form of the periodic table consists of *eighteen vertical columns* and *seven horizontal rows*. These have been obtained by arranging the elements in order of increasing atomic numbers in such a way that the elements with similar electronic configurations are placed under each other in the same vertical column. *These vertical columns are known as* **groups** *while the horizontal rows are called* **periods** (See Table 2.2).

2.6.1 Groups

(*i*) The long form of the periodic table has eighteen vertical columns called groups. Each group consists of elements having the same electronic configuration of the outermost shell. These groups are numbered from 1 to 18. In the modified Mendeleev's periodic table, these eighteen vertical columns were divided into sixteen groups designated as IA, IIA .... VIIA, IB IIB .... VIIB, VIII and zero.

(*ii*) In the elements of the first two groups, *i.e.* 1 and 2 on the extreme left, last electrons are filled in *s*-orbitals while those of the last six groups, *i.e.* 13-18 lying on the extreme right involve the filling of electrons in the *p*-orbitals of the valence shell. The elements of group 18 are called **inert gases** or **noble gases**. Their valence shell electronic configuration is ns^2np^6. The elements of the remaining seven groups, *i.e.* 1, 2, 13, 14, 15, 16 and 17 are called **normal or representative elements**.

(*iii*) The elements of groups 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 are called **transition elements**. This is because their properties lie between the properties of the alkali and alkaline earth metals placed on the extreme left and non-metals placed on the extreme right of the periodic table.

In these elements, filling of the *d*-orbitals of the penultimate shell occurs. As such, their general outer electronic configuration can be represented as $(n-1)d^{1-10}\ ns^{1-2}$.

The series of the elements with Z = 58 to Z = 71 occurring after lanthanum in the periodic table are called **lanthanides** while the second series of elements with Z = 90 to Z = 103 which occur in the periodic table after actinium are called **actinides**. These elements are also called **inner transition elements**.

These elements have their general outer electronic configuration as $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$.

2.6.2 Periods

Long form of the periodic table has seven horizontal rows called **periods**. These are numbered as 1, 2, 3, 4, 5, 6 and 7 from top to bottom. Each period begins with the filling of electrons in a new energy shell. Each of these periods is described as under:

The **first period** corresponds to the filling of electrons in the first energy shell, *i.e.* $n = 1$. Since this energy shell has only *one orbital i.e.* 1*s* which can accommodate only two electrons. Therefore, *first period has only two elements.* These are hydrogen and helium.

The **second period** corresponds to the filling of electrons in the 2nd energy shell, *i.e.* $n = 2$. This shell has four orbitals (one 2*s* and three 2*p*) which can accommodate eight electrons. Therefore, *second period contains eight elements.* It starts with lithium (Z = 3) in which one electron enters the 2*s*-orbital. Neon (Z = 10) in which the second shell is complete, is the last element of this period.

Table 2.2: Long Form of Periodic Table

Groups

s-Block

d-Block Elements

Transition Elements

p-Block

Bohr's	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
IUPAC	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Periods 1.	1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
2.	3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.81	6 **C** Carbon 12.01	7 **N** Nitrogen 14.01	8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
3.	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31											13 **Al** Aluminium 26.98	14 **Si** Silicon 28.09	15 **P** Phosphorous 30.97	16 **S** Sulphur 32.07	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
4.	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.90	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.70	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.59	33 **As** Arsenic 74.92	34 **Se** Selenium 78.96	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.80
5.	37 **Rb** Rubidium 85.47	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.91	40 **Zr** Zirconium 91.22	41 **Nb** Niobium 92.91	42 **Mo** Molybdenum 95.94	43 **Tc** Technelium 98.91	44 **Ru** Ruthenium 101.1	45 **Rh** Rhodium 102.9	46 **Pd** Palladium 106.4	47 **Ag** Silver 107.9	48 **Cd** Cadmium 112.4	49 **In** Indium 114.8	50 **Sn** Tin 118.7	51 **Sb** Antimony 121.8	52 **Te** Tellurium 127.6	53 **I** Iodine 126.9	54 **Xe** Xenon 131.3
6.	55 **Cs** Cesium 132.9	56 **Ba** Barium 137.3	57 ***La** Lanthanum 138.9	72 **Hf** Hafnium 178.5	73 **Ta** Tantalum 180.9	74 **W** Tungsten 183.9	75 **Re** Rhenium 186.2	76 **Os** Osmium 190.2	77 **Ir** Iridium 192.2	78 **Pt** Platinum 195.1	79 **Au** Gold 197.0	80 **Hg** Mercury 200.6	81 **Tl** Thallium 204.4	82 **Pb** Lead 207.2	83 **Bi** Bismuth 209.0	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7.	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **†Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (276)	110 **Ds** Darmstadtium (281)	111 **Rg** Roentgenium (280)	112 **Cn** Copernicium (285)	113 **Uut** Ununtrium (284)	114 **Fl** Flerovium (289)	115 **Uup** Ununpentium (288)	116 **Lv** Livermorium (293)	117 **Uus** Ununseptium (294)	118 **Uuo** Ununoctium (294)

f-Block Elements (Inner Transition Elements)

6 * Lanthanide Series	58 **Ce** Cerium 140.1	59 **Pr** Praseodimium 140.9	60 **Nd** Neodymium 144.2	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.4	63 **Eu** Europium 152.0	64 **Gd** Gadolinium 157.3	65 **Tb** Terbium 158.9	66 **Dy** Dysprosium 162.5	67 **Ho** Holmium 164.9	68 **Er** Erbium 167.3	69 **Tm** Thulium 168.9	70 **Yb** Ytterbium 173.0	71 **Lu** Lutetium 175.0
7† Actinide Series	90 **Th** Thorium 232.0	91 **Pa** Protoactinium (231)	92 **U** Uranium 238.0	93 **Np** Neptunium 237	94 **Pu** Plutonium (242)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (260)

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

The **third period** corresponds to the filling of electrons in the third shell, *i.e.* $n = 3$. This shell has *nine orbitals* (one 3*s*, three 3*p* and five 3*d*). But, 3*d*-orbitals have higher energy than 4*s*-orbitals. Therefore, 3*d*-orbitals are filled only after filling 4*s*-orbitals. Consequently, third period involves the filling of only *four orbitals* (one 3*s* and three 3*p*) and, thus, *contains eight elements from sodium to argon.*

The **fourth period** involves filling of electrons in the fourth energy level, *i.e.* $n = 4$. It starts with the filling of 4*s*-orbitals. However, after filling 4*s*-orbital, the filling of five 3*d*-orbital begins since the energy of 3*d*-orbitals is lower than those of 4*p*-orbitals but higher than that of 4*s*-orbitals. It may be noted that filling of 4*d* and 4*f*-orbitals does not occur in this period since their energies are higher than those of 5*s*-orbitals. Therefore, in the fourth period, the filling of only *nine orbitals* (one 4*s*, five 3*d* and three 4*p*) occurs which can accommodate at the maximum eighteen electrons. *There are eighteen elements from potassium* (Z = *19*) *to krypton* (Z = *36*) *in this period.*

The **fifth period**, like the fourth period also contains eighteen elements since only *nine orbitals* (one 5*s*, five 4*d* and three 5*p*) are available for filling with electrons. It begins with rubidium (Z = 37) in which one electron enters the 5*s*-orbitals and ends up with xenon (Z = 54) in which the filling of 5*p*-orbitals is complete.

The **sixth period** involves the filling of sixth energy level, *i.e.* $n = 6$. In this period, *sixteen orbitals* (one 6*s*, seven 4*f*, five 5*d* and three 6*p*) are available for filling with electrons. Therefore, *sixth period contains thirty-two elements.* It begins with caesium (Z = 55) in which one electron enters the 6*s*-orbitals and ends up with radon (Z = 86) in which the filling of 6*p*-orbitals is complete. In this period, after the filling of 6*s*-orbitals, the filling of seven 4*f*-orbitals begins with cerium (Z = 58) and ends up with lutetium (Z = 71). These fourteen elements constitute the **first** (**or 4*f***) **inner transition series** called **lanthanides**. These are separated from the main frame of the periodic table and are placed at the bottom of the periodic table for convenient size and easy handling of the periodic table.

The **seventh period** corresponds to the filling of seventh energy shell, *i.e.* $n = 7$. This period is also expected to involve filling of *sixteen orbitals* (one 7*s*, seven 5*f*, five 6*d* and three 7*p*). This period also contains thirty-two elements. It begins with francium (Z = 87) to ununoctium (Z = 118). In this period, the filling of seven 5*f*-orbitals begins with thorium (Z = 90) and ends up with lawrencium (Z = 103). These fourteen elements constitute the **second (or 5*f*) inner transition series** which is commonly called as **actinides**.

The first three periods (1st, 2nd and 3rd) containing 2, 8, 8 elements respectively are known as **short periods** while the next three periods (4th, 5th and 6th) containing 18, 18, 32 elements respectively are called **long periods**.

2.6.3 Classification of Elements into Four Blocks

Elements in the long form of the periodic table have been divided into four blocks, *i.e. s*, *p*, *d* and *f* (Fig. 2.1). *This division is based upon the name of the orbital where the last electron enters.* A brief description of each block is given below:

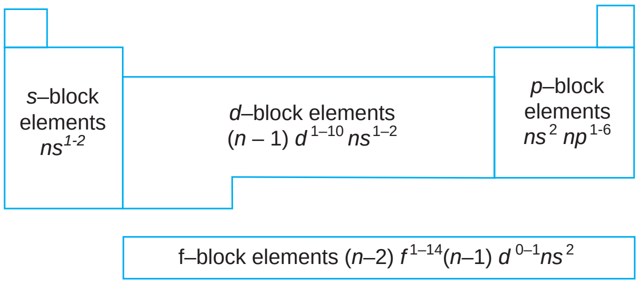


Fig. 2.1: *Division of periodic table into s, p, d and f-blocks*

1. ***s*-Block Elements.** *Elements in which the last electron enters the s-orbital are called s-block elements*. Since *s*-subshell has only one orbital which can accommodate only two electrons, therefore, there are only two groups corresponding to *s*-block elements. Thus, elements of group 1 (alkali metals) and group 2 (alkaline earth metals) form *s*-block elements. For example, consider elements of group 1. Hydrogen has only one electron and this enters 1*s*-orbital. In the rest of the elements, viz., Li, Na, K, Rb, Cs and Fr the last electron enters 2*s*, 3*s*, 4*s*, 5*s*, 6*s* and 7*s*-orbitals respectively.

   Now consider the elements of group 2, *i.e.* Be, Mg, Ca, Sr, Ba and Ra. The last electron in these elements also enters the *s*-orbitals. Hence, these elements also belong to *s*-block and have ns^2 as their general outer shell electronic configuration.

Hydrogen and helium also belong to *s*-block since the filling of the electrons in both cases ($1s^1$ for H and $1s^2$ for He) takes place in the *s*-orbital.

Thus, the elements of groups 1 and 2, including hydrogen and helium in which the s-orbitals are being progressively filled in, are called **s-block elements**.

Characteristics of *s*-Block Elements

(*i*) All are good conductors of heat and electricity.
(*ii*) They have low ionization energies and are highly electropositive.
(*iii*) They are very reactive metals.
(*iv*) They are soft metals with low melting and boiling points.
(*v*) They are strong reducing agents.
(*vi*) Hydroxides of these elements are strongly basic in nature.
(*vii*) Most of the metals of this block impart characteristic colours to the flame.
(*viii*) They form ionic compounds by losing one or two valence electrons and thus show oxidation states of +1 and +2.

2. **p-Block Elements.** *p*-block is present on the extreme right hand side of the periodic table. It consists of group 13-17. In all these elements the last electron enters in *p*-orbital of their outermost shell. The inner energy shells are complete. The general electronic configuration for *p*-block atoms may be written as $ns^2\ np^{1-6}$; *i.e.* $ns^2\ np^1$, $ns^2\ np^2$, $ns^2\ np^3$ ....., etc. (Table 2.3).

Table 2.3

$_5$B	$1s^2\ 2s^2\ 2p^1$
$_7$N	$1s^2\ 2s^2\ 2p^3$
$_{10}$Ne	$1s^2\ 2s^2\ 2p^6$
$_{14}$Si	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
$_{17}$Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

In case of *p*-block elements also, we can predict group number and period from the electronic configuration of the elements.

In boron, the last electron is going in *p*-orbital of the outermost shell. Therefore, it belongs to *p*-block. Now, there are 3 electrons in the outermost shell. Therefore, it belongs to group 13 of the periodic table. And since, there are two shells in its electronic configuration. Therefore, it belongs to **second period**.

The *s*- and *p*-block elements are known as the **representative** or **normal elements** because the inner shells in such atoms are already completely filled.

Characteristics of *p*-Block Elements

(*i*) The general electronic configuration of *p*-block elements may be written as $ns^2\ np^{1-6}$, *i.e.* $ns^2\ np^1$, $ns^2\ np^2$, $ns^2\ np^3$, ..., etc.
(*ii*) As we move from left to right along a period, metallic character decreases and non-metallic character increases.
(*iii*) They mainly form covalent compounds.
(*iv*) Their reactivity is less with a few exceptions (*e.g.*, fluorine is highly reactive element).
(*v*) They exhibit negative as well as positive oxidation states.
(*vi*) Along a period, from left to right reducing character decreases and oxidising character increases.

3. **d-Block Elements.** It consists of groups 3-12. In all these elements, last electron is going in *d*-orbital of (n – 1) shell, *i.e.* second last shell. *d*-Block lies in between *s* and *p*-blocks. The elements of *d*-block are known as **transition elements** because there is a change (*transition*) from highly electropositive elements

to highly electronegative elements of *p*-block. The general electronic configuration for *d*-block atoms is $(n-1)\ d^{1-10}\ ns^{1-2}$.

For example, the electronic configuration of $_{26}$Fe is given below:

$$_{26}\text{Fe} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$$

The last electron, during filling of the orbital is entering *d*-orbital of second last shell, (in this case second last shell is 3rd shell). The *d*-orbitals of the penultimate shell are not completely filled. As the electrons are going in *d*-orbital, they are named as ***d*-block elements**.

Basis of Division of d-block Elements into Different Transition Series

The first transition series forms a part of the fourth period of the long form of the periodic table. It contains ten elements from scandium to zinc, *i.e.* Sc (21) to Zn (30) in which 3*d*-orbitals are being progressively filled in.

The second transition series which forms a part of the fifth period also contains ten elements from yttrium to cadmium, *i.e.* Y (39) to Cd (48) in which 4*d*-orbitals are being progressively filled in.

The third transition series which forms a part of the sixth period also contains ten elements, *i.e.* lanthanum La (58) and from hafnium to mercury, *i.e.* Hf (72) to Hg (80) in which 5*d*-orbitals are being progressively filled in.

The fourth transition series which forms a part of the seventh period contains elements from actinium Ac (89) and those beyond rutherfordium Rf (104).

Characteristics of *d*-Block Elements

(*i*) The general electronic configuration for *d*-block elements is $(n-1)d^{1-10}\ ns^{1-2}$.

(*ii*) All the transition elements are metallic in character. They are hard and brittle. They possess high melting point.

(*iii*) They exhibit variable oxidation states.

(*iv*) They form a number of complexes in which the cations of these elements constitute the central ion.

(*v*) *d*-block elements form mostly coloured compounds due to the presence of incomplete *d*-orbitals.

(*vi*) Most of the transition elements and their compounds are paramagnetic in nature (*i.e.* they are attracted by magnetic lines of forces). This is due to the presence of unpaired electrons in one or more orbitals of an atom or an ion.

(*vii*) They are used as catalysts.

4. ***f*-Block Elements.** *f*-block elements lie at the bottom of the table. It includes Lanthanoids and Actinoids series. These elements are, commonly known as **inner transition elements** or **rare earth elements**. In such elements, the second last and third last shells are incomplete.

In these elements, last electron is going in *f*-orbital of $(n-2)$ shell. They have last two shells incomplete, *i.e.* they have incomplete *f*-subshell in addition to incomplete *d*-subshell.

For example, electronic configuration of element $_{58}$Ce is given below:

$$_{58}\text{Ce (cerium)}: 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^1\ 5s^2\ 5p^6\ 5d^1\ 6s^2$$

In the order of the filling of the orbitals, the last electron enters in *f*-orbital of $(n-2)$th shell (in this case last shell is sixth).

Therefore, the last electron is going in *f*-orbital of 4th shell, *i.e.* $(6-2)$ shell.

Transition and Inner Transition Elements. The *d*-block elements are known as transition elements because their properties are intermediate between those of *s*- and *p*-block elements. The *f*-block elements are known as inner transition elements because in the transition elements of *d*-block, the electrons are filled in $(n-1)$ *d* subshell while in the inner transition elements of *f*-block, the filling of electrons takes place in $(n-2)$ *f* subshell which happens to be one inner subshell. These include two series of elements called lanthanoids and actinoids.

Characteristics of *f*-Block Elements

(*i*) Their general electronic configuration is $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$.

(*ii*) They have generally high melting points, high boiling points and high densities.

(*iii*) They show variable valencies and multioxidation states.

(*iv*) They form complexes. The compounds formed by them are *coloured* and usually *paramagnetic*.

(*v*) Many of them are *radioactive* in nature.

5. **Noble Gases.** At the end of each period, there is a noble gas. There are in all six noble gases, *viz.*, helium, neon, argon, krypton, xenon, and radon, the last one is radioactive. They are also called **inert gases** because they exhibit no reactivity. But in recent years, some compounds of xenon like XeF_2, XeF_4 and XeF_6 have been reported. All these elements, except helium, possess eight electrons in the outermost orbit. Helium possesses two electrons. As these elements show no reactivity, it was proposed that octet structure (eight elements in the outermost orbit) is responsible for this inertness. Consequently, the stability of a compound was related to the octet configuration and the idea that it is because of the tendency to gain eight electrons in the outermost orbit, the substance reacting, gained strength. The atomic number and electronic configuration in the last orbit of the noble gases are given below:

At. No.	2	10	18	36	54	86
Noble gas	He	Ne	Ar	Kr	Xe	Rn
Electronic configuration	$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6$	$4s^2\ 4p^6$	$5s^2\ 5p^6$	$6s^2\ 6p^6$

2.6.4 Merits of the Long Form of the Periodic Table

The long form of the periodic table has a large number of advantages as given below:

(*i*) It is easy to remember and reproduce. The elements can be reproduced more easily in sequence of atomic numbers.

(*ii*) The elements in the same group show marked similarities due to similar outer electronic configurations.

(*iii*) It relates the position of an element in the table to its electronic configuration.

(*iv*) Based on their electronic configuration, elements have been grouped into *s*, *p*, *d* and *f*-blocks. This has helped us to study their properties systematically.

(*v*) The elements are classified into *normal elements* and *transition elements* on the basis of their outer electronic configurations.

(*vi*) The elements are also classified as *active metals* placed in groups 1 and 2, heavy metals placed in groups 3 – 12 and *non-metals* placed in the upper right corner (groups 13-18) of the periodic table.

(*vii*) A satisfactory position has been provided to the elements of groups 8-10 consisting of nine elements of group VIII of the Mendeleev's periodic table.

2.7 PREDICTION OF PERIOD, GROUP AND BLOCK OF A GIVEN ELEMENT

The period, group and block of an element can be easily predicted from its electronic configuration as follows:

(*i*) The group of an element is predicted from the number of electrons in the valence shell or/and penultimate shell (last but one, *i.e.* $n-1$) as follows:

- (*a*) **For *s*-block elements**, *group number is equal to the* **number of valence electrons**.
- (*b*) **For *p*-block elements**, *group number is equal to* **10 + number of electrons in the valence shell**.
- (*c*) **For *d*-block elements**, *group number is equal to the number of electrons in* **(*n* – 1) *d*-subshell + number of electrons in the valence shell (*n*th shell)**.

(*ii*) The period of an element corresponds to the principal quantum number of the valence shell.

(*iii*) The block of an element corresponds to the type of orbital which receives the last electron.

PROBLEMS FOR PRACTICE

1. The outer electronic configurations of some elements are given below:

   (*i*) $3s^2\ 3p^3$ (*ii*) $3d^5\ 4s^1$ (*iii*) $5d^1\ 6s^2$ (*iv*) $4f^1\ 5d^1\ 6s^1$

   State to which block of the periodic table each of these elements belongs.

   [**Ans.** (*i*) *p*; (*ii*) *d*; (*iii*) *d*; (*iv*) *f*]

2. An element X with atomic number 112 has recently been discovered. Predict its electronic configuration and suggest the group in which this element would be placed.

   [**Ans.** [Rn] $5f^{14}\ 6d^{10}\ 7s^2$, 12th group]

3. Write the names and atomic numbers of the following elements:

   (*i*) The fourth alkali metal (*ii*) The third alkaline earth metal

   (*iii*) The fifth element of the first transition series (*iv*) The first inner transition element

   [**Ans.** (*i*) Rb (Z = 37), (*ii*) Ca (Z = 20), (*iii*) Mn (Z = 25), (*iv*) Ce (Z = 58)]

4. The outer electronic configurations of some elements are:

   (*i*) $2s^2\ 2p^5$ (*ii*) $3s^2\ 3p^6$ (*iii*) $3d^{10}\ 4s^2$ (*iv*) $3s^2\ 3p^6\ 4s^1$

   Assign the block to which each element belongs.

   [**Ans.** (*i*) $2s^2\ 2p^6$ configuration...............*p*-block, (*ii*) $3s^2\ 2p^6$ configuration...............*p*-block
   (*iii*) $3d^{10}\ 4s^2$ configuration.............*d*-block, (*iv*) $3s^2\ 3p^6\ 4s^2$ configuration........*s*-block]

5. The electronic configurations of some elements are given below:

   (*i*) $1s^2\ 2s^2\ 2p^6\ 3s^1$ (*ii*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ (*iii*) $1s^2\ 2s^2\ 2p^6$ (*iv*) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

   Name these elements and indicate which of them is (*a*) an alkali metal, (*b*) an alkaline earth metal, (*c*) a halogen and (*d*) a noble gas.

   [**Ans.** Names of the elements are (*i*) sodium (*ii*) calcium (*iii*) neon and (*iv*) chlorine.
   (*a*) sodium is an alkali metal
   (*b*) calcium is an alkaline earth metal
   (*c*) chlorine is a halogen
   (*d*) neon is a noble gas]

2.8 ATOMIC OR PERIODIC PROPERTIES

Atomic properties of elements are those properties which depend upon the atomic structure or electronic configuration of elements.

In long form of periodic table, the elements are arranged in order of their electronic configurations, which show *periodicity*. Therefore, the atomic properties are also referred to as the **periodic properties** of the elements.

Atomic properties which are periodic in character include a long list of them. But the following are the most important:

(*a*) Atomic radius, (*b*) Ionization energy and (*c*) Electron affinity.

Most of the physical and chemical properties of elements vary periodically with the atomic number. These properties are directly related to the atomic structure and electronic configuration. The main factors which influence the properties of elements are:

(*i*) The magnitude of the nuclear charge.
(*ii*) The number of electrons and their distribution around the nucleus.
(*iii*) The electronic configuration of the outermost energy level, *i.e.* valence shell.

Depending upon these factors, the properties show a gradual variation as we move down a group or across a period in the periodic table, as discussed below:

2.9 ATOMIC RADIUS

It is difficult to determine the size of an atom because of the following reasons:

(*i*) Atom is too small, a particle to be isolated for measuring its size.

(*ii*) If we take a cluster of atoms, the atomic interactions are bound to affect the size and therefore we have to use certain arbitrary definitions for the size of the atom, which would take into account the molecular interactions present in the cluster.

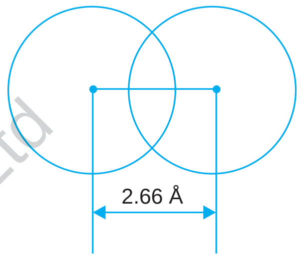


Fig. 2.2: *I_2 molecule*

Atomic radius is the radius of the atom bound by a single bond. Thus, it is half the distance between the nuclei of the two atoms linked by a covalent bond. This is shown in Fig. 2.2. The nuclei of two iodine atoms are separated by a distance of 2.66 Å.

$$\text{Hence, the atomic radius is } \frac{2.66\text{Å}}{2} = 1.33 \text{ Å}$$

$$\text{or} \quad 133 \text{ pm (picometre)}$$

$$1 \text{ pm} = 10^{-12} \text{ metre.}$$

Similarly, the atomic radius in hydrogen is 37 pm. The Table 2.7 gives the atomic radii of the halogens.

Types of atomic radius. There are three types of atomic radii. These are (*a*) *Covalent radii*, (*b*) *van der Waals' radii* and (*c*) *Metallic radii.*

(*a*) Covalent radius. *It is defined as one-half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule* (*Fig. 2.3*).

Thus, for a homonuclear diatomic molecule

$$r_{\text{covalent}} = \frac{1}{2}$$

[Internuclear distance between two bonded atoms]

Since, the internuclear distance between two bonded atoms is called the bond length. Therefore,

$$r_{\text{covalent}} = \frac{1}{2} \text{ [Bond length]}$$

For example, the internuclear distance between two hydrogen atoms in H_2 molecule is 74 pm (0.74 Å). Hence, the covalent radius of hydrogen is 74/2 = 37 pm (0.37 Å). Similarly, the internuclear distance between chlorine atoms in Cl_2 molecule is 198 pm (1.98 Å) and the covalent radius of chlorine is 198/2 = 99 pm (0.99 Å).

(*b*) van der Waals' radius. *It is defined as one-half of the distance between the nuclei of two non-bonded isolated atoms or two adjacent atoms belonging to two neighbouring molecules of an element in the solid state.*

van der Waals' radius denotes that the forces existing between the non-bonded isolated atoms or neighbouring molecules are the weak van der Waals' forces of attraction. Consequently, the magnitude of the van der Waals radii depends upon the packing of the atoms when the element is in the solid state. These are obtained from X-ray studies of the various atoms in the solid state. For example, the internuclear distance between the adjacent

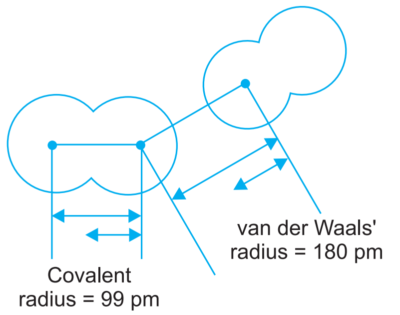


Fig. 2.3: *van der Waals' and covalent radii of chlorine*

chlorine atoms of the two neighbouring molecules in the solid state is 360 pm or 3.6 Å. Therefore, the van der Waals' radius of chlorine atom = 360/2 = 180 pm or 1.8 Å.

Comparison of covalent radius and van der Waals' radius. van der Waals' radius of an element is always greater than its covalent radius because the van der Waals' forces of attraction are weak. Therefore, the internuclear distances in case of atoms held by van der Waals' forces are much larger than those between covalently bonded atoms. Therefore, *van der Waals' radii are always larger than covalent radii.*

(*c*) **Metallic radius.** *It is defined as one-half of the distance between the centres of nuclei of the two adjacent atoms in the metallic crystal.*

Metallic radius of an element is always greater than its covalent radius. This is because a metallic bond is weaker than a covalent bond and hence the internuclear distance between the two adjacent atoms in a metallic crystal is longer than the internuclear distance between the two atoms held by a covalent bond. For example, metallic radius and covalent radius of potassium are 231 and 203 pm respectively.

2.9.1 Variation of Atomic Radii in the Periodic Table

(*a*) **Variation in a period.** *In general, the atomic radii (covalent or van der Waals') decrease with increase in atomic number as we move from left to right in a period.* The atomic (covalent) radii of the elements of second period are given in Table 2.4.

Table 2.4: Variation in Atomic (Covalent) Radii in the Second Period

Element	Li	Be	B	C	N	O	F	Ne
Nuclear charge	+3	+4	+5	+6	+7	+8	+9	+10
Other electronic configuration	$2s^1$	$2s^2$	$2s^2\ 2p^1$	$2s^2\ 2p^2$	$2s^2\ 2p^3$	$2s^2\ 2p^4$	$2s^2\ 2p^5$	$2s^2\ 2p^6$
Atomic radii (pm)	123	90	80	77	75	74	72	112*

*van der Waals' radius

The above table leads us to the following conclusions:

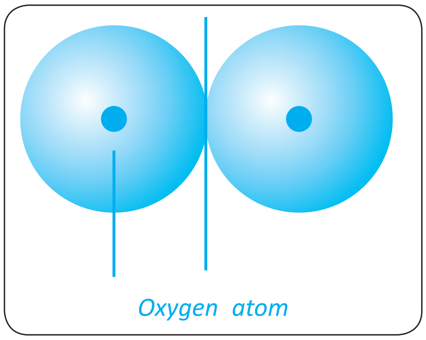
(*i*) The alkali metals at the extreme left of the periodic table have the largest size in a period.

(*ii*) The halogens at the extreme right of the periodic table have the smallest size.

(*iii*) The sizes of the atoms of the inert gases are, however, larger than those of the preceding halogens. This is a break in the trend of decreasing size from left to right in the period.

Explanation. As we move from left to right in a period, nuclear charge increases by one unit in each succeeding element while the number of the shells remains the same. Due to increased nuclear charge, the electrons of the shells are pulled closer to the nucleus thereby making electron shell smaller and smaller. This results in a decrease of the atomic radius as we move from left to right in a period.

Perusal of the table reveals that the atomic radius abruptly increases as we move from halogen (F) to the inert gas (Ne). This is due to the reason that in case of inert gases all the orbitals are completely filled and hence the inter-electronic repulsion is maximum. This results in the spread of electron cloud. Moreover, in case of inert gases, the atomic size is actually the *van der Waals' radius* since they do not form covalent bonds. By definition, van der Waals' radii are larger than covalent radii. Therefore, the atomic size of an inert gas in a period is much higher than that of the preceding halogen.



(*b*) **Variation in a group.** *The atomic (covalent) radii of elements increase with increase in atomic number as we move from top to bottom in a group.* Consider the atomic (covalent) radii of the members of the alkali metals group (Table 2.5).

Table 2.5: Variation in Atomic (Covalent) Radii of the Alkali Metals Group

Element	Li	Na	K	Rb	Cs	Fr
Nuclear charge	+3	+11	+19	+37	+55	+87
Outer electronic configuration	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$	$7s^1$
Covalent radii (pm)	123	157	202	216	235	–

The above table shows that the atomic radii increase as we move down the group from lithium to caesium among alkali metals.

Explanation. As we move down a group, a new shell is added at each succeeding element. In other words, electrons in the outer shell of each succeeding element lie farther and farther away from the nucleus. With the increase in atomic number, the nuclear charge also increases. As a result, the force of attraction of the nucleus for the electrons increases and hence we expect the atomic radii to decrease. But the effect of the increased nuclear charge on the valence electrons is reduced due to the screening or shielding effect of the electrons present in the inner shells. K and L shells in Na-atom act as screens between the nucleus and outer electron in M-shell. This will reduce the force of attraction between the nucleus and outer electron (Fig. 2.4). Thus, the effect of adding a new energy shell is so large that it outweighs the contractive effect of the increased nuclear charge. Hence, *the increase in atomic radii as we move down the group (from Li to Cs among alkali metals and from F to I among halogens) is primarily due to the addition of a new energy shell.*

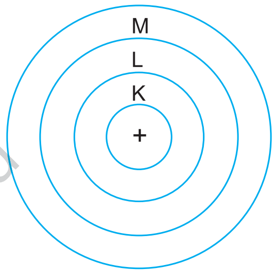


Fig. 2.4: *Screening effect in Na-atom*

Thus, the hold of the nucleus on outer electrons decreases with the addition of new shells. This is because the force of attraction between the two is inversely proportional to the square of the distance between them. This results in increase of atomic radius as move down the group.

Ionic Radii. The ionic radii relate to the radii of ions situated in ionic crystals. Ions are formed when neutral atoms lose or gain electrons. A *positive ion* or **cation** is formed when a neutral atom loses one or more electrons while a *negative ion* or **anion** is formed when a neutral atom gains one or more electrons. Ionic radius may be defined as follows:

***Ionic radius** may be defined as the effective distance from the centre of the nucleus of the ion upto which it exerts its influence on its electron cloud.*

To determine the ionic radius, the internuclear distance in any ionic compound is determined from X-ray measurements. Assuming that the positive and negative ions are touching each other, *this internuclear distance is then taken as the sum of the radii of two ions involved* (Fig. 2.5). *Knowing the radius of one, that of the other can be obtained by difference.*

For example, the internuclear distance between Na^+ and Cl^- ions in sodium chloride crystal has been determined to be 276 pm from X-ray measurements. This distance is then taken as sum of the radii of Na^+ and Cl^- ions. Based upon Pauling's method, the absolute value of the ionic radius of Na^+ ion has been determined to be 95 pm. Therefore, the ionic radius of Cl^- ion = 276 – 95 = 181 pm. Further, the radius of Na^+ ion, thus, obtained may be used to calculate the radii of other anions, such as Br^- and I^- ions, by measuring the internuclear distances in NaBr and NaI. Similarly, the radius of the Cl^- ion may be used to calculate the radii of other cations such as Li^+, K^+, etc., by measuring internuclear distances in LiCl and KCl crystals respectively.

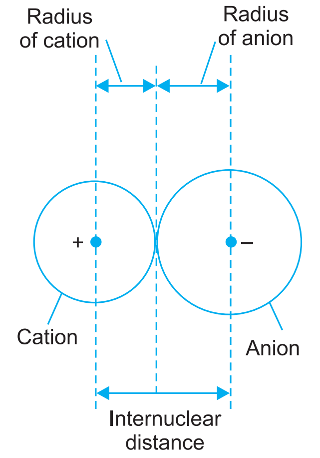


Fig. 2.5: *Internuclear distance and ionic radius*

2.9.2 Comparison of the Ionic and Atomic Radii

A study of ionic radii of cations and anions leads to the following conclusions:

(*a*) **The radius of the cation is always smaller than that of its parent atom.** A cation is obtained by loss of one or more electrons from the neutral gaseous atom. This causes the removal of the outermost (*valence*) shell of electrons. For example, sodium atom loses the third shell (3*s*), when an electron is removed to get sodium ion.

$$\begin{array}{cccc} \mathrm{Na} & \rightarrow & \mathrm{Na}^+ & + \; e^- \\ 1s^2\,2s^2\,2p^6\,3s^1 & & 1s^2\,2s^2\,2p^6 & \end{array}$$

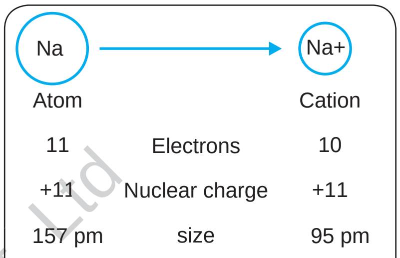


Fig. 2.6: *Relative sizes of Na atom and Na$^+$ ion*

Due to the removal of the valence shell, the number of shells in the cation decreases. As a result, the size of the cation is smaller than the parent atom from which it is formed. Further, due to the removal of electrons from the parent atom, the number of electrons in the cation decreases (Fig. 2.6) but its nuclear charge remains the same as that of the atom. As a result, the force of attraction by the nucleus on the electrons increases and hence the size of the atom decreases.

Even if the outer shell is not removed completely, we expect similar result. This is because after the removal of electrons, the nuclear charge will outweigh the electronic charge. Therefore, the electron cloud will be pulled inwards resulting in the decrease in the size of the cation.

The size of a cation is always smaller than that of the corresponding atom due to decrease in the number of shells and increase in the effective nuclear charge resulting in greater force of attraction by the nucleus on the electrons. The above generalization is illustrated in Table 2.6.

Table 2.6: Comparative Sizes of Atoms and their Cations

Atom	Li	Na	K	Be	Mg	Al
Atomic radii (pm)	123	157	202	89	136	125
Corresponding cations	Li^+	Na^+	K^+	Be^{2+}	Mg^{2+}	Al^{3+}
Ionic radii (pm)	60	95	133	39	65	50

Variation of ionic (cationic) radii within a group. Like covalent radii of atoms, *the ionic radii of cations also increase as we move from top to bottom within a group because more and more shells are added as we move down the group.* For example, the ionic radii of Li^+ is 60 pm, that of Na^+ is 95 pm and that of K^+ is 133 pm.

(*b*) **The radius of the anion is always larger than that of its parent atom.** An anion is obtained when a neutral gaseous atom gains one or more electrons (Fig. 2.7). This increases the number of electrons in the anion while its nuclear charge remains the same as that on the neutral atom. Since the same nuclear charge now attracts greater number of electrons, therefore, the force of attraction by the nucleus on the electrons of all the shells decreases. *Hence, the electron cloud of the atom expands. Expansion of the electron cloud takes place due to increased inter-electronic repulsions also.* In other words, the distance between the centre of the nucleus and the last shell increases thereby increasing the ionic radius. Thus, *the size of an anion is always larger than the corresponding atom mainly because of decrease in the effective nuclear charge, i.e. lesser force of attraction by the nucleus on the electrons.* Table 2.7 illustrates the above conclusions.

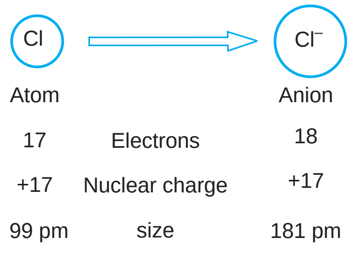


Fig. 2.7: *Relative sizes of Cl atom and Cl$^-$ ion*

Table 2.7: Comparative Sizes of Atoms and their Anions

Atom	F	Cl	Br	I	O	S
Atomic radii (pm)	72	99	114	133	74	102
Corresponding anion	F^-	Cl^-	Br^-	I^-	O^{2-}	S^{2-}
Ionic radii (pm)	136	181	196	219	142	184

Variation of ionic (anionic) radii within the group. *Ionic radii of anions increase as we move down the group due to introduction of more and more shells between the nucleus and the outermost shell of electrons.* For example, the ionic radii of F^-, Cl^-, Br^- and I^- ions are 136, 181, 196 and 219 pm respectively.

PROBLEMS FOR PRACTICE

1. Arrange the following in the order of increasing radii?

   (*i*) I, I^+, I^- (*ii*) C, N, Si (*iii*) O^{2-}, N^{3-}, S^{2-}

   [**Ans.** (*i*) $I^+ < I < I^-$ (*ii*) N < C < Si (*iii*) $O^{2-} < N^{3-} < S^{2-}$]

2. Which one of the following pairs would have a larger size? Explain.

   (*i*) K or K^+ (*ii*) Br or Br^- (*iii*) Li^+ or Na^+ (*iv*) P or As.

   [**Ans.** (*i*) K, (*ii*) Br^-, (*iii*) Na^+, (*iv*) As]

2.10 IONIZATION ENTHALPY OR IONIZATION ENERGY OR IONIZATION POTENTIAL

When energy is supplied to an atom, the electrons are raised to higher energy levels. If energy is increased, the electron is completely dislodged from the atom, *i.e.* it is out of the influence of the nucleus. In other words, it is completely detached resulting in the formation of a positively charged ion. *This process is called* **ionization**. Ionization enthalpy is defined as:

The minimum energy required to completely remove the most loosely bound outermost electron from an isolated gaseous atom to form a gaseous ion is called the **ionization enthalpy** (or **ionization energy**). This process is written as:

$$X\,(g) + \text{Energy} \rightarrow X^+\,(g) + e^-$$

where X (*g*) and $X^+(g)$ represent the gaseous atom and the gaseous cation respectively.

We have taken gas phase because in the gas phase, the atom and the ion are isolated from all external influences.

The energy necessary to effect the ionization is exactly the energy with which the atom binds its electron. *Thus, the magnitude of the ionization energy gives a quantitative measure of the stability of the electronic structure of the isolated atom.*

Usually, the ionization potential is expressed in units of electron volts. It is also expressed in kJ/mole of atoms. 1 eV = 96.49 kJ $mole^{-1}$.

Ionization potential can be measured experimentally. To measure ionization energy experimentally, the vapours of the atoms are placed in a discharge tube and then gradually the voltage between the two plates is increased. Practically no current flows through the tube until the voltage reaches a value high enough that electrons get ripped off (split) the atoms. From the voltage, the ionization potential can be calculated, *i.e.* the energy corresponding to this voltage gives the ionization energy of the element.

2.10.1 Successive Ionization Enthalpies (Energies)

The energy required to pull only one electron from an atom in the gaseous state is known as **first ionization enthalpy or ionization energy**. This is denoted by E_1.

It is represented as:

$$X\,(g) + E_1 \rightarrow X^{1+}\,(g) + e^-$$

The energy required to remove one more electron from the 1+ ion to form 2+ ion is called **second ionization energy**. It is denoted by E_2 and is represented as:

$$X^{1+}(g) + E_2 \rightarrow X^{2+}(g) + e^-$$

Similarly, the energy required to pull the third electron is known as **third ionization energy, E_3**. This is represented as:

$$X^{2+}(g) + E_3 \rightarrow X^{3+}\,(g) + e^-$$

Thus, the energies required to remove the succeeding electrons from an atom are known as **successive ionization energies.**

When the first electron is removed from the atom to get the 1+ ion, the effective nuclear charge increases, number of electrons decreases and the number of protons remains the same and, thus, the pull of the nucleus is greater on the remaining electrons, *i.e.* nucleus holds the remaining electrons more firmly. Therefore, the second ionization energy will be greater than the first ionization energy.

Similarly, third ionization energy will be greater than the second ionization energy. Thus, the higher ionization energies will be more and more than their preceding grades. If these ionization energies are expressed as E_1, E_2, E_3, etc., then their magnitudes will be as:

$$E_1 < E_2 < E_3 \text{ ... and so on}$$

e.g., First ionization energy:

$$\text{Li}\,(g) \rightarrow \text{Li}^+\,(g) + e^-;\ E_1 = 520\ \text{kJ mol}^{-1}$$

Second ionization energy:

$$\text{Li}^+(g) \rightarrow \text{Li}^{2+}(g) + e^-;\ E_2 = 7298\ \text{kJ mol}^{-1}$$

Third ionization energy:

$$\text{Li}^{2+}(g) \rightarrow \text{Li}^{3+}(g) + e^-;\ E_3 = 11810\ \text{kJ mol}^{-1}$$

Table 2.8 lists successive ionization energies of some elements:

Table 2.8: Successive I.E. of the Elements (kJ mol^{-1})

Element	H	He	Li	Be	B	C
E_1	1312	2371	520	900	800	1086
E_2	–	5250	7297	1757	2427	2352
E_3	–	–	11810	14850	3658	4619
E_4	–	–	–	21000	25024	6220
E_5	–	–	–	–	32824	37820
E_6	–	–	–	–	–	47820

2.10.2 Factors on which Ionization Enthalpy (Energy) Depends

Ionization potential depends upon the following factors:

1. **Atomic size.** Force of attraction between two electrical charges varies inversely as the square of the distance between them. Therefore, if the distance of the outer electron increases from the nucleus then there is a smaller force of attraction, *i.e.* it is less firmly held. Hence, less energy is required to knock it out. Thus, the ionization energy decreases from top to bottom in a group of the periodic table due to increase in the size of the atom, as illustrated by the following table.

Element	Li	Na	K	Rb	Cs
I.E. (kJ mol^{-1})	520	495	418	403	374

It is obvious, ionization potential is inversely proportional to the atomic size.

2. **Nuclear charge.** With the increase in atomic number, the positive charge on the nucleus of the atom is increased. Therefore, the electrons of the outermost shell are more firmly held by the nucleus. In other words, the force of attraction holding the outer electrons towards the nucleus increases. Hence, it will be difficult to remove the outer electrons. That is why, ionization energy increases, generally, on moving along a period from left to right because the nuclear charge (atomic number) also increases.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
First I.E. (in kJ mol^{-1})	495	738	889	787	1060	1004	1255	1522

Evidently, the ionization potential is directly proportional to the nuclear charge.

3. **Screening effect, *i.e.* Effect of electrons in the inner shells.** The electrons in the inner shell shield the electrons in the valency shell from the nucleus. Therefore, the nuclear charge is partly obstructed by the inner electrons. This is known as **screening effect**.

As a result, the electrons to be removed are less firmly held by the nucleus, *i.e.* hold of the nucleus on the valency electrons becomes weak. Therefore, it is easier to pull out the electrons. Hence, the ionization energy will be low. *Thus, increase in the number of electrons in the inner shells tends to increase the screening effect. Therefore, larger the screening effect, the lower is the ionization energy.*

The actual charge experienced by the valence electrons is called **effective nuclear charge (Z_{eff})** and the repulsive force experienced by valence electrons from the inner shell electrons is called **screening effect** or **shielding effect**. Effective nuclear charge is given by the relation:

Z_{eff} = Total nuclear charge (Z) – Screening effect (s)

Screening effect (s) is calculated with the help of **Slater Rule**.

4. **Type of the electron.** It is easier to pull off a p-electron than a s-electron in the same shell. This is due to the fact that s-electrons are relatively nearer to the nucleus than p-electrons of the same shell. Hence, within a given shell, the binding energy of electrons in various subshells is in the order $s > p > d > f$.

For example, the first ionization potential of Al is lower than that of Mg. Because, in case of $_{13}$Al ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$), p-electron of 3rd shell is pulled out and in case of $_{12}$Mg ($1s^2\ 2s^2\ 2p^6\ 3s^2$), s-electron of the same shell (3rd) is pulled out.

5. **Electronic configuration.** (*Effect of half-filled and fully filled orbitals*). Completely filled and exactly half-filled orbitals possess *extra stability*.

In other words, the elements with stable configurations have high ionization energy. On this basis, we can account for the following:

(*a*) The ionization potentials of noble gases (inert gases) are greater than those of their immediate neighbours because they possess stable configurations with eight electrons in the outermost shell. It is specially hard to pull an electron-off an atom having 8 electrons in its outermost shell.

(*b*) Ionization energy of Be is greater than that of Li. In case of $_4Be$ ($1s^2 2s^2$), electron is to be removed from completely filled 2*s* orbital while in case of $_3Li$ ($1s^2 2s^1$) it is not so.

Similarly, ionization energy of $_{12}Mg$ ($1s^2\ 2s^2\ 2p^6\ 3s^2$) is higher than that of $_{11}Na$ ($1s^2\ 2s^2\ 2p^6\ 3s^1$).

(*c*) From exactly half-filled subshells too, it is more difficult to remove electron.

Ionization energy of nitrogen ($_7N$) is higher than that of $_6C$ and $_8O$.

C	N	O
1086 kJ mol^{-1}	1402 kJ mol^{-1}	1314 kJ mol^{-1}

This is because in case of $_7N$ ($1s^2\ 2s^2\ 2p_x^{\ 1}\ p_y^{\ 1}\ p_z^{\ 1}$), electron is extracted from the exactly half-filled *p*-orbitals. On the other hand, it is not so in case of $_6C$ ($1s^2\ 2s^2\ 2p_x^{\ 1}\ p_y^{\ 1}\ p_z^{\ 0}$) and $_8O$ ($1s^2\ 2s^2\ 2p_x^{\ 2}\ p_y^{\ 1}\ p_z^{\ 1}$). Similarly, we can explain why the ionization potential of $_{15}P$ is higher than that of $_{14}Si$.

Thus, unexpectedly high ionization energy in case of N and P is due to the fact that it is required to break-up a half-filled subshell to remove an electron.

Example 1. *Calculate the energy required to convert all the atoms of magnesium to magnesium ions present in 6 mg of magnesium vapours? First and second ionization energies of Mg are 7.646 and 15.035 eV respectively.*

Solution. According to the definition of successive ionization energies:

$$Mg(g) + IE_1 \rightarrow Mg^+(g) + e^-;\ IE_1 = 7.646 \text{ eV}$$

$$Mg^+(g) + IE_2 \rightarrow Mg^{2+}(g) + e^-;\ IE_2 = 15.035 \text{ eV}$$

∴ Total amount of energy needed to convert Mg-atom into $Mg^{2+}(g)$ ion

$$= IE_1 + IE_2$$
$$= 7.646 + 15.035 \text{ eV} = 22.681 \text{ eV}$$
$$= 22.681 \times 96.49 \text{ kJ mol}^{-1}$$
$$= 2188.489 \text{ kJ mol}^{-1}.$$

$$6 \text{ mg of Mg} = \frac{6}{1000}\text{g} = \frac{6}{1000 \times 24} \text{ mole}$$
$$= 0.25 \times 10^{-3} \text{ mole}$$

∴ Amount of energy needed to ionize 10^{-3} mole of Mg vapours

$$= 2188.489 \times 0.25 \times 10^{-3} = 0.547 \text{ kJ}$$

2.10.3 Ionization Enthalpy (Energy) is a Function of Atomic Number

If the values of ionization energies of atoms be plotted against atomic numbers, there are variations in the magnitude of ionization energy of the elements according to their atomic numbers.

Thus, ionization energy of the atoms of the various elements, is the periodic function of their atomic number, as shown in the Fig. 2.8.

From the graph, it is clear that inert gases (He, Ne, Ar, etc.) have the highest values while the alkali metals (Li, Na, K, Rb, Cs) have low values.

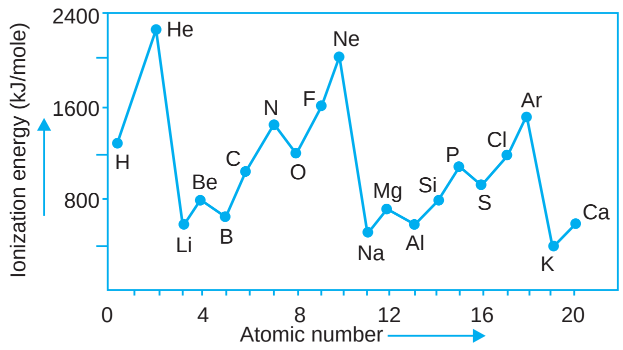


Fig. 2.8: *Periodic variation of ionization energy with atomic number*

In general, ionization energy (i.e. first I.E.) gradually increases from left to right in a period and decreases from top to bottom in a group of the periodic table.

This has already been explained in terms of atomic size and nuclear charge.

Example 2. *The electronic configurations for the following neutral atoms are given for use in the question:* *(a)* $1s^2 2s^2 2p^6 3s^2$; *(b)* $1s^2 2s^2 2p^6 3s^1$; *(c)* $1s^2 2s^2 2p^4$; *(d)* $1s^2 2s^2 2p^5$; *and (e)* $1s^2 2s^2 2p^6$.

(i) Which of the electronic configurations given above would you expect for inert gas?

(ii) Which of the electronic configurations given above would you expect to have the lowest ionization energy?

(iii) List the above configurations in order of increasing ionization energy.

Solution.

(*i*) Since the outer electronic configuration, of inert gases is ns^2np^6, thus, the electronic configuration, $1s^2\ 2s^2\ 2p^6$ [option (*e*)] represents an inert gas.

(*ii*) The option (*b*) with electronic configuration, $1s^2\ 2s^2\ 2p^6\ 3s^1$ has the lowest ionization energy.

(*iii*) Arrange the electronic configurations of all the atoms in order of increasing atomic number in such a manner that atoms belonging to a particular energy level are grouped together. Thus, we get

$$\underset{(c)}{1s^2\ 2s^2\ 2p^4;} \quad \underset{(d)}{1s^2\ 2s^2\ 2p^5;} \quad \underset{(e)}{1s^2\ 2s^2\ 2p^6;} \qquad \text{(......L-shell)}$$

$$\underset{(b)}{1s^2\ 2s^2\ 2p^6\ 3s^1;} \quad \underset{(a)}{1s^2\ 2s^2\ 2p^6\ 3s^2;} \qquad \text{(......M-shell)}$$

As the M-shell is at a greater distance from the nucleus than L-shell so lesser amount of energy is required to remove an electron from M-shell than from L-shell. In other words, ionization energy (I.E.) of atoms (*a*) and (*b*) should be lower than that of atoms (*c*), (*d*) and (*e*). Further, in case of atom (*a*), the electron is to be removed from more stable completely filled 3*s*-orbital, whereas in case of atom (*b*) it is not so. Therefore, the I.E. of atom (*b*) should be lower than that of atom (*a*). The nuclear charge on atoms (*c*), (*d*) and (*e*) is +8, +9 and +10 respectively. Since, the I.E. increases with the increase in nuclear charge, the I.E. of atoms (*c*), (*d*) and (*e*) follow the sequence:

$$(e) > (d) > (c).$$

From the above discussion, we find that the ionization energies of the five atoms increase in the following order:

$$b < a < c < d < e.$$

i.e., $1s^2\ 2s^2\ 2p^6\ 3s^1 < 1s^2\ 2s^2\ 2p^6\ 3s^2 < 1s^2\ 2s^2\ 2p^4 < 1s^2\ 2s^2\ 2p^5 < 1s^2\ 2s^2\ 2p^6$

2.10.4 Variation of Ionization Enthalpy (Energy) in a Group

The ionization energies go on decreasing regularly as we move down a group from one element to the other (Table 2.9).

Table 2.9: Ionization Energies of the Elements of Some Groups

Group 1		Group 17		Noble Gases (Group 18)	
Element	**I.E. (kJ/mole)**	**Element**	**I.E. (kJ/mole)**	**Element**	**I.E. (kJ/mole)**
Li	520	F	1680	He	2370
Na	495	Cl	1254	Ne	2081
K	418	Br	1133	Ar	1517
Rb	403	I	1007	Kr	1346
Cs	374			Xe	1166

On moving from top to bottom in a group, the nuclear charge, no doubt, increases with the increased atomic number. But at the same time, the number of main energy levels also increases. Consequently, the distance of the outermost electron from the nucleus increases. In addition, the number of electrons lying in between the nucleus and the outermost electron also increases. The increase in atomic radius and the shielding effect more than neutralise the effect of increased nuclear charge. As a result, the ionization energy goes on decreasing regularly.

Fig. 2.9 gives the variation of first ionization energy with atomic number in the case of alkali metal group.

The combined effect of the increase in the atomic size and the screening effect more than compensates the effect of the increased nuclear charge. Consequently, the valence electrons become less and less firmly held by the nucleus and, hence, the ionization energies gradually decrease as we move down the group.

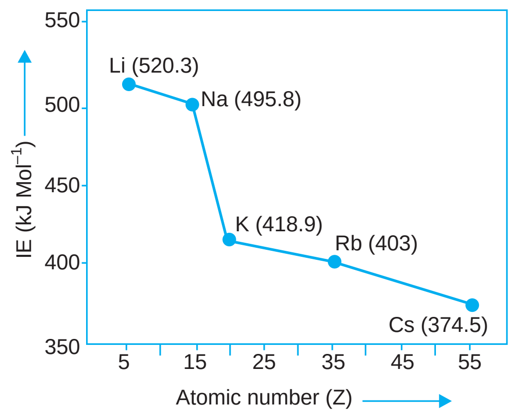


Fig. 2.9: *The variation of first ionization energies with atomic number in group I (alkali metals)*

2.10.5 Variation of Ionization Enthalpy (Energy) in a Period

Generally speaking, the ionization energies of the elements *show an increase* on moving from left to right in a period of the periodic table (Table 2.10).

Table 2.10: Trends in First Ionization Energy of Second Period and Third Period Elements (kJ mol^{-1})

Li 520	Be 894	B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
Na 496	Mg 737	Al 577	Si 786	P 1012	S 999	Cl 1255	Ar 1521

The general increase in ionization energy along a period can be explained as follows:

(*a*) With the increase in atomic number from left to right, the nuclear charge increases but the number of main energy level remains the same. So, the distance of the outer electron from the nucleus decreases *i.e.* the size of the atom decreases. As a result, the force of attraction between the electron and the nucleus increases and it becomes more difficult to remove the electron.

(*b*) The lower value of ionization energy in case of B as compared to Be is due to the fact that the outermost electron in B ($1s^2\ 2s^2\ 2p^1$) is present in a 2*p*-orbital while that in Be ($1s^2\ 2s^2$) it is in 2*s*-orbital. An electron in *p*-orbital is easier to remove than that in 2*s*-orbital of the same energy level.

The lower value of ionization energy in case of O ($1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$) as compared to N ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) is due to the fact that N has the outermost sublevel exactly half-filled while in O it is neither half-filled nor completely filled. As a result, it is easier to remove an electron from an oxygen atom than from a N atom.

(*c*) The nuclear charge (at. no.) of Mg being 12, its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2$.

The atomic number (nuclear charge) of Na being 11, its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^1$.

As nuclear charge of Mg is higher, therefore, first ionization energy of Mg is higher than that of Na. After the removal of first electron, the next electron in case of Na is removed from the lower energy level, *i.e.* 2*p*. The ionization energies of such electrons are comparatively very high while second electron in case of Mg is removed from third energy level, *i.e.* 3*s*. Obviously, it would require lesser second ionization energy as compared to Na.

Electronegativity

Electronegativity is the relative tendency of an atom to attract the shared pair electrons towards itself. It measures the power of attracting electrons pairs. The concept of electronegativity was introduced by Pauling in 1932. An arbitrary value of 4.0 has been assigned to fluorine (the most electronegative element) and the electronegativities of other elements have been calculated against this standard by the following formula:

$$X_A - X_B = 0.208\left[E_{A-B} - \frac{1}{2}(E_{A-A} + E_{B-B})\right]^{1/2}$$

Where X_A and X_B are the electronegativities of two atoms A and B and E_{A-B}, E_{A-A} and E_{B-B} are bond energies of molecules A – B, A_2 and B_2, respectively in Kcal mol^{-1}.

According to Mulliken

$$\text{Electronegativity} = \frac{\text{Ionization enthalpy} + \text{Electron gain enthalpy}}{2}$$

Variation of electronegativity in period

- From left to right across a period of elements, electronegativity increases. If the valence shell of an atom is less than half full, it requires less energy to lose an electron than to gain one. Conversely, if the valence shell is more than half full, it is easier to pull an electron into the valence shell than to donate one.

Variation of electronegativity in group

- From top to bottom down a group, electronegativity decreases. This is because the atomic number increases down a group, and thus there is an increased distance between the valence electrons and nucleus, or a greater atomic radius.
- Important exceptions of the above rules include the noble gases, lanthanodes, and actinodes. The noble gases possess a complete valence shell and do not usually attract electrons. The lanthanodes and actinodes possess a very complicated chemistry that does not generally follow any trends. Therefore, noble gases, lanthanodes and actinodes do not have electronegativity values.
- As for the transition metals, although they have electronegativity values, there is little variance among them across the period and up and down a group. This is because their metallic properties affect their ability to attract electrons as easily as the other elements.

PROBLEMS FOR PRACTICE

1. The electronic configurations of some neutral atoms are given below:

   (*i*) $1s^2\ 2s^2$ (*ii*) $1s^2\ 2s^2\ 2p^1$ (*iii*) $1s^2\ 2s^2\ 2p^4$.

   Which of these electronic configurations would be expected to have the highest

   (*a*) IE_2 (*b*) IE_3 (*c*) IE_4. [**Ans.** (*a*) (*iii*), (*b*) (*i*), (*c*) (*ii*)]

2. For each of the following pairs, predict which one has lower first ionization energy?

   (*i*) N or O (*ii*) Be^+ or Mg^{2+} (*iii*) I or I^- [**Ans.** (*i*) O, (*ii*) Be^+, (*iii*) I]

3. In each of the following pairs of elements which element would you expect to have lower first ionization energy? Explain.

   (*i*) Cl or F (*ii*) Cl or S (*iii*) Kr or Xe. [**Ans.** (*i*) Cl (*ii*) S (*iii*) Xe]

4. Among the elements Li, K, Ca and Kr, which one has the lowest first ionization energy? Which one has the highest first ionization energy? [**Ans.** Lowest: K, Highest: Kr]

5. The ionization potential of hydrogen is 13.60 eV/mole. Calculate the energy in kJ required to produce 0.2 mole of H^+ ions. (Given, 1 eV = 96.49 kJ mol^{-1}). [**Ans.** 262.452 kJ]

6. Calculate the energy in joules required to convert all the atoms of sodium to sodium ions present in 23 mg of sodium vapours. Ionization energy of sodium is 495 kJ mol^{-1} (Atomic mass of Na = 23).
[**Ans.** 495 J]

7. Arrange the following in the order of increasing ionization energy.
(*i*) $1s^2\ 2s^2\ 2p^6\ 3s^2$ (*ii*) $1s^2\ 2s^2\ 2p^6\ 3s^1$ (*iii*) $1s^2\ 2s^2\ 2p^6$ (*iv*) $1s^2\ 2s^2\ 2p^2$
[**Ans.** (*ii*) < (*i*) < (*iv*) < (*iii*)]

8. The first (IE_1) and second (IE_2) ionization energies (kJ mol^{-1}) of a few elements designated by Roman numerals are shown below:

	IE_1	IE_2
I.	2372	5251
II.	520	7300
III.	1680	3380

Which one of the above elements is likely to be
(*a*) a reactive metal,
(*b*) a reactive non-metal and
(*c*) a noble gas?
[**Ans.** (*a*) II (*b*) III (*c*) I]

2.11 MELTING POINTS AND BOILING POINTS

It is quite interesting to observe the variation in melting and boiling points of elements in the second and third periods of the periodic table as given in Tables 2.11 and 2.12.

Table 2.11: Variation in melting and boiling points of elements in the second period

Element	Symbol	Melting Point (°C)	Boiling Point (°C)
Lithium	Li	180.5	1342
Beryllium	Be	1287	2471
Boron	B	2075	4000
Carbon	C	3550	3825
Nitrogen	N	– 210	– 195.58
Oxygen	O	– 218.8	– 183
Fluorine	F	– 219.6	– 188.1
Neon	Ne	– 248.6	– 246

Table 2.12: Variation in melting and boiling points of elements in the third period

Element	Symbol	Melting Point (°C)	Boiling Point (°C)
Sodium	Na	97.8	888
Magnesium	Mg	650	1107
Aluminium	Al	660.3	2519
Silicon	Si	1414	3265
Phosphorus	P	44.2	277
Sulphur	S	115.2	444.6
Chlorine	Cl	– 101.5	– 34.6
Argon	Ar	– 189.35	– 185.85

We observe that in second period as well as third period, the melting and boiling points show an increase upto some point as we move from the left hand side to the right hand side in the period. After that the melting and boiling point decrease upto the end.

Explanation: Melting and boiling points depend upon the nature of chemical bonding between the atoms of these elements. Elements on the extreme left of the period are metals, they involve metallic bonding. A small amount of energy is required to separate the atoms from one another. Therefore, they show low melting and boiling points. As we move towards the right, we come across network solids having two dimensional or three dimensional giant molecules. A greater amount of energy is required to break the bonds between them. Therefore, the melting and boiling points increase. The extreme right elements like N_2 and O_2 are molecular substances bound to each other by weak van der Waals forces. The attractive force between the atoms in these diatomic gas molecules is strong but the force between the molecules is very weak. Therefore, they melt and boil at very low temperature.

2.12 PROPERTIES OF PERIOD 3 OXIDES

2.12.1 Physical Properties

The oxides that we shall be looking at are:

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
				P_4O_6	SO_2	Cl_2O

These oxides are known as the highest oxides of these elements. These are the oxides where the period 3 elements are in their highest oxidation states. Na_2O, MgO and Al_2O_3 are metallic oxides having ionic character. The metal cations and oxide ions are arranged in the crystal lattice such that each metal ion is surrounded by oxide ions and vice versa. Silicon oxide exists as a giant covalent oxide. The oxides of P, S and Cl are molecular oxides.

Melting and boiling points: SiO_2 having a giant structure possesses high melting and boiling points because a lot of energy is required to break the strong bonds operating in three dimensions. The oxides of P, S and Cl consist of individual molecules and have weak van der Waals forces between them. A small amount of energy is required to overcome forces between them. Therefore, they exhibit smaller melting and boiling points.

Electrical conductivity: None of these oxides has any free or mobile electrons. That means none of them will conduct electricity when they are in solid state. However, ionic oxides participate in electrolysis in the molten state because of the movement of ions towards oppositely charged electrodes.

2.12.2 Chemical Properties

Na_2O MgO Al_2O_3	SiO_2	P_4O_{10} SO_3 Cl_2O_7 P_4O_6 SO_2 Cl_2O
Basic	Amphoteric Both basic and acidic	Acidic

Aluminium oxide also shows amphoteric character.

Ionic oxides (Na_2O, MgO and Al_2O_3) contain O^{2-}. They are strongly basic, they react with water to produce OH^- ions.

$$O^{2-}\ (aq) + H_2O\ (l) \rightarrow 2\ OH^-\ (aq)$$

Thus, all ionic oxides are basic.

Covalent oxides (SiO_2) do not contain ions but have a strong positive pole on the atom other than O. This attracts lone pair of electrons on water towards itself.

$$MO + H_2O\ (l) \rightarrow MO(OH^-)\ (aq) + H^+\ (aq)$$

Thus all covalent oxides are acidic.

Intermediate oxides (for example Al_2O_3) can act both ways. They are amphoteric (basic as well as acidic).

$$Al_2O_3(s) + 6H^+ (aq) \rightarrow Al^{3+} (aq) + 3\,H_2O\ (l) \qquad \text{(Basic)}$$

$$Al_2O_3\ (s) + 3H_2O + 6\,OH^- \rightarrow 2Al\ (OH)_6^{3-} \qquad \text{(Acidic)}$$

pH changes when these oxides are dissolved in water

$$Na_2O + 2H_2O \rightarrow 2NaOH \qquad (pH = 14)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (pH = 9)$$

Al_2O_3 is insoluble in water. It is amphoteric. (pH = 7)

SiO_2 is insoluble in water. It is an acidic oxide. (pH = 7)

P_4O_{10} is an acidic oxide. It dissolves in water to give acids.

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4 \qquad (pH = 3)$$

Thus, we find that pH of the solution when the oxides are added to water decreases as we move from Na_2O to Cl_2O_7. We can say that the oxides become more and more acidic on moving from left to right.

Harmful effects of SO_2 and SO_3 in acid rain

Combustion of fossil fuels in automobiles and industrial units produces large quantities of SO_2 and SO_3. These gases go up in the air and are washed down by rain water. These gases dissolve in water to form acids.

$$SO_2 + H_2O \rightarrow \underset{\text{(Sulphurous acid)}}{H_2SO_3}$$

$$SO_3 + H_2O \rightarrow \underset{\text{(Sulphuric acid)}}{H_2SO_4}$$

Thus, rain water gets contaminated with acids. Such a rainfall is harmful for the soil and the crops. It also has a detrimental effect on the aquatic animals.

2.13 PERIODICITY IN PROPERTIES OF HALIDES, CARBONATES, HYDROXIDES AND SULPHATES OF ALKALI AND ALKALINE EARTH METALS

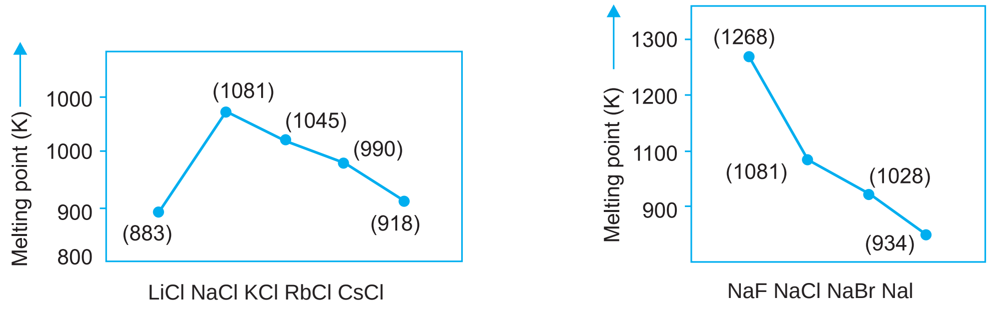
2.13.1 Halides of Alkali Metals

1. **Melting and boiling points.** All the halides of alkali metals are *high-melting colourless crystalline solids.* The high melting points of these halides are due to their ionic nature and high lattice energies. The melting and boiling points of alkali metals follow the following trends:

   (*i*) **For the same halide ion**, *the melting points of lithium halides are lower than those of the corresponding sodium halides and thereafter they decrease as we move down the group from Na to Cs.* The trend in the variation of melting points of alkali metal chlorides is illustrated in Fig. 2.10 (*a*).

   Explanation. *The low melting point of LiCl as compared to NaCl is probably because LiCl is covalent in nature while NaCl is ionic. Covalent compounds have lower m.p. and b.p.* Thereafter, the melting points decrease as we move from NaCl → KCl → RbCl → CsCl because the lattice energies decrease as the size of the alkali metal atom increases. Smaller ions pack more closely and have higher lattice energies.

   (*ii*) **For the same alkali metal**, *the melting and boiling points decrease in the order: fluoride > chloride > bromide > iodide.* Fig. 2.10 (*b*) depicts the trend in the melting points of different halides of sodium.



(a) Alkali metal chlorides

(b) Sodium halides

Fig. 2.10: *(a) Variation in melting points of alkali metal chlorides*
(b) Variation in melting points of sodium halides

Explanation. This trend can be easily explained on the basis of *lattice energy* of these halides. For the same alkali metal ion, the lattice energy decreases as the size of the halide ion increases. As the *lattice energy decreases, energy required to break the lattice (melting points) decreases and, hence, the melting points of sodium halides decrease from NaF (1298 K) → NaCl (1081 K) → NaBr (1028 K) → NaI (934 K).*

2. **Solubility.** *The alkali metal halides are soluble in water. LiCl has much higher solubility than NaCl* because Li^+ ion being smaller in size has much higher hydration energy. For the same halide ion, the solubilities of the halides of alkali metals in water increase regularly from Na to Cs. This can be explained in terms of decrease in lattice energies.

2.13.2 Hydroxides of Alkali and Alkaline Earth Metals

Solubility

(*i*) **The hydroxides of alkali metals (MOH)** *are appreciably soluble in water* and their solubilities further increase as we move from LiOH → NaOH → KOH → RbOH → CsOH due to a decrease in their lattice energies as the size of the alkali metal ion increases.

(*ii*) **The hydroxides of alkaline earth metals $M(OH)_2$** *are sparingly soluble in water*. Lower solubility of alkaline earth metal hydroxides is due to the greater ionization energy of alkaline earth metal atoms. Lower solubility of alkaline earth metal hydroxides can also be due to higher lattice energy because of comparable sizes of cation and anion. However, their solubilities in water increase markedly as we move down the group (Fig. 2.11) mainly due to a decrease in their lattice energies as the size of the metal ion increases from Be^{2+} to Ba^{2+}.

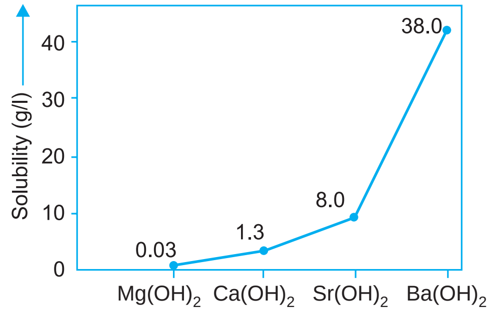


Fig. 2.11: *Solubilities of hydroxides of alkaline earth metals in water at 298 K*

Basic strength

(*i*) **The hydroxides of alkali metals** *behave as strong bases due to their low ionization energies.* Due to low ionization energies, the M—O bond in M—O—H can be easily broken giving M^+ and OH^- ions.

$$MOH \rightarrow M^+ + OH^- \text{ (basic nature)}$$

As we move down the group, the ionization energy decreases. As a result, the M—OH bond is more and more easily broken and, hence, the basic strength increases down the group from LiOH to CsOH.

LiOH NaOH KOH RbOH CsOH

$\longrightarrow$

Basic strength increases

(*ii*) The hydroxides of alkaline earth metals *are relatively less basic than the hydroxides of the corresponding alkali metals of the same period.* This is due to their higher ionization energies, smaller ionic size and higher lattice energies. As a result, OH^- ions are more tightly held by M^{2+} ions and the M—O—H bond does not break readily. On moving down the group, the basic character of the hydroxides increases markedly from Be to Ba mainly due to decreasing ionization energies of the metal atoms. For example,

$Be(OH)_2$	$Mg(OH)_2$	$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
Amphoteric	Weak base	Moderately bases	Strong	As strong a base as alkali metal hydroxide

$\longrightarrow$

Basic strength increases

2.13.3 Carbonates and Bicarbonates of Alkali and Alkaline Earth Metals

Solubility

(*i*) *The carbonates and bicarbonates of alkali metals are soluble in water.* Their solubility increases as we move down the group from Li to Cs due to decreasing lattice energies as the size of atom increases.

(*ii*) *The carbonates of alkaline earth metals are sparingly soluble in water.* Their solubility decreases from Be to Ba down the group. For example, $MgCO_3$ is slightly soluble in water but $BaCO_3$ is almost insoluble.

As we move down the group, the lattice energies of carbonates remain approximately the same. The reason being that carbonate ion is so large that relatively small changes in the size of the cations from Be^{2+} to Ba^{2+} do not make any material difference. However, the *hydration energies* of the metal cations decrease from Be^{2+} to Ba^{2+}. Smaller cations are associated with greater hydration energies. Hence, *the solubilities of carbonates of the alkaline earth metals decrease while moving down the group.*

Stability

(*i*) *Except Li_2CO_3, the carbonates of other alkali metals are stable to heat and hence do not decompose on heating.* Li_2CO_3 on heating, however, gives Li_2O and CO_2.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

The instability of Li_2CO_3 is due to the small size of Li^+ ion in the lattice compared to size of CO_3^{2-}. The other alkali metal ions are larger in size and, hence, can easily stabilize the larger CO_3^{2-} ion. Therefore, the carbonates of alkali metals other than Li_2CO_3 are stable towards heat. Li_2O is produced on decomposition of Li_2CO_3 and forms a stable lattice.

(*ii*) *The carbonates of alkaline earth metals are comparatively less stable than those of alkali metals and decompose on heating to give CO_2.* Stability towards heat, however, increases from $BeCO_3$ to $BaCO_3$. This can be explained in terms of more and more stable lattices as we move down.

Carbonate:				
$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
Decomposition temperature:				
< 373 K	813 K	1173 K	1563 K	1635 K

Sulphates of alkaline earth metals. *The sulphates of alkaline earth metals are less soluble in water. The solubility, however, decreases further down the group from Be to Ba.* For example,

$BeSO_4$	$MgSO_4$	$CaSO_4$	$SrSO_4$	$BaSO_4$
Fairly soluble	Soluble	Sparingly soluble	Insoluble	Insoluble

$$\xrightarrow{\hspace{12em}}$$

Solubility decreases

This is because, the hydration energies of the metal cations decrease from Be^{2+} to Ba^{2+}. Hence, *the solubilities of sulphates of the alkaline earth metals decrease down the group.*

MISCELLANEOUS SOLVED QUESTIONS

1. *The first ($\Delta_i H_1$) and second ($\Delta_i H_2$) ionization enthalpies (in kJ mol^{-1}) and the electron gain enthalpies (in kJ mol^{-1}) of a few elements are given below:*

Element	$\Delta_i H_1$	$\Delta_i H_2$	$\Delta_{eg} H$
I	*520*	*7300*	*–60*
II	*419*	*3051*	*–48*
III	*1681*	*3374*	*–328*
IV	*1008*	*1846*	*–295*
V	*2372*	*5251*	*+48*
VI	*738*	*1451*	*–40*

Which of the above elements is likely to be:

(a) the least reactive element

(b) the most reactive metal

(c) the most reactive non-metal

(d) the least reactive non-metal

(e) the metal which can form a stable binary halide of the formula MX_2 (X = halogen)

(f) the metal which can form a pre-dominantly stable covalent halide of the formula MX (X = halogen)?

Ans. (*a*) Element V as it has very high values of first and second ionization enthalpies.

(*b*) Element II is the most reactive metal as it has low value of $\Delta_i H_1$ and very high value of $\Delta_i H_2$.

(*c*) Element III as it has high value of $\Delta_i H_1$.

(*d*) Element V as it has very high value of $\Delta_i H_1$ and positive value of $\Delta_{eg} H$.

(*e*) Element VI because the difference between $\Delta_i H_1$ and $\Delta_i H_2$ is not large.

(*f*) Element I as it has low value of $\Delta_i H_1$ and very high value of $\Delta_i H_2$.

2. *Explain, why cations are smaller and anions larger in radii than their parent atoms.*

Ans. Cations are obtained by the loss of electrons and anions are obtained by the gain of electrons. As a result force of attraction in cations is more and it is less in anions than their parent atoms.

3. *What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down a group?*

Ans. The main factors due to which the ionization enthalpy of the main group elements tend to decrease down a group are:

(*i*) The attraction of electron towards the nucleus. As we move down the group attraction of electron towards nucleus decreases and therefore ionization enthalpy decreases.

(*ii*) Screening effect: Attractive force between the nucleus and valency electron decreases due to the presence of intervening core electrons present in between.

4. *How does atomic radius vary in a period and in a group? How do you explain the variation?*

Ans. Atomic radius increases as we go down the group and it decreases as we move from left to right in a period. As we go down the group, the electrons are added in a different shell and the force of attraction between the nucleus and outermost electrons decreases, hence the size increases. As we move from left to right in a period, the electrons are filled in the same shell, there is no new shell formation but nuclear charge increases, therefore force of attraction between nucleus and electrons increases, as a result atomic size decreases.

5. *Consider the following species:*

N^{3-}, O^{2-}, F^{-}, Na^{+}, Mg^{2+} and Al^{3+}

(a) What is common in them?

(b) Arrange them in order of increasing ionic radii.

Ans.

(*a*) N^{3-}, O^{2-}, F^{-}, Na^{+}, Mg^{2+} and Al^{3+} have same 10 electrons each (they are iso-electronic).

(*b*) $Al^{3+} < Mg^{2+} < Na^{+} < F^{-} < O^{2-} < N^{3-}$

6. *What is the basic difference between electron gain enthalpy and electronegativity?*

Ans. Difference between electron gain enthalpy and electronegativity.

Electron gain enthalpy	*Electronegativity*
1. Electron gain enthalpy is an absolute value.	1. Electronegativity has a relative value.
2. Electron gain enthalpy is defined for an isolated gaseous atom.	2. Electronegativity is defined for a bonded atom.
3. It is measured in terms of energy (eV, kJ mol^{-1}).	3. It is a relative number and has no unit.

QUICK SCAN (FOR REVISION)

1. **Mendeleev's periodic law** states that physical and chemical properties of elements are a periodic function of their atomic weights.
2. **Mendeleev's periodic table.** In Mendeleev's periodic table, the elements are arranged in order of their increasing atomic weights in such a way that elements with similar properties are placed in the same group.

   Mendeleev's original table consists of 8 vertical columns called **groups**. These are numbered as I, II, III ..... VIII. However, 9th vertical column called **zero group** was added with the discovery of inert gases. Except for groups VIII and zero, each group is further divided into two sub-groups designated as A and B. Group VIII consists of 9 elements arranged in three sets each containing three elements. There are 7 horizontal rows called periods in the Mendeleev's table.
3. **Modern periodic law** states that physical and chemical properties of the elements are a periodic function of their atomic numbers, *i.e.* if the elements are arranged in order of their increasing atomic numbers, the elements with similar properties are repeated after regular intervals.
4. **Cause of periodicity** in properties of elements is due to repetition of similar outer electronic configuration after certain regular intervals. These regular intervals being 2, 8, 8, 18, 18 and 32. These numbers are also called as **magic numbers**.
5. **Modern periodic table** is also called **long form of the periodic table** or **Bohr's table**. In this table, the elements are arranged in order of their increasing atomic numbers. It consists of 18 groups numbered from 1–18 and 7 periods numbered from 1–7. The first period involves the filling of 1*s*-orbital and contains only **2 elements** and, hence, is the **shortest period**. The **second period** involves the filling of 2*s* and 2*p*-orbitals and, hence, contains **8 elements**. Likewise, the **third period** involves the filling of 3*s* and 3*p*-orbitals and thus contains **8 elements**. Both second and the third periods are called **short periods**. The **fourth period** involves the filling of 4*s*, 3*d* and 4*p* orbitals and, hence, contains **18 elements**. Similarly, the **fifth period** involves the filling of 5*s*, 4*d* and 5*p* orbitals and, hence, contains **18 elements**. Both fourth and fifth periods are called **long periods**. The **sixth period** involves the filling of 6*s*, 4*f*, 5*d* and 6*p* orbitals and, thus, contains 32 elements. It is, therefore, the **longest period**. The **seventh period** should involve the filling of 7*s*, 5*f*, 6*d* and 6*p* orbitals and should also contain 32 elements. However, this period is incomplete and with the number of elements discovered so far, it contains only 24 elements.
6. All the elements in the long form of the periodic table have been further divided into *s*, *p*, *d* and *f*-blocks.
7. ***s*-Block elements.** These elements contain 1 or 2 electrons in the *s*-orbital of their respective outermost

shells. Their outer shell electronic configuration being ns^{1-2}, where n = 1 to 7. They include elements of **group** 1 (hydrogen and alkali metals) and **group** 2 (alkaline earth metals and helium). Thus, in all, there are 14 *s*-block elements in the periodic table.

8. ***p*-Block elements.** These elements contain 1-6 electrons in the *p*-orbitals of their respective outermost shells. Their general outer shell electronic configuration is $ns^2\ np^{1-6}$ where n = 2 to 7. They include elements of groups 13, 14, 15, 16, 17 and 18 excluding helium. Thus, in all, there are 30 *p*-block elements in the periodic table.
9. ***d*-Block elements** also called **transition elements** contain 1 to 10 electrons in the *d*-orbitals of their respective penultimate shells. Their general outer shell electronic configuration being $(n-1)d^{1-10}\ ns^{1-2}$. They are further divided into four series. The **first transition series** involves the filling of 3*d*-orbitals and contains ten elements from $_{21}$Sc – $_{30}$Zn. The **second transition series** involves the filling of 4*d*-orbitals and contains ten elements from $_{39}$Y – $_{48}$Cd. Similarly, **third transition series** involves the filling of 5*d*-orbitals and contains ten elements from $_{72}$Hf – $_{80}$Hg including $_{58}$La. The **fourth transition series** is, however, incomplete and contains only six elements at present. Thus, in all there are 36 known *d*-block elements so far.
10. ***f*-Block elements** also called **inner transition elements** have last electron in the *f*-orbitals of $(n-2)$ shells. Their general outer shell electronic configuration is $(n-2)f^{1-14}\ (n-1)d^{0-1}\ ns^2$. There are two series of *f*-block elements each containing 14 elements. Thus, in all, there are 28 *f*-block elements in the periodic table. These are placed at the bottom of the periodic table.

    The 14 elements of the first series from $_{58}$Ce – $_{71}$Lu in which 4*f*-orbitals are being progressively filled in are called **lanthanides**.

    The fourteen elements of the second series from $_{90}$Th – $_{103}$Lr in which 5*f*-orbitals are being progressively filled in are called **actinides**. All the actinides are radioactive elements. The first three elements, *i.e.* $_{90}$Th, $_{91}$Pa and $_{92}$U occur in nature but the remaining 11 elements from $_{93}$Np – $_{103}$Lr have been prepared artificially. These 11 elements are usually called **transuranic elements**.
11. **Representative elements or Normal elements.** All the elements of *s*- and *p*-blocks with the exception of noble gases are called representative elements. They include elements of groups 1, 2, 13, 14, 15, 16 and 17.
12. The properties of Zn, Cd and Hg resemble more to the *d*-block elements rather than *s*-block elements and hence are better considered as *d*-block elements even though, the last electron in these elements goes to the *s*-orbital of their respective outermost shells.
13. The atomic numbers of the next halogen, inert gas, alkali metal and alkaline earth metal, if discovered in future shall have atomic numbers of 117, 118, 119 and 120 respectively.
14. Maximum no. of metals are present in *d*-block.
15. If we draw a diagonal line from B to At in *p*-block, the elements that fall on that line are metalloids (semi-metals).
16. Most of the transuranic elements have been produced by G.T. Seaborg and his colleagues.
17. The electrons present in the outermost shell are called **valence electrons**.
    (*i*) **For *s*-block elements**, group number is equal to the number of valence electrons.
    (*ii*) **For *p*-block elements**, group number is equal to 10 + number of valence electrons.
    (*iii*) **For *d*-block elements**, group number is equal to the number of electrons in $(n-1)d$ subshell + number of electrons in the valence shell (***n*th shell**).
18. The valency of *s*-block elements = number of valence electrons. For *p*-block elements, valency = 8 minus number of valence electrons. In contrast, transition and inner transition elements exhibit variable valence due to involvement of not only the valence electrons but *d* or *f*-electrons as well.
19. **Periodic properties** are directly or indirectly related to their electronic configuration and show a regular gradation on moving from left to right in a period or from top to bottom in a group. Some important periodic properties are: atomic radii, ionization energy, electron affinity, electronegativity, valence, density, m.p. and b.p.
20. **van der Waals'** radius of an element is always larger than its covalent radius.
21. **Atomic and ionic radii** are determined from X-ray studies.
22. Distance between the nucleus and a point where the electron probability is maximum, is called the **atomic radius**. It may also be defined as the distance between nucleus and the last electron in the outermost orbit.
23. Covalent radii are additive.
24. The IE decreases from top to bottom in a group due to increase in atomic size and screening effect.

25. In general, the IE increases from left to right in a period due to corresponding increase in the nuclear charge, with some exceptions. These are attributed either to the stability of the electronic configuration or penetration effect of the electrons.

26. The IE_1 of N is higher than that of O even though the nuclear charge of O is higher than that of N. This is due to the greater stability of the exactly half-filled electronic configuration of N ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) as compared to that of O ($1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$).

27. The IE_2 of O is higher than that of F even though the nuclear charge of F is higher than that of O. This is again due to the reason that the second electron in oxygen has to be removed from the more stable exactly half filled electronic configuration of O^+ ($1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$) while, the removal of the second electron from F^+ ($1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$) gives the more stable exactly half-filled electronic configuration, *i.e.* F^{2+} ($1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$).

28. The IE_1 of B is lower than that of Be even though the nuclear charge of B is higher than that of Be. The reason being that in case of B, a less tightly held *p*-electron is to be removed while in case of Be, the more tightly held *s*-electron of the same shell is to be removed.

29. The number of valence electrons in an atom can be determined by examining its successive ionization energies one by one till a large jump in its value is found in going from one to the next higher successive ionization energy. For example, the number of valence electrons in Na is **one** because the value of IE_2 is much greater than that of IE_1. Similarly, the number of valence electrons in Mg is **two** because the value of its IE_3 is much greater than that of IE_2.

30. Greater the extent of penetration, greater is the ionization energy. The order of penetration of orbitals of same energy level is: $s > p > d > f$.

31. The electron affinities of elements having exactly half-filled and completely filled orbitals are essentially zero, *i.e.* electron affinities of Be, Mg, Ca, N, etc. and inert gases are zero.

32. **For the same alkali metal**, the melting points and boiling points of the halides decrease in the order *Fluoride > Chloride > Bromide > Iodide* due to a corresponding decrease in their lattice energies.

33. **For the same halide ion**, the melting points and boiling points of the alkali metal halides follow the order: $NaCl > KCl > RbCl > CsCl > LiCl$.

34. **Solubility of alkali metal halides in H_2O follows the order:** $NaCl < KCl < LiCl < RbCl < CsCl$ as the lattice energies regularly decrease from Na to Cs. LiCl is, however, more soluble than NaCl and KCl due to high hydration energy of Li^+ because of its small size.

35. Dense element is osmium while lightest element is hydrogen.

    Most abundant element in air is nitrogen followed by oxygen.

    Element with highest melting point 3757°C is carbon (diamond).

    Element with highest boiling point is rhenium (5870ºC).

36. **Solubility of alkali metal hydroxides in H_2O follows the order:** $LiOH < NaOH < KOH < RbOH < CsOH$; increases as the lattice energies decrease from Li to Cs.

37. **Basicity of alkali metal hydroxides follows the order:** $LiOH < NaOH < KOH < RbOH < CsOH$ as the I.E. of the alkali metal decreases from Li to Cs.

38. **Solubility of alkaline earth metal hydroxides in water follows the order:** $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$ as the lattice energies decrease from Be^{2+} to Ba^{2+}.

39. **Basicity of alkaline earth metal hydroxides follows the order:** $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$ as the I.E. of the metal atom decreases from Be to Ba. $Be(OH)_2$ is, however, amphoteric in nature.

40. Hydroxides of alkaline earth metals are relatively less basic than the hydroxides of the corresponding alkali metals of the same period.

41. The solubility of carbonates and bicarbonates of alkali metals in water increases from Li to Cs.

42. The bicarbonates of all metals are soluble in H_2O. Only alkali metal bicarbonates exist as crystalline solids while bicarbonates of all other metals are stable only in solution.

43. The solubilities of the carbonates of alkaline earth metals decrease down the group mainly due to decreasing hydration energies from Be^{2+} to Ba^{2+}.

44. Alkaline earth metal carbonates decompose on heating evolving CO_2. However, their thermal stability increases in the order: $BeCO_3 < MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$.

45. Li_2CO_3 decomposes ($Li_2CO_3 \rightarrow Li_2O + CO_2$) on heating while all other alkali metal carbonates are stable to heat.

46. Solubility of alkaline earth metal sulphates decrease in the order: $BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$. It is due to the decreasing hydration energies from Be^{2+} to Ba^{2+}.

EXERCISES

Very Short Answer Type Questions

1. To which block do the normal elements belong?
2. How many vertical columns (groups) are there in the long form of the periodic table?
3. Name the fundamental property of the element upon which modern periodic law is based.
4. What is the total number of periods of the periodic table?
5. What is the number of elements present in 3rd period of the periodic table?
6. What is the reason for the similar properties of elements belonging to the same group?
7. What is the total number of elements in the long form of the periodic table?
8. What is the type of the first element in a row of the periodic table?
9. How many elements are there in the 1st period?
10. To which block do the transition elements belong?
11. Which of the halogens has highest ionization energy?
12. In case of inner transition elements, to which orbital does the last electron go?
13. To which orbital in *s*-block elements, does the last electron go?
14. What are the atomic numbers of elements which constitute *f*-block (lanthanides and actinides)?
15. Which element amongst the alkali metals has the smallest atomic radius?
16. Define first ionization energy.
17. Which of the halogens has highest ionization energy?
18. Name the factors affecting ionization energy.

Short Answer Type Questions

1. Explain why does the electron affinity of the atom increase from left to right along a row in the periodic table.
2. How does the ionization energy vary: (*i*) in a group and (*ii*) along a period?
3. State Modern Periodic Law. What is the cause of periodicity?
4. Which one of the following pairs of elements would have a higher electron affinity? Explain.
   (*i*) N or O (*ii*) F or Cl.
5. For each of the following pairs state which one has greater ionization energy and greater electron affinity:
   (*i*) I, I^- (*ii*) Br, K
   (*iii*) Li, Li^+
6. The electron affinity of chlorine is more than that of fluorine. Explain.
7. Define covalent radius and van der Waals' radius. Which of the two is larger?
8. Which element will have the greatest electron affinity?
   (*i*) $[Ne]\ 3s^2\ 3p^3$ (*ii*) $[Ne]\ 3s^3\ 3p^4$
   (*iii*) $[Ne]\ 3s^2\ 3p^5$ (*iv*) $[Ne]\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
9. Define ionization energy. What are its units? Name the factors affecting I.E.
10. What is meant by ionization energy? Explain why the second ionization energy is greater than the first one.
11. How does the ionization energy vary in a group and along a period?
12. Write the difference between electron gain enthalpy and electronegativity.

Long Answer Type Questions

1. State modern periodic law. What is long form of periodic table? What are its main features? How is it superior to Mendeleev's table?
2. What is meant by periodic classification of elements? State Mendeleev's periodic law and discuss the main features of Mendeleev's periodic table.
3. Explain classification of elements into *s*, *p*, *d* and *f*-blocks, justifying the basis of this classification.
4. Give the characteristics of *s*, *p*, *d* and *f*-block elements.
5. (*i*) If the electronic configuration of neon (Z = 10) can be written as $1s^2, 2s^2, 2p^6$, write the electronic configuration of the elements A, B and C having Z = 17, 18 and 19 respectively and indicate which one of them is an alkali metal and which one is an inert element and why?

   A (Z = 17) ....
   B (Z = 18) ....
   C (Z = 19) ....
   Alkali element ... A, B or C

   (*ii*) Calculate the atomic number of the element having the configuration in its last orbit as $4s^2$, $4p^5$.
6. How do the atomic and ionic radii vary with increasing atomic number in a particular group and in a particular period?

7. Explain with reason why the ionization potential of Li is higher than that of Na.

8. The electronic configuration of an element A is:
$1s^2, 2s^2, 2p_x^{\ 2}, 2p_y^{\ 2}, 2p_z^{\ 2}, 3s^2$.
   - (*i*) Which is the group of the periodic table to which A belongs?
   - (*ii*) Write down the formula of the nitrate of A.
   - (*iii*) State whether a solution of the nitrate is a conductor of electricity or not.
   - (*iv*) How many electrons are present in each of the principal energy levels of the atoms of A?

9. The following are some of the elements of the periodic table:
Li, Be, B, C, N, O, F, Ne, Na, Mg, Al, Si, P, S, Cl, Ag, K and Ca
Which is the most electropositive and which is the most electronegative element? Which are the chemically inactive elements?

10. Arrange the elements with atomic numbers 17, 18 and 19 in the order of increasing first ionization potential.

11. (*i*) Which of the following elements N, F, Na and K, will have the smallest and which one will have the largest atomic radius?
   - (*ii*) Among the following elements Li, Cs, Cl and F, which is the most electronegative and which is the least electronegative?

12. Explain the following:
   - (*i*) Ionization energy of Mg is more than that of both Na and Al.
   - (*ii*) Ionization energy of nitrogen is more than that of oxygen.

13. (*i*) How does electronegativity very long a period?
   - (*ii*) Among alkali metals which element do you expect to be least electronegative and why?

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. *s*- and *p*-blocks
2. 18
3. At. number
4. 7
5. 8
6. Similar electronic configuration in the valence shell
7. 105
8. An alkali metal
9. 2
10. *d* and *f*-blocks
11. F
12. $(n-2)f$
13. *ns* orbital
14. Lanthanides: 58 to 71, Actinides: 90 to 103
15. Lithium

COMPETITION FILE

SUBJECTIVE PROBLEMS

Problem 1. *Which of the following pairs of elements would you expect to have lower first ionization energy? Explain your answer.*

(*a*) *Cl or F*	(*b*) *Cl or S*
(*c*) *K or Ar*	(*d*) *Kr or Xe*

Solution.

(*a*) Cl as it belongs to higher period, lower in the group and has a large size.

(*b*) Sulphur as it precedes chlorine (Cl) in the period.

(*c*) Potassium as it is an alkali metal while Kr is a noble gas with ns^2np^6 configuration.

(*d*) Xe as it is lower in the group and has a large size.

Problem 2. *Among the elements of the second period Li to Ne pick out the element:*

(*a*) *with the highest first ionization energy.*

(*b*) *with the highest electronegativity.*

(*c*) *with the largest atomic radius.*

(*d*) *that is the most reactive non-metal.*

(*e*) *that is the most reactive metal.*

Solution. (*a*) Ne; (*b*) F; (*c*) Li; (*d*) F; (*e*) Li.

Problem 3. *Which of the following pairs would have a larger size? Explain your answer.*

(*a*) *K or* K^+	(*b*) *Br or* Br^-
(*c*) O^{2-} *or* F^-	(*d*) Li^+ *or* Na^+
(*e*) *P or As*	(*f*) Na^+ *or* Mg^{2+}

Solution.

(*a*) K, as it has a similar effective nuclear charge.

(*b*) Br, as it has more electrons and nuclear charge is less.

(*c*) O^{2-} has a large size as it has smaller nuclear charge (8) compared to that of F^- (9) though both are isoelectronic.

(*d*) Na^+, as it is of a lower element in the group.

(*e*) As, as it is lower in the group with bigger size.

(*f*) Na^+, has a bigger size as its effective nuclear charge is smaller though both are isoelectronic.

Problem 4. *The valency of a representative element is either equal to the number of the valence electrons or eight minus this number. What is the basis of this rule?*

Solution. The basis is electronic configuration which is $ns^{1-2}np^{1-6}$. Since representative elements are only in 8 groups, the valency cannot be more than 8. Thus, it is normally equal to the valence electron or 8 minus this number.

Problem 5. *Explain why the first ionization energy of Na is lower than that of Mg while the second ionization energy of Na is higher than that of Mg?*

Solution. The first electron in both the cases has to be removed from the 2*s* orbital but nuclear charge of Na is less than that of Mg. After the loss of first electron, the electronic configuration of Na^+ is $1s^2\ 2s^2\ 2p^6$, *i.e.* that of noble gas which is very stable, and hence, the removal of second electron is very difficult. In case of Mg, after the loss of one electron, electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^1$. The second electron to be removed is from 3*s*-orbital which is easier.

Problem 6. *Copper is regarded as a transition element though it has completely filled d-orbitals (d^{10}).*

Solution. This is because in the most common oxidation state (+2) the *d*-orbitals are incompletely filled:

$$Cu\ (Z = 29) = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$$

$$Cu^{2+} = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9.$$

Problem 7. *Why has the zero group been placed at the extreme right of the periodic table?*

Solution. This is in accordance with the electronic configurations because each period starts with the filling of *s*-subshell and is complete after the filling of *p*-subshell of the same main shell.

Problem 8. *How many elements can be accommodated in the present set up of the long form of the periodic table? Explain.*

Solution. In the present set up of the long form of the periodic table, we have seven periods and four blocks. Each period ends up with an inert gas with its outermost shell complete having $ns^2\ np^6$ configuration. The 6th period ends up with Radon (Z = 86) having valence shell electronic configuration $6s^2\ 6p^6$. The 7th period will end up with a hypothetical inert gas (Z = 86 + 32 = 118) having valence shell electronic configuration $7s^2\ 7p^6$. Therefore, the maximum number of elements which can be accommodated in the present set up of the long form of the periodic table is 118.

Problem 9. *What are representative elements?*

Solution. The *s*-block and *p*-block elements are called representative elements. Representative elements include the elements of the following groups:

(*i*) Group 1 (alkali metals) and group 2 (alkaline earth metals)

(*ii*) Group 13 (boron family) and group 14 (carbon family), group 15 (nitrogen family), group 16 (oxygen family), group 17 (halogen family).

Problem 10. *Arrange the following in order of decreasing van der Waals' radii: Cl, H, O and N.*

Solution. van der Waals' radii increase as the number of energy shells increases, and decreases as the nuclear charge increases. Since H has only one energy shell, and Cl has three, therefore van der Waals' radius of H is the lowest while that of Cl is the highest. Further, both N and O have two energy shells but the nuclear charge on O (+8) is higher than that on N (+7). Therefore, the *van der Waals' radius* of N is higher than that of O.

Thus, the overall decreasing order is:

$$Cl > N > O > H.$$

Problem 11. *The solubilities of the carbonates of the alkali metals increase while those of the alkaline earth metals decrease when we move from top to bottom in their respective groups. Explain why?*

Solution. The solubilities of alkali metal carbonates increase down the group due to decreasing lattice energies, with the increase in size from Li to Cs. The solubilities of alkaline earth metals decrease down the group because their lattice energies remain almost the same whereas hydration energies decrease from Be^{2+} to Ba^{2+}.

Problem 12. *Arrange Na, Rb, K and Mg in order of increasing atomic radius.*

Solution. Na < Mg < K < Rb.

Problem 13. *Arrange the following ions in order of their increasing ionic radii: Li^+, Mg^{2+}, K^+ and Al^{3+}.*

Solution.

(*i*) The ionic radius of any cation increases as the number of energy shells increases and decreases as the magnitude of the positive charge increases.

(*ii*) Mg^{2+} ($1s^2\ 2s^2\ 2p^6$) and Al^{3+} ($1s^2\ 2s^2\ 2p^6$) are isoelectronic ions and each has two energy-shells. Since the positive charge on Al^{3+} is higher than that of Mg^{2+}, therefore, ionic radius of Al^{3+} is lower than that of Mg^{2+}.

(*iii*) Since K^+ ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$) has three shells and Mg^{2+} and Al^{3+} have two shells each, ionic radius of K^+ is the largest followed by Mg^{2+} and then Al^{3+}.

(*iv*) Now Li^+ ($1s^2$) has one shell and +1 charge but Al^{3+} has two shells and +3 charge. Increase in the ionic radius of Al^{3+} due to the presence of two shells is more than counter balanced by the decrease in its size due to an increase in charge from +1 in Li^+ to +3 in Al^{3+}, therefore, *the ionic radius of* Al^{3+} *is lower than that of* Li^+*. Thus, the ionic radii of these four ions increase in the order:* $Al^{3+} < Li^+ < Mg^{2+} < K^+$.

Problem 14. *The first ionization energy of carbon atom is greater than that of boron whereas the reverse is true for the second ionization energy. Explain.*

Solution. The electronic configuration of C-atom is $1s^2\ 2s^2\ 2p^2$ and that of B-atom is $1s^2\ 2s^2\ 2p^1$. The first electron to be removed in both the cases is from 2*p*-orbital but nuclear charge of C is more than that of B. After the removal of first electron, the second electron to be removed from C-atom is from 2*p*, whereas that from B-atom is from 2*s* which is more penetrating and hence, is more strongly attracted by the nucleus.

Problem 15. *Explain why the first ionization energy of Na is lower than that of Mg while the second ionization energy of Na is higher than that of Mg?*

Solution. The first electron in both the cases has to be removed from the 2*s* orbital but nuclear charge of Na is less than that of Mg. After the loss of first electron, the electronic configuration of Na^+ is $1s^2\ 2s^2\ 2p^6$, *i.e.* that of noble gas which is very stable, and hence, the removal of second electron is very difficult. In case of Mg, after the loss of one electron, electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^1$. The second electron to be removed is from 3*s*-orbital which is easier.

Problem 16. *Arrange the following elements in the increasing order of their ionization energy:*

Hydrogen, Helium and Lithium.

Solution. Li < H < He.

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. The electronic configuration of the element with atomic number 110, if discovered, will be
   (*a*) $(n-1)\ d^7\ ns^2\ np^1$ (*b*) $(n-1)\ d^8\ ns^2$
   (*c*) $(n-1)\ d^6\ ns^2\ np^2$ (*d*) $(n-1)\ d^5\ ns^2\ np^3$
2. The atomic numbers of Cl and K are 17 and 19 respectively and Cl^- and K^+ ions are isoelectronic. If r_a and r_c are the ionic radii of Cl^- and K^+ respectively, then which one of the following relations would hold good?
   (*a*) $r_a = r_c$ (*b*) $17r_a = 19r_c$
   (*c*) $r_a \approx 1.36\ r_c$ (*d*) $r_a \approx 0.73\ r_c$
3. The ionic radii of N^{3-}, O^{2-}, F^- and Na^+ follows the order
   (*a*) $N^{3-} > O^{2-} > F^- > Na^+$
   (*b*) $Na^{3-} > Na^+ > O^{2-} > F^-$
   (*c*) $Na^+ > O^{2-} > N^{3-} > F^-$
   (*d*) $O^{2-} > F^- > Na^+ > N^{3-}$
4. The set representing the correct order of first ionization potential is
   (*a*) K > Na > Li (*b*) Be > Mg > Ca
   (*c*) B > C > N (*d*) Ge > Si > C
5. The correct order of radii is
   (*a*) N < Be < B (*b*) $F^- < O^{2-} < N^{3-}$
   (*c*) Na < Li < K (*d*) $Fe^{3+} < Fe^{2+} < Fe^{4+}$
6. Which one of the following ions has the highest value of ionic radius?
   (*a*) Li^+ (*b*) B^{3+}
   (*c*) O^{2-} (*d*) F^-
7. The increasing order of the first ionization enthalpies of the elements B, P, S and F (lowest first) is
   (*a*) F < S < P < B (*b*) P < S < B < F
   (*c*) B < P < S < F (*d*) B < S < P < F
8. Following statements regarding the periodic trends of chemical reactivity of the alkali metals and the halogens are given. Which of these statements gives the correct picture?
   (*a*) The reactivity decreases in the alkali metals but increases in the halogens with increase in atomic number down the group.
   (*b*) In both the alkali metals and the halogens the chemical reactivity decreases with increase in atomic number down the group.
   (*c*) Chemical reactivity increases with increase in atomic number down the group in both the alkali metals and halogens.

(*d*) In alkali metals the reactivity increases but in the halogens it decreases with increase in atomic number down the group.

9. The set representing the correct order of ionic radius is
   (*a*) $Li^+ > Be^{2+} > Na^+ > Mg^{2+}$
   (*b*) $Na^+ > Li^+ > Mg^{2+} > Be^{2+}$
   (*c*) $Li^+ > Na^+ > Mg^{2+} > Be^{2+}$
   (*d*) $Mg^{2+} > Be^{2+} > Li^+ > Na^+$

10. The increasing order of the ionic radii of the given isoelectronic species is
    (*a*) S^{2-}, Cl^-, Ca^{2+}, K^+
    (*b*) Ca^{2+}, K^+, Cl^-, S^{2-}
    (*c*) K^+, S^{2-}, Ca^{2+}, Cl^-
    (*d*) Cl^-, Ca^{2+}, K^+, S^{2-}

11. Amongst the elements with the following electronic configuration, which one of them may have the highest ionization energy?
    (*a*) Ne $[3s^2 3p^2]$
    (*b*) Ar $[3d^{10} 4s^2 4p^3]$
    (*c*) Ne $[3s^2 3p^1]$
    (*d*) Ne $[3s^2 3p^3]$

(B) Fill in the Blanks

Fill in the blank spaces:

1. .... block elements are called inner .... elements.
2. Electronegativity of an atom is given by the average of electron affinity and ....
3. Electron affinity of fluorine is .... than that of chlorine.
4. Ca^{2+} ion has a smaller ionic size than K^+ ion because it has ....

(C) True/False Statements

Write T for True and F for False statements:

1. Whenever an atom is converted into anion, energy is released.
2. Size of an atom increases with an increase in the atomic number.
3. Electronegativity always increases with the increase in atomic number.
4. Effective nuclear charge of an atom increases when an atom loses electrons.
5. Decreasing order of electron affinity of F, Cl and Br is F > Cl > Br.

(D) Assertion-Reason Type Questions

The questions below (1 to 4) consist of an ***Assertion*** *in column 1 and the* ***Reason*** *in column 2. Use the following key to choose the appropriate answer:*

(*a*) Both *Assertion* and *Reason* are correct, and *Reason* is the correct explanation of the *Assertion*.
(*b*) Both *Assertion* and *Reason* are correct, but *Reason* is not the correct explanation of the *Assertion*.
(*c*) The *Assertion* is correct, but *Reason* is incorrect.
(*d*) The *Assertion* is incorrect, but *Reason* is correct.

Assertion (Column 1)	**Reason (Column 2)**
1. The first ionization energy of Be is greater than that of B.	1. 2*p* orbital is lower in energy than 2s.
2. Long form of the periodic table is based on atomic number.	2. Chemical behaviour of an element is decided by its atomic number.
3. Third period of periodic table involves filling of 3*s* and 3*p* orbitals.	3. General outer shell configuration of transition elements is $(n-1)d^{1-10}\ ns^{1-2}$.
4. Basicity of alkali metal hydroxides decreases in the order LiOH > NaOH > KOH > RbOH	4. Basicity of alkaline earth metal hydroxides increases in the order $Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2$

(E) Multiple Choice Questions

Choose one or more than one correct answer(s):

1. Ionization energy of nitrogen (Z = 7) is more than that of oxygen (Z = 8) because
   (*a*) half-filled *p*-orbitals in nitrogen ($2p^3$) are most stable.
   (*b*) electrons are more attracted towards the nucleus.
   (*c*) nitrogen atom is small.
   (*d*) ionization energy is low in oxygen as it becomes comparatively stable by losing an electron.

2. Long form of the periodic table consists of
   (*a*) nine groups
   (*b*) eight groups
   (*c*) seven periods
   (*d*) eighteen groups.

3. The values of which property increases from left to right in a period
   (*a*) ionization potential
   (*b*) electron affinity
   (*c*) size of an atom
   (*d*) electronegativity

4. Change of $Zn \rightarrow Zn^{2+} + 2e^-$ is accompanied by a decrease in
   (*a*) no. of valence electrons
   (*b*) atomic mass
   (*c*) atomic number
   (*d*) no. of shells.

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. Consider the isoelectronic species, Na^{+}, Mg^{2+}, F^{-} and O^{2-}. The correct order of increasing length of their radii is

   (*a*) $F^{-} < O^{2-} < Mg^{2+} < Na^{+}$

   (*b*) $Mg^{2+} < Na^{+} < F^{-} < O^{2-}$

   (*c*) $O^{2-} < F^{-} < Na^{+} < Mg^{2+}$

   (*d*) $O^{2-} < F^{-} < Mg^{2+} < Na^{+}$

2. The order of screening effect of electrons of *s*, *p*, *d* and *f* orbitals of a given shell of an atom on its outer shell electrons is:

   (*a*) $s > p > d > f$ (*b*) $f > d > p > s$

   (*c*) $p < d < s > f$ (*d*) $f > p > s > d$

3. The first ionization enthalpies of Na, Mg, Al and Si are in the order:

   (*a*) Na < Mg > Al < Si   (*b*) Na > Mg > Al > Si

   (*c*) Na < Mg < Al < Si   (*d*) Na > Mg > Al < Si

4. The statement that is not correct for periodic classification of elements is:

   (*a*) The properties of elements are periodic function of their atomic numbers.

   (*b*) Non-metallic elements are less in number than metallic elements.

   (*c*) For transition elements, the 3*d*-orbitals are filled with electrons after 3*p*-orbitals and before 4*s*-orbitals.

   (*d*) The first ionization enthalpies of elements generally increase with increase in atomic number as we go along a period.

5. The period number in the long form of the periodic table is equal to

   (*a*) magnetic quantum number of any element of the period.

   (*b*) atomic number of any element of the period.

   (*c*) maximum Principal quantum number of any element of the period.

   (*d*) maximum Azimuthal quantum number of any element of the period.

6. Electronic configurations of four elements A, B, C and D are given below:

   (A) $1s^2\ 2s^2\ 2p^6$ (B) $1s^2\ 2s^2\ 2p^4$

   (C) $1s^2\ 2s^2\ 2p^6\ 3s^1$ (D) $1s^2\ 2s^2\ 2p^5$

   Which of the following is the correct order of increasing tendency to gain electron?

   (*a*) A < C < B < D

   (*b*) A < B < C < D

   (*c*) D < B < C < A

   (*d*) D < A < B < C

7. Which of the following sequences contain atomic numbers of only representative elements?

   (*a*) 3, 33, 53, 87   (*b*) 2, 10, 22, 36

   (*c*) 7, 17, 25, 37, 48   (*d*) 9, 35, 51, 88

8. Which of the following elements will gain one electron more readily in comparison to other elements of their group?

   (*a*) S (g)   (*b*) Na (g)

   (*c*) O (g)   (*d*) Cl (g)

9. Which of the following sets contain only isoelectronic ions?

   (*a*) Zn^{2+}, Ca^{2+}, Ga^{3+}, Al^{3+}

   (*b*) K^{+}, Ca^{2+}, Sc^{3+}, Cl^{-}

   (*c*) P^{3-}, S^{2-}, Cl^{-}, K^{+}

   (*d*) Ti^{4+}, Ar, Cr^{3+}, V^{5+}

10. Ionic radii vary in

    (*a*) inverse proportion to the effective nuclear charge.

    (*b*) inverse proportion to the square of effective nuclear charge.

    (*c*) direct proportion to the screening effect.

    (*d*) direct proportion to the square of screening effect.

II. Assertion-Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below in each question.

1. ***Assertion (A):*** Generally, ionization enthalpy increases from left to right in a period.

   Reason (R): When successive electrons are added to the orbitals in the same principal quantum level, the shielding effect of inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus.

   (*a*) Assertion is correct statement and reason is wrong statement.

   (*b*) Assertion and reason both are correct statements and reason is correct explanation of assertion.

   (*c*) Assertion and reason both are wrong statements.

   (*d*) Assertion is wrong statement and reason is correct statement.

2. ***Assertion (A):*** Boron has a smaller first ionization enthalpy than beryllium.

   Reason (R): The penetration of a 2*s* electron to the nucleus is more than the 2*p* electron hence 2*p* electron is more shielded by the inner core of electrons than the 2*s* electrons.

(*a*) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(*b*) Assertion is correct statement but reason is wrong statement.

(*c*) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(*d*) Assertion and reason both are wrong statements.

3. ***Assertion (A):*** Electron gains enthalpy and becomes less negative as we go down a group.

   Reason (R): Size of the atom increases on going down the group and the added electron would be farther from the nucleus.

   (*a*) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

   (*b*) Assertion and reason both are correct statements and reason is correct explanation for assertion.

   (*c*) Assertion and reason both are wrong statements.

   (*d*) Assertion is wrong statement but reason is correct statement.

III. Short Answer Type Questions

1. All transition elements are *d*-block elements, but all *d*-block elements are not transition elements. Explain.
2. Choose the correct order of atomic radii of fluorine and neon (in pm) out of the options given below and justify your answer.

   (*i*) 72, 160 (*ii*) 160, 160

   (*iii*) 72, 72 (*iv*) 160, 72

3. Illustrate by taking examples of transition elements and non-transition elements that oxidation states of elements are largely based on electronic configuration.
4. First member of each group of representative elements (i.e., *s* and *p*-block elements) shows anomalous behaviour. Illustrate with two examples.
5. *p*-block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water.
6. How would you explain the fact that first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium?
7. Arrange the elements N, P, O and S in the order of

   (*i*) increasing first ionization enthalpy.

   (*ii*) increasing non-metallic character.

   Give reason for the arrangement assigned.
8. The radius of Na^+ cation is less than that of Na atom. Give reason.
9. Among alkali metals which element do you expect to be least electronegative and why?

ANSWERS

(A) Multiple Choice Questions

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

(B) Fill in the Blanks

1. *f*, transition 2. ionization energy 3. less 4. higher

(C) True/False Statements

1. F 2. F 3. F 4. T 5. F

(D) Assertion-Reason Type Questions

1. (*c*) 2. (*a*) 3. (*b*) 4. (*d*)

(E) Multiple Choice Questions (More than one correct answers)

1. (*a*), (*d*) 2. (*c*), (*d*) 3. (*a*), (*b*), (*d*) 4. (*a*), (*d*)

Some Additional Questions

I. Multiple Choice Questions

1. (*b*) 2. (*a*) 3. (*a*) 4. (*c*) 5. (*c*) 6. (*a*) 7. (*a*), (*d*) 8. (*a*), (*d*)
9. (*b*), (*c*) 10. (*a*), (*c*)

II. Assertion-Reason Type Questions

1. (*b*) 2. (*c*) 3. (*d*)

3
CHAPTER

Chemical Bonding

LEARNING OBJECTIVES

- Ionic bonding
  - Explain that ionic bonding results from the electrostatic attraction between oppositely charged ions.
  - Draw dot and cross diagrams to show the electron arrangement of ions in ionic bonding.
  - Predict the charge on the ions of an element from its group number in the Periodic Table.
  - State the formulae for a range of ions including the nitrate ion, nitrite ion, carbonate ion, sulphate ion, sulphite ion, phosphate ion and ammonium ion.
- Covalent bonding and dative covalent bonding (coordinate bonding).
  - Describe the nature of the covalent bond.
  - Draw dot and cross diagrams to describe single covalent bonding (e.g. Cl_2, HCl, H_2O, CH_4), multiple covalent bonding (e.g. O_2, N_2, CO_2), dative covalent (coordiante) bonding (e.g. H_3C^+, NH_4^+, H_2SO_4, HNO_3, oxyacids of chlorine), molecules and ions (e.g. NO_3^-, SO_4^{2-}, CO_3^{2-}).
- The shapes of molecules and ions
  - Explain the factors that determine the shapes of molecules including hybridisation of orbitals.
  - Explain the shapes and bond angles in molecules and ions with up to six electron pairs (including lone pairs) surrounding a central atom e.g. BF_3 (trigonal planar), CH_4 and NH_4^+ (tetrahedral), SF_6 (octahedral), NH_3 (pyramidal), H_2O (non linear), CO_2 (linear).
  - Predict the shapes of molecules and their bond angles for other molecules and ions.
- Polar molecules
  - Define term electronegativity and explain that the atoms of some elements are more electronegative than others.
  - Use the concept of electronegativity to explain that some molecules, e.g. HCl, CH_3Cl, have polar bonds and are permanent dipole.
- Intermolecular forces
  - Describe the origin of intermolecular forces e.g. van der Waals forces (based on induced dipoles e.g. N_2, H_2, O_2), dipole-dipole forces (based on permanent dipoles e.g. HCl and CH_3Cl).
  - Describe hydrogen bonding in molecules such as H_2O, NH_3, HF.
  - Explain, using hydrogen bonding, the anomalous properties of the hydrides of the second period e.g. NH_3, H_2O and HF.
- Metallic bonding
  - Describe the structure of metals in terms of the attraction of positive metal ions to a delocalised 'sea' of electrons.

3.1 INTRODUCTION

Atom rarely exists free. Most of the substances exist in the form of groups of atoms called molecules. A molecule is a small, electrically neutral group or aggregate of atoms. The attractive force which holds together the atoms of a molecule is called a **chemical bond**. Water molecule is a group of two atoms of hydrogen bonded to one atom of oxygen. Similarly, diamond is an aggregate of large number of carbon atoms and sulphur, in solid state, is a cluster of eight atoms bonded together. In nineteenth century, the chemical bond was represented by a line drawn between the symbols of two chemical elements which expressed many chemical facts, but had only qualitative significance with regard to molecular structure. The nature of bond was completely unknown. After the discovery of electron, numerous attempts were made to develop an electronic theory of chemical bond. A satisfactory theory of chemical bond should provide answers to the following questions:

(*i*) Why do atoms combine?

(*ii*) Why do they combine in a definite ratio (*e.g.*, HCl exists but H_2Cl or HCl_2 do not) and sometimes in several ratios (*e.g.*, SO_2 and SO_3)?

(*iii*) Why do molecules and crystals have discrete structures?

Lewis, in 1916 made the first attempt to develop the modern electronic theory of chemical bond.

3.2 MODERN ELECTRONIC THEORY OF VALENCY

A bonded atom is more stable than unbonded atom. Thus, the formation of a chemical bond is accompanied by a decrease in energy of the system, thereby giving it more stability. The study of inert gases of zero group (group 18) has revealed that they are quite stable and do not combine with any other element or with each other under ordinary conditions. The electronic configurations of these inert gases are given in Table 3.1.

Table 3.1: Electronic Configuration of Noble Gases

Symbol	At. No.	Electronic Configuration
He	2	$1s^2$
Ne	10	$1s^2\ 2s^2\ 2p^6$
Ar	18	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Kr	36	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$
Xe	54	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$
Rn	86	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6$

The study of electronic configuration of these stable inert gases become the basis of modern electronic theory of valency. According to this theory:

(*i*) An atom, having eight electrons in its outermost orbit (except He which has two electrons) has no tendency to undergo chemical combination. It is chemically inert.

(*ii*) Every atom (except H, Li and Be) has a tendency to have eight electrons, called octet, in its outermost orbit. In order to attain the stable configuration of the nearest noble gas, an atom loses, gains or shares the electrons to have the *octet. This is called the* **octet rule** *and is the real cause of chemical combination or bonding.*

(*iii*) The valency of an element is the number of electrons gained, lost or contributed for sharing by its atom to attain the stable configuration.

From the electronic theory of valency, it follows that, **chemical bonding** *may be defined as the combination of two or more atoms through rearrangement of electrons in their outermost shells, by sharing or transferring of electrons among themselves, so that all the atoms attain a stable configuration of nearest inert gas.*

3.3 KOSSEL-LEWIS APPROACH

There are number of assumptions to explain the formation of chemical bonds in terms of electrons, but it was only in 1916 that Kossel and Lewis succeeded in giving a satisfactory explanation. Since their theory was based on the electronic concept of atom, it is referred to as *Electronic Theory of Valency*. Whereas Kossel's field of study was largely limited to inorganic compounds, Lewis focused his attention mainly to organic compounds.

The study of inert gases (group 18) suggests that neither they combine chemically with any other element nor among themselves. Their electronic configurations are as follows:

Element	*Atomic No.*	*Electronic Configuration*
Helium	2	2
Neon	10	2, 8
Argon	18	2, 8, 8
Krypton	36	2, 8, 18, 8
Xenon	54	2, 8, 18, 18, 8
Radon	86	2, 8, 18, 32, 18, 8

From the study of electronic configurations of the inert gases, it is clear that inert gases are chemically inactive because they have 8 electrons in their outermost orbit except in case of helium which has 2. Hence, it was suggested that they possess stable electronic configurations. In case of all other elements, the number of electrons in their outermost shell is less than 8 and hence they are chemically reactive. This led to the following conclusion:

The atoms of different elements combine with each other in order to complete their respective octets (i.e. 8 electrons in their outermost shell) or duplet (i.e. outermost shell having 2 electrons in case of H, Li and Be) to attain stable inert gas configuration.

3.4 LEWIS SYMBOLS

In the formation of a molecule, only the outer shell electrons are involved and they are known as **valence electrons**. The inner shell electrons are well protected and are generally not involved in the combination process.

G.N. Lewis introduced simple symbols to denote the valence shell electrons in an atom. The outer shell electrons are shown as dots surrounding the symbol of the atom. These symbols are known as **Lewis symbols** or electron dot symbols. These symbols ignore the inner shell electrons. Examples are:

Significance of Lewis Symbols. The number of dots around the symbol gives the number of electrons present in the outermost shell. This number of electrons helps to calculate the *common valency* of the element. That is why these electrons are called **valence shell electrons**.


G.N. Lewis

The common valency of the element is either equal to the number of dots in the Lewis symbol (if these are ≤ 4) *or 8 minus the number of dots (if these are* > 4).

For example, Li, Be, B and C have valencies 1, 2, 3 and 4 respectively, *i.e.*, equal to the number of dots whereas the valencies of N, O, F and Ne are 3, 2, 1 and 0 respectively, *i.e.*, 8 minus the number of dots.

3.5 TYPES OF CHEMICAL BONDS

On the basis of electronic theory, the following types of combinations are possible between atoms:

(i) **Electrovalent or ionic bond** which involves the *transfer of one or more electrons* from one atom to another.

(ii) **Covalent bond** which involves *mutual sharing of electrons* between two atoms contributing equal number of electrons.

(iii) **Coordinate bond** which also involves sharing of *electrons* by two atoms but the *shared pair is contributed by only one of the two atoms.*

Each one of these bonds is discussed below:

3.6 ELECTROVALENT BOND OR IONIC BOND

Atoms are electrically neutral. If an atom loses electrons, it will become positively charged and is called a **cation**. On the other hand, the atom which gains electrons will become negatively charged and is called an **anion**. The cation and anion are held by electrostatic force of attraction which is known as the *ionic* or *electrovalent bond.* It is shown in Fig. 3.1.

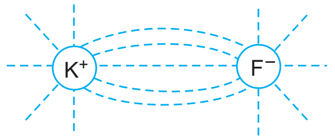


Fig. 3.1: *Electrostatic forces in KF*

An **electrovalent** bond involves the complete transference of one or more electrons from one atom to another dissimilar atom so that both the atoms acquire stable inert gas configuration. Combination of sodium and chlorine to form sodium chloride is a common example of electrovalent bond.

In the examples that follow, the electrons possessed by the metal in the outermost orbit have been represented by a cross (x), while those possessed by the non-metal have been represented by dot (•).

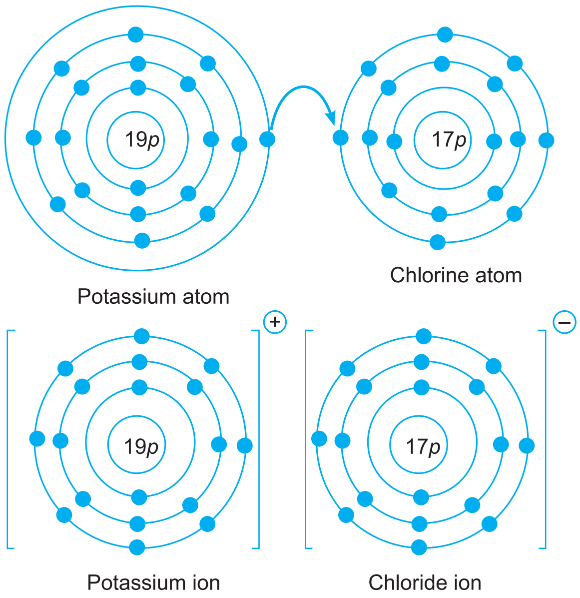


Fig. 3.2: *Ionic bond between K^+ and Cl^-*

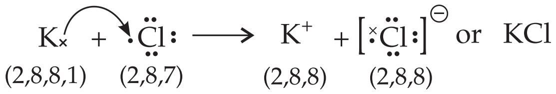
Formation of Potassium Chloride (KCl)

The electronic configuration of potassium (At. No. 19) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$. It loses one electron from outermost shell, *i.e.*, $4s$ and attains the configuration of inert gas argon ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$). The electrons of potassium are shown in Fig. 3.2.

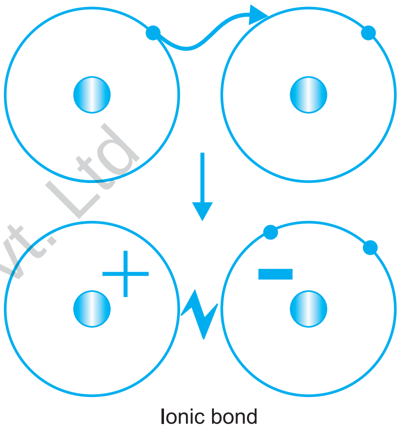
On the other hand, the electronic configuration of chlorine (At. No. 17) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. It gains one electron and attains the configuration of argon, *i.e.*, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

In this way, by the transfer of one electron from potassium to chlorine, both the atoms attain stable configuration. Potassium atom is converted into cation (written as K^+) while chlorine atom is converted into anion (written as Cl^-), the oppositely charged ions are held by electrovalent bond. The formation of potassium chloride can easily be depicted by using **Electron**

Dot Symbols or **Lewis Symbols** in which only the outer shell electrons are shown as dots surrounding the symbols of the elements. In terms of Lewis symbols, the reaction between potassium and chlorine, can be written as shown in Fig. 3.2.



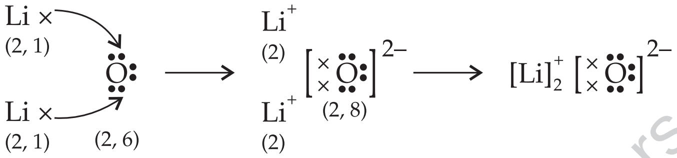
Some other examples for the formation of ionic bond are given below. The electrons possessed by the metal in the outermost shell are represented by a cross (x) and those possessed by the non-metal in the outermost orbit are represented by a dot (•).



Representation of an ionic bond

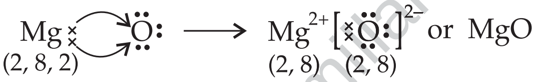
Formation of Lithium Oxide (Li_2O)

Lithium (At. No. 3) has electronic configuration $1s^2\ 2s^1$, while oxygen (At. No. 8) has electronic configuration $1s^2\ 2s^2\ 2p^4$. Thus, lithium readily gives the electron in $2s$ orbital to attain stable configuration (duplet). Oxygen is short of two electrons from the octet. It has a tendency to gain two electrons to complete the octet. Thus, two lithium atoms lose one electron each and these two electrons are gained by oxygen. Thus, lithium and oxygen complete their *duplet* and *octet* respectively. This is represented as under:



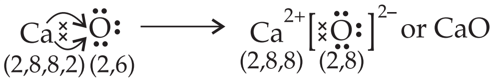
Formation of Magnesium Oxide (MgO)

Magnesium (At. No. 12) has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2$ while oxygen (At. No. 8) has electronic configuration $1s^2\ 2s^2\ 2p^4$. An examination of the electronic configurations reveals that magnesium has two electrons more and oxygen has two electrons less than octet configuration. Thus, magnesium readily loses two electrons and oxygen readily gains two electrons to attain octet structure. This is represented as under:



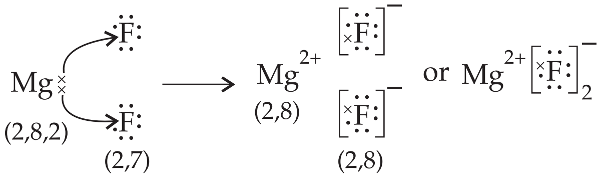
Formation of Calcium Oxide (CaO)

Calcium (At. No. 20) has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ while oxygen (At. No. 8) has electronic configuration $1s^2\ 2s^2\ 2p^4$. In order to complete octet, calcium loses two electrons and oxygen gains two electrons. This is represented as under:



Formation of Magnesium Fluoride (MgF_2)

Magnesium having at. no. 12 (electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2$) loses two electrons shown as ×, one each to two fluorine atoms (electronic configuration $1s^2\ 2s^2\ 2p^5$)



PROBLEMS FOR PRACTICE

Explain the formation of ionic bond in the case of the following compounds:

(*i*) Barium chloride

(*ii*) Sodium sulphide

(*iii*) Aluminium oxide

Factors Influencing the Formation of Ionic Compounds

Following are the important factors which favour the formation of ions:

(*i*) **Appropriate number of valence electrons.** The atom A which is converted into the cation A^+ should possess 1, 2 or 3 valence electrons while the atom B which is converted into anion, B^- should have 5, 6 or 7 valence electrons. The elements of groups 1, 2 and 13 satisfy this condition for atom A and those of groups 15, 16 and 17 satisfy this condition for atom B. It is energetically not favourable to lose or gain more than three electrons.

(*ii*) **Low ionisation energy of the metal atom.** Ionisation energy is the minimum amount of energy required to remove the most loosely bound electron from a neutral isolated gaseous atom. Thus:

$$\underset{\substack{\text{Gaseous}\\ \text{neutral atom}}}{A(g)} \quad + \quad \underset{\text{(Ionisation energy)}}{\text{Energy required}} \longrightarrow \underset{\text{Cation}}{A^+(g)} \quad + \quad e^-$$

Obviously, *if an atom has low ionisation energy, it will be easier for it to lose the electron and hence, get converted into a cation. Thus, low ionisation energy of the metal favours the formation of cation.*

(*iii*) **High electron affinity of the non-metal.** Electron affinity is the amount of energy released when an electron is added to a neutral isolated gaseous atom. Thus:

$$\underset{\substack{\text{Gaseous}\\ \text{neutral atom}}}{B(g)} \quad + \quad e^- \longrightarrow \underset{\text{Anion}}{B^-(g)} \quad + \quad \underset{\text{(Electron affinity)}}{\text{Energy released}}$$

Release of energy is always favoured by a system, therefore, the atoms with high electron affinity will favour the formation of anions.

(*iv*) **High lattice energy of the ionic compound formed.** The energy released when one gram mole of a crystal is formed from its gaseous ions is called the lattice energy of the crystal. Thus:

$$\underset{\text{1 mole}}{A^+(g)} \quad + \quad \underset{\text{1 mole}}{B^-(g)} \longrightarrow \underset{\text{1 mole}}{A^+B^-\ \text{(crystal)}} \quad + \quad \underset{\text{(Lattice energy)}}{\text{Energy released}}$$

Higher the value of lattice energy of a crystal, the greater is the ease of its formation and hence, greater is the stability of the ionic crystal.

For lattice energy to have a high value, the electrostatic force of attraction between the constituent ions of the ionic compound should be high. According to Coulomb's law, the force of attraction (F) between two oppositely charged ions having charges equal to q_1 and q_2 and separated by a distance equal to d is given by:

$$F = \frac{q_1 q_2}{d^2} = \frac{q_1 q_2}{(r_A^+ + r_B^-)^2}$$

d is equal to the sum of the radii of the positive and negative ions (r_A^+ and r_B^- respectively). From this equation, it is clear that to have a large value of force of attraction (or lattice energy), the following two conditions should be satisfied.

(*a*) *The electric charge on the ions* (*i.e.,* q_1 *and* q_2) *should be large.* For example, the force of attraction between the doubly charged Mg^{2+} ion and the doubly charged O^{2-} ion in $Mg^{2+}O^{2-}$ ionic crystal is four times as much as between monovalent Na^+ and Cl^- ions in Na^+Cl^- crystal assuming that the distance (*d*) between the ions in both the ionic compounds is the same. Consequently, MgO is more stable than NaCl.

(*b*) *As d is in the denominator in the above equation, it should be small, i.e., the cation and the anion constituting the ionic compound should be small in size.* Thus, for a given anion, the smaller the radius of the cation, the greater is the strength of the ionic bond. For example, since Na^+ ion is smaller than K^+ ion, the force of attraction between Na^+ and Cl^- ions in Na^+Cl^- ionic crystal is more than that between K^+ and Cl^- ions in K^+Cl^- ionic crystal. Thus, the lattice energy of Na^+Cl^- is higher than that of K^+Cl^-. Consequently, Na^+Cl^- compound is formed more easily than K^+Cl compound or Na^+Cl^- is more stable than K^+Cl^-.

Similarly, for a given cation, the smaller the radius of the anion, the greater is the strength of the ionic bond or the greater is the stability of the ionic compound.

(*v*) Electronegativity difference of A and B. Atoms A and B will form an ionic bond, if they have sufficient electronegativity difference. In fact, a difference of 2 or more is necessary for the formation of an ionic bond between atoms A and B. For example, difference in electronegativities of Na and Cl is 2.1 (Na = 0.9, Cl = 3.0). Therefore, Na and Cl will form an ionic bond.

Formation of Ionic Bonds and Periodic Table

The relative tendency of the atoms to turn into cations and anions decides their position in the periodic table. Conversely, from the position of an element in the periodic table, we can assess its tendency to change into cation or anion. The elements having *low ionisation energies, i.e., elements of groups 1 and 2 have a strong tendency to form cations.* The elements of groups 16 and 17 having *high electron affinities have a strong tendency to turn into anions.*

Thus, the binary compounds having ionic bonding are most readily formed by the elements of groups 1 and 2 with those of groups 16 and 17.

3.7 ELECTROVALENCY

Electrovalency *of an element is equal to the number of electrons lost by an atom of that element in forming a positive ion or gained by it in forming a negative ion to attain the noble gas configuration in their outermost shell.* The elements which lose electrons show positive electrovalency while the elements which gain electrons show negative electrovalency. For example, in the formation of NaCl, the electrovalency of Na is equal to +1 while that of Cl is equal to –1. An element which gains or loses *one, two, three, four, ...,* etc., electrons is called *mono* (*or uni*) *valent, di* (*or bi*) *valent, trivalent, tetravalent, ..., etc., element.* Some examples are given below:

Na, K, Cl, F ...	Monovalent elements
Mg, Ca, O, S, ...	Divalent elements
Al, B, N, ...	Trivalent elements
C, Si, ...	Tetravalent elements

3.7.1 Variable Electrovalency

There are some elements which show different electrovalencies in different electrovalent compounds. This phenomenon is called variable electrovalency. It is due to the following two reasons:

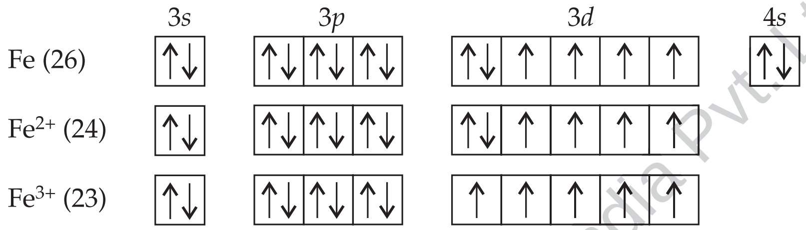
(*i*) **Unstable electronic configuration of the core.** The outermost levels of the elements like Fe, Co, Ni, Cu, etc., contain only one or two electrons. When these electrons are lost, the remaining part which is called the **core** or **kernel**, is unstable and, hence, some more electrons from the core can be further lost. For example:

(*a*) The electrovalency of iron equal to +2 in ferrous compounds and equal to +3 in ferric compounds can be explained as follows:

Fe (26) $\longrightarrow$ 2, 8, 14, 2 or 2, 8, $3s^2p^6d^6$, $4s^2$

Fe^{2+} (24) $\longrightarrow$ 2, 8, 14 or 2, 8, $3s^2p^6d^6$

Orbital diagrams of Fe, Fe^{2+} and Fe^{3+} in the last two shells are given below:



$3s^2p^6d^5$ configuration is more stable than $3s^2p^6d^6$ configuration and hence, Fe^{2+} loses one more electron to forms Fe^{3+} ion.

Fe^{3+} (23) $\longrightarrow$ 2, 8, 13 or 2, 8, $3s^2p^6d^5$

Electronic configurations with half-filled and fully-filled orbitals are more stable than other electronic configurations. There are five *d*-orbitals and if each of them contains one electron, the electronic configuration containing five electrons in *d*-orbitals will be more stable than that containing six electrons. In fact, there is not much energy difference between 4*s* and 3*d* electrons. If only 4*s* electrons are lost, we get Fe^{2+} ions. If two 4*s* and one 3*d* electrons are lost, we get Fe^{3+} ions.

(*b*) An increase in the nuclear charge tends to prevent the removal of electrons from a lower energy level. For example, Co (Z = 27) atom forms Co^{3+} ion with great difficulty because 3*d* electrons are more firmly retained by cobalt nucleus with positive charge equal to +27 which is one unit higher than that of iron nucleus (= +26).

Co(27) $\longrightarrow$ 2, 8, 15, 2 or 2, 8, $3s^2p^6d^7$, $4s^2$

Co^{2+}(25) $\longrightarrow$ 2, 8, 15 or 2, 8, $3s^2p^6d^7$

Co^{3+}(24) $\longrightarrow$ 2, 8, 14 or 2, 8, $3s^2p^6d^6$

(*c*) The variable electrovalency of Cu equal to +1 (cuprous ion) and +2 (cupric ion) can be explained by the electronic configurations given below:

Cu(29) $\longrightarrow$ 2, 8, 18, 1 or 2, 8, $3s^2p^6d^{10}$, $4s^1$

Cu^{+}(28) $\longrightarrow$ 2, 8, 18 or 2, 8, $3s^2p^6d^{10}$

Cu^{2+}(27) $\longrightarrow$ 2, 8, 17 or 2, 8, $3s^2p^6d^9$

Cu^{+} (cuprous ion) is preferred because it gives rise to more stable (fully-filled *d*-orbitals) electronic configuration. But if sufficient energy is available under the reaction conditions, there is also the possibility of formation of Cu^{2+} (cupric ions).

(*ii*) **Inert electron pair effect.** Some elements of *p*-block having ns^2p^{1-4} valency shell configuration (*e.g.*, Ga, In, Tl, Ge, Sn, Pb, As, Sb, Bi, Te and Po) show variable electrovalency. These variable electrovalencies differ from each other by two units. The following examples illustrate:

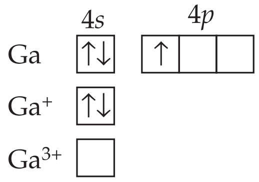
(*a*) *Electrovalencies of Ga = +1 and +3.* In chemical combinations, Ga (Z = 31) atom which has $4s^2p^1$ as valence-shell configuration initially loses its $4p^1$ electron, forming Ga^+ ion and, thus, shows an electrovalency of +1. In Ga^+ ion, $4s^2$ electron pair is called **inert electron pair** and does not participate in bonding. If sufficient energy is available, the $4s^2$ electron pair participates in bonding. Both the electrons of $4s^2$ pair are lost by Ga^+ ion and Ga^{3+} ion is formed. Thus, the variable electrovalencies of +1 and +3 of Ga atom are explained.

$$Ga\ (31) \longrightarrow 2, 8, 18, 3 \text{ or } 2, 8, 18, 4s^2p^1$$

$$Ga^+\ (30) \longrightarrow 2, 8, 18, 2 \text{ or } 2, 8, 18, 4s^2$$

$$Ga^{3+}\ (28) \longrightarrow 2, 8, 18 \text{ or } 2, 8, 3s^2p^6d^{10}$$

Orbital diagrams of Ga, Ga^+ and Ga^{3+} in the last shell are given below.



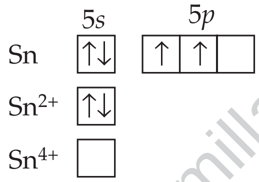
(*b*) *Electrovalencies of Sn = +2 and +4.* These are explained as follows:

$$Sn(50) \longrightarrow 2, 8, 18, 18, 4 \text{ or } 2, 8, 18, 18, 5s^2p^2$$

$$Sn^{2+}(48) \longrightarrow 2, 8, 18, 18, 2 \text{ or } 2, 8, 18, 18, 5s^2$$

$$Sn^{4+}(46) \longrightarrow 2, 8, 18, 18 \text{ or } 2, 8, 18, 4s^2p^6d^{10}$$

Orbital diagrams of Sn, Sn^{2+} and Sn^{4+} in the last shell are given below.



3.7.2 Formation of Ionic Bond is Accompanied by Decrease in Energy

Let us consider the formation of one gram molecule of solid sodium chloride, NaCl(*s*), from one mole of sodium and half mole of chlorine. The following steps are involved:

(*i*) **Sublimation of Na(s) to Na(g).** *In this step, one mole of Na(s) absorbs energy equal to its sublimation energy and changes to gaseous state, Na(g). Energy absorbed in the sublimation of Na(s) to Na(g) is shown at the left hand side of the equation.*

$$Na(s) + \underset{(108.5\ \text{kJ/mole})}{\text{Sublimation energy}} \longrightarrow Na(g)$$

(*ii*) **Dissociation of 1/2 Cl_2(g) molecules to Cl(g) atom.** *In this step, half a mole of $Cl_2(g)$ absorbs energy equal to the half of the dissociation energy of $Cl_2(g)$ and is converted into Cl(g).*

$$1/2\ Cl_2(g) + \text{Dissociation energy} \longrightarrow Cl(g)$$

$$(= 243\ \text{kJ/mole of } Cl_2(g))$$

$$(= 121.5\ \text{kJ/mole of } Cl(g))$$

***(iii)* Ionisation of Na(g) to Na^+(g).** Each Na(*g*) formed in step (*i*) *absorbs* energy equal to its *ionisation energy* (or ionisation potential) and loses its outermost electron to form $Na^+(g)$.

$$\underset{(= 496 \text{ kJ})}{Na(g) + \text{Ionisation energy}} \longrightarrow Na^+ (g) + e^-$$

***(iv)* Conversion of Cl(g) into Cl^- (g).** $Cl^-(g)$ atom adds the electron given out by Na(*g*) to form Cl(*g*). In this process, Cl(*g*) *releases* energy equal to its *electron affinity*. Energy *released in the reaction is shown at the right hand side of the equation.*

$$Cl(g) + e^- \longrightarrow Cl^- (g) + \underset{(= 394 \text{ kJ mole})}{\text{Electron affinity}}$$

***(v)* Combination of Na^+ (g) and Cl^- (g) ions to form NaCl(s).** This is the final step in which Na^+ (*g*) formed in step (*iii*) and Cl^- (*g*) obtained in step (*iv*) combine together to form one mole of NaCl(*s*). In this step, *energy equal to lattice energy* (or crystal energy) *of NaCl is released.*

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) + \underset{(= 760 \text{ kJ/mole of NaCl})}{\text{Lattice energy}}$$

Now,

$$\begin{aligned} \text{Total energy absorbed} &= 108.5 + 121.5 + 496 \\ &= 726 \text{ kJ} \end{aligned}$$

$$\text{and} \quad \begin{aligned} \text{Total energy released} &= 394 + 760 \\ &= 1154 \text{ kJ.} \end{aligned}$$

Since total energy released is greater than total energy absorbed, in the formation of NaCl, ionic crystal energy will be released equal to (1154 – 726)kJ or 428 kJ/mole of NaCl.

Hence, the formation of an ionic bond in NaCl ionic solid is followed by the release of energy which produces a very strong bond.

3.8 GENERAL PROPERTIES OF IONIC COMPOUNDS

The ionic compounds possess the following properties:

1. **Physical state.** These compounds usually exist in the solid state.
2. **Solubility.** Ionic compounds are soluble in water which is polar in nature and has high dielectric constant. It is due to the reason that the polar solvent interacts with the ions of the crystals and further, the high dielectric constant of the solvent cuts off the force of attraction between these ions. Furthermore, the ions may combine with the solvent to liberate energy called the hydration energy which is sufficient to overcome the attractive forces between the ions.

   Non-polar solvents like carbon tetrachloride, benzene, etc., having low dielectric constants do not cut attractive forces between the ions and are not capable of dissolving ionic solids. Hence, ionic solids are soluble in polar solvents but insoluble in non-polar solvents.

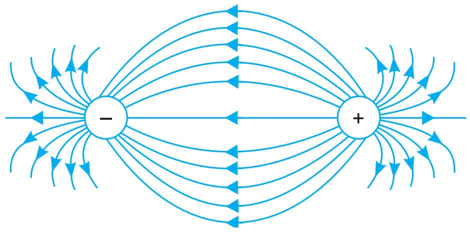


Fig. 3.3: *Dissolution of an ionic solid in water*

3. **Ionic reactions.** The reactions of the ionic compounds are, in fact, the reactions between the ions produced in solution. As the oppositely charged ions combine quickly, these reactions are, therefore, quite fast. For example,

$$Na^+Cl^-(aq) + Ag^+NO_3^-(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

   Precipitation of silver chloride takes place in a fraction of second.

4. **High melting and boiling points.** Ionic compounds possess high melting and boiling points. This is because ions are tightly held together by strong electrostatic forces of attraction and, hence, a huge amount of energy is required to break the crystal structure.

5. **Crystal structure.** X-ray analysis of the ionic compounds shows that they exist as ions and not as molecules. These ions are arranged in a regular pattern to form a lattice.

   Crystal structure, however, depends upon the sizes and charges of the ions. For example, in case of sodium chloride, each sodium ion is surrounded by six chloride ions and each chloride by six sodium ions, giving rise to octahedral crystal structure.

6. **Electrical conductivity.** Ionic compounds are good conductors of electricity in solution or in the molten state. In solution or molten state, their ions are free to move. As the ions are charged, they are attracted towards electrodes and, thus, act as carriers of electric current in the electrochemical processes.

7. **Highly brittle.** Ionic solids are highly brittle. If a lattice external force is applied on ionic crystals, they are easily broken. This property is called **brittleness** and can be explained as follows:

   Ionic solids are composed of parallel layers which contain cations and anions in alternate positions so that the opposite ions in the various parallel layers lie over each other. When a little external force is applied on an ionic crystal, one layer of ions slides a bit over the other layer along a plane. As a result of sliding, the like ions come close to each other and, hence, begin to repel each other (Fig. 3.4). Consequently, the application of a little external force brings about repulsion between the two layers and the ionic solid breaks.

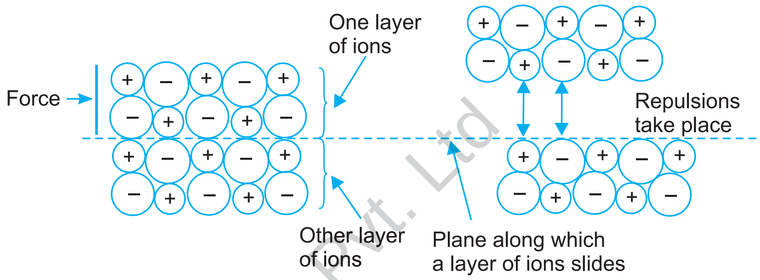


Fig. 3.4: *Explanation of high brittleness of ionic solids*

8. **High density.** The electrostatic force of attraction between the cations and anions in an ionic crystal brings these ions very close to one another. This decreases the volume of the crystal and consequently, the ionic crystals have *high density*.

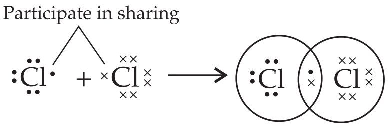
9. **They do not exhibit isomerism.** Ionic bond involving electrostatic force of attraction between opposite ions is non-rigid and non-directional. The ionic compounds are, therefore, incapable of exhibiting isomerism.

10. **They show isomorphism.** Ionic solids made up of ions with identical electronic configurations exist in similar crystalline form. This phenomenon is called **isomorphism**. Two such pairs of isomorphous compounds are (*a*) NaF and MgO, and (*b*) $CaCl_2$ and K_2S.

(*a*)	Sodium	fluoride	and	Magnesium	oxide
	Na^+	F^-		Mg^{2+}	O^{2-}
	(2, 8)	(2, 8)		(2, 8)	(2, 8)
(*b*)	Calcium	chloride	and	Potassium	sulphide
	Ca^{2+}	Cl^-		K^+	S^{2-}
	(2, 8, 8)	(2, 8, 8)		(2, 8, 8)	(2, 8, 8)

3.9 COVALENT BOND – LEWIS CONCEPT

The formation of ionic bond or ionic compounds is valid for the combination of two atoms – *one which attains stable configuration by losing electrons, while other by gaining electrons.* However, there may be a case where both the atoms tend to gain electrons for achieving the stable configuration, *e.g.*, two similar H atoms combine to form H_2 molecule or two dissimilar atoms H and Cl combine to form HCl. In such cases, gain or loss of electrons is not possible. According to Lewis, in such cases atoms share pairs of electrons to complete their octets, *e.g.*,



The shared pair of electrons counts towards both the atoms to have their octet complete. When two atoms are held together by shared pair of electrons, the two are said to have a covalent bond between them.

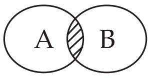
3.9.1 Types of Bonds

We come across the following types of bonds in the formation of molecules from constituent atoms.

Single bond: When two atoms share one pair of electrons, a single bond is said to be formed between them. Such a bond is formed by the overlap of the orbitals along the internuclear axis. We call it a *sigma* (σ) *bond*. A single bond formation between two atoms may be represented as

$$A{\times} + {\bullet}B \longrightarrow A \overset{\times}{\bullet} B \longrightarrow A - B$$

Lewis representation

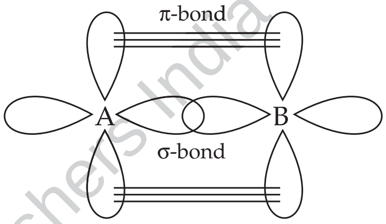


Orbital representation

Double bond: When two atoms share two pairs of electrons between them, a double bond is said to be formed between them. Out of the two bonds, one bond is *sigma* (σ) which is formed by the overlap of orbitals along the internuclear axis and the second bond is *pi* (π) which is formed by the lateral overlap of *p*-orbitals of the two atoms. A double bond between two atoms A and B may be represented as

$$A\overset{\times}{\underset{\times}{}} \quad {:}B \longrightarrow A{=}B$$

Lewis representation

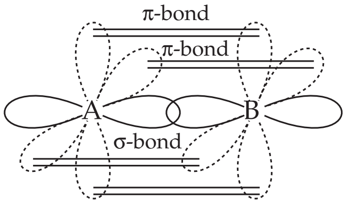


Orbital representation

Triple bond: When two atoms share three pairs of electrons between them, a triple bond is said to be formed between them. Out of the three bonds, one bond is *sigma* (σ) which is formed by the overlap of orbitals along the internuclear axis and two bonds are *pi* (π) bonds which are formed by the lateral overlap of two sets of orbitals at right angles to each other.

$$A\overset{\times}{\underset{\times}{\times}} \quad \vdots B \longrightarrow A \equiv B$$

Lewis representation



Orbital representation

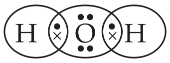
3.9.2 Examples of Single Bonds

Formation of Hydrogen Molecule

$H{\bullet} + {\times}H \longrightarrow H\overset{\bullet}{\times}H$ or H – H (Hydrogen tends to have two electrons in its outermost orbit)

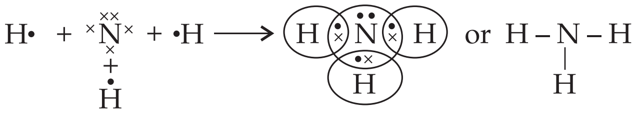
Formation of Water Molecule

$$H{\bullet} + \overset{\times\times}{\underset{\times\times}{{\times}O{\times}}} + {\bullet}H \longrightarrow$$



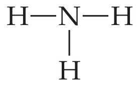
or H – O – H

Formation of Ammonia Molecule



As is seen, oxygen and nitrogen have six and five electrons respectively in their outermost orbits and share 2 and 3 electrons respectively with hydrogen. The remaining 4 electrons of oxygen and 2 of nitrogen which are not involved in sharing are called **lone pairs** or **unshared pairs**.

While showing covalent bonding in a molecule, the shared pairs are shown by a line drawn between two atoms for each shared pair. Lone pairs are not shown, *e.g.*,

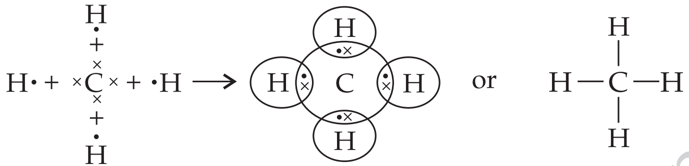


Ammonia

H—O—H

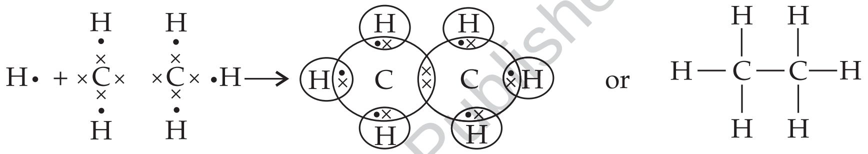
Water

Formation of Methane



Methane

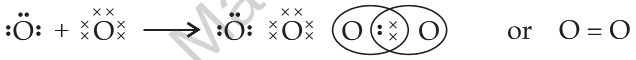
Formation of Ethane



Ethane

3.9.3 Example of Double and Triple Bonds

Let us consider the **formation of O_2** molecule from two atoms of oxygen. Oxygen atom has six electrons in its outermost orbit and require the sharing of two electrons. This can be achieved as follows:



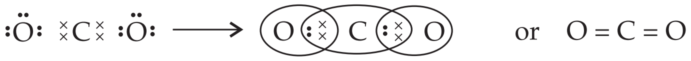
In this way, two oxygen atoms are held by two shared pairs of electrons. These shared pairs of electrons are shown by two lines, *i.e.*,

$$O = O$$

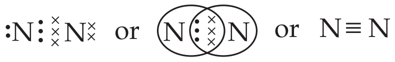
Such a bond is called a **double bond**.

Octet of both oxygen atoms is completed in this way. Two pairs of electrons mean four electrons. These four electrons in oxygen molecules count towards the octet of both oxygen atoms.

In **carbon dioxide**, the four electrons of carbon are shared with two electrons of each oxygen atom.

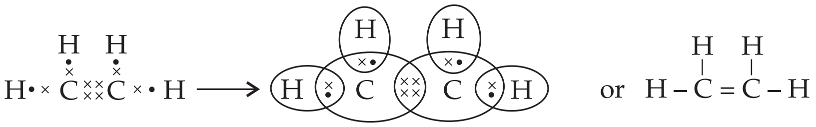


Similarly, if three electrons are shared between atoms, a *triple bond* is formed, *e.g.*, in N_2 molecule.

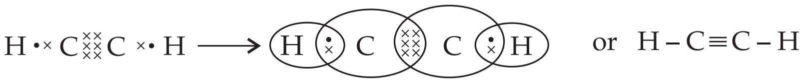


The total number of electrons shared by an atom of an element in a covalent compound is known as its covalency.

Formation of ethylene (C_2H_4) and acetylene (C_2H_2) molecules. In C_2H_4, each C-atom achieves the stable octet by sharing its four electrons with two H-atoms and the other C-atom. In this way each C-atom forms two single bonds with two H-atoms and one double bond with the other C-atom.



In C_2H_2, each C-atom forms one single bond with one H-atom and one triple bond with the other C-atom.



3.10 COVALENCY

The valency of an element in a covalent compound is called its covalency. *Covalency of an element in a covalent compound is equal to the number of electrons shared by one atom of it with other atoms.* Consequently, *the covalency of an element in a covalent compound is equal to the number of covalent bonds formed by one atom of it with other atoms.* Thus, the covalency of Cl in Cl_2 molecule = 1, of H in H_2 and H_2O molecule = 1, of O in O_2 and H_2O molecule = 2, of N in N_2 molecule = 3, and of C in CH_4 molecule = 4.

3.10.1 Variable Covalency

It has been observed that the elements containing vacant *d*-orbitals (*e.g.*, P, S, Cl etc.) show different values of covalency in different covalent compounds. This phenomenon is called variable covalency. Examples of elements showing different covalencies are given in Table 3.2.

Table 3.2: Variable Covalencies of Elements in different Compounds

Element	Different Covalencies	Examples of Compounds
Phosphorus	3	PCl_3
	5	PCl_5
Sulphur	2	SCl_2
	4	SF_4
	6	SF_6
Halogens (other than fluorine)	1	ICl
	3	ICl_3
	5	IF_5
	7	IF_7

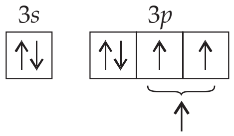
3.10.2 Cause of Variable Covalency

Variable covalency of an element arises due to the increase in the number of unpaired electrons in the different excited states of the atom. For example, the covalencies of S, P and Cl atoms can be explained as follows:

(*i*) Variable covalency of S-atom (2, 4, 6).

(*a*) *Covalency of 2.* Normal configuration of the valence shell of sulphur atom is $3s^2\ 3p^2_x\ 3p^1_y\ 2p^1_z$. Sulphur atom having this configuration is said to be in the *ground state* or *normal state.*

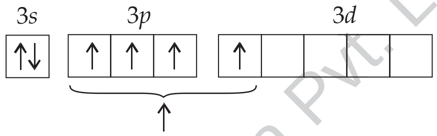
Sulphur atom in its ground state $(3s^2\,3p_x^2\,3p_y^1\,3p_z^1)$



Two unpaired electrons explain covalency of 2

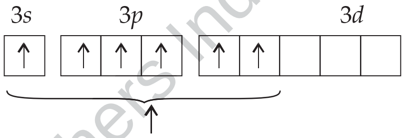
(*b*) *Covalencies of 4 and 6.* When sulphur atom forms covalent bonds with other atoms, one 3*p* electron or both 3*s* and 3*p* electrons jump to the vacant 3*d*-orbital. Now sulphur atom is said to be in the **excited state**. When only 3*p* electron jumps, we get *four* unpaired electrons which explain the covalency of 4 for sulphur atom. However, when both 3*s* and 3*p* electrons jump, we get *six* unpaired electrons which account for the covalency of 6 for sulphur atom.

Sulphur atom in its first excited state $(3s^2\,3p_x^1\,3p_y^1\,3p_z^1\,3d^1)$



Four unpaired electrons explain covalency of 4

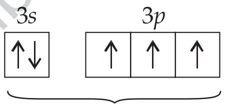
Sulphur atom in its second excited state $(3s^1 3p_x^1\,3p_y^1\,3p_z^1\,3d^2)$



Six unpaired electrons explain covalency of 6

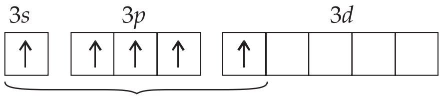
(*ii*) Variable covalencies of phosphorus. Variable covalency of phosphorus (3, 5) is explained as under:

Phosphorus atom in its ground state $(3s^2 3p_x^1\,3p_y^1\,3p_z^1)$



Three unpaired electrons explain covalency of 3

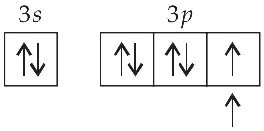
Phosphorus atom in its excited state $(3s^1 3p_x^1\,3p_y^1\,3p_z^1\,3d^1)$



Five unpaired electrons explain covalency of 5

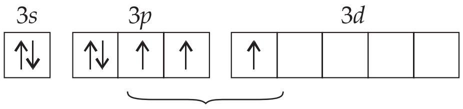
(*iii*) Variable covalency of chlorine. Variable covalency of chlorine (1, 3, 5 and 7) is explained as under:

Chlorine atom in its ground state $(3s^2\,3p_x^2\,3p_y^2\,3p_z^1)$



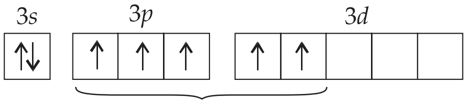
One unpaired electron explains covalency of 1

Chlorine atom in its first excited state $(3s^2\,3p_x^2\,3p_y^1\,3p_z^1\,3d^1)$



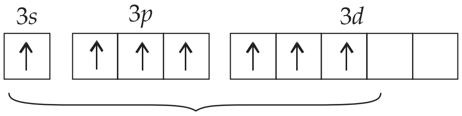
Three unpaired electrons explain covalency of 3

Chlorine atom in its second excited state
($3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^2$)



Five unpaired electrons explain covalency of 5

Chlorine atom in its third excited state
($3s^1\ 3p_x^1\ 3p_y^1\ 3p_z^1\ 3d^1 3d^1 3d^1$)



Seven unpaired electrons explain covalency of 7

Maximum number of covalent bonds formed by the atom of an element is called its maximum covalency. For example, the maximum covalencies of P, S and Cl atoms are 5, 6 and 7 respectively.

3.10.3 Formation of Covalent Bonds and Periodic Table

Covalent bonds are formed between the same or different kinds of atoms which should have high electronegativity, since the elements with high electronegativity do not ionise and have an equal attraction for electrons to complete their octets. Such elements are found in right-hand portion of the periodic table.

Factors favouring the formation of covalent compounds

Following are the main factors which favour the formation of covalent bond:

(*i*) **High Ionisation Energy.** The atoms which have high value of ionisation energy cannot easily lose electrons, to form cations. Thus, these elements cannot form ionic bonds. Such elements form covalent bonds between them.

(*ii*) **Comparable Electron Affinities.** For covalent bonding, the two atoms must have equal attraction for electrons. In other words, the combining atoms must have comparable electron affinities.

(*iii*) **Number of Valence Electrons.** Each of the two atoms should have 5, 6 or 7 valence electrons (H-atom has only one electron) so that both the atoms achieve the stable octet by sharing 3, 2 or 1 electron-pair. The nonmetals of groups 15, 16 and 17 respectively satisfy this condition.

(*iv*) **Equal Electronegativity.** Both atoms should have comparable electronegativities so that the transfer of electron(s) from one atom to the other may not take place. When the electronegativity of both the atoms is equal, sharing of electron pair occurs and covalent bond is formed.

PROBLEMS FOR PRACTICE

Draw the Lewis structures of following molecules:

(*i*) PCl_3 (*ii*) CCl_4 (*iii*) H_2S

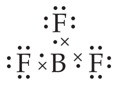
3.11 VIOLATION OF OCTET RULE (DEVIATION FROM OCTET RULE)

(*a*) **Atoms having less electrons than inert gas configuration**

According to octet rule, the elements whose atoms have 1, 2 or 3 electrons in their outermost orbits, should never form covalent bonds because even after sharing all the valence electrons, they cannot attain the octet state. But there are some compounds known, in which the octet is not completed, *e.g.*, BF_3 and $BeCl_2$.

Boron (At. No. 5) has three and beryllium (At. No. 4) has two electrons respectively in their valence shells which are shared with F and Cl atoms.

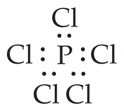
BF_3



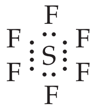
$BeCl_2$

(*b*) **Atoms having more electrons than inert gas configuration**

In PCl_5 and SF_6, phosphorus and sulphur have 10 and 12 electrons respectively in their valence shells. Phosphorus which has five and sulphur which has six electrons in their valence shells, share them with same number of Cl and F atoms respectively.



PCl_5 (10 electrons around P)



SF_6 (12 electrons around S)

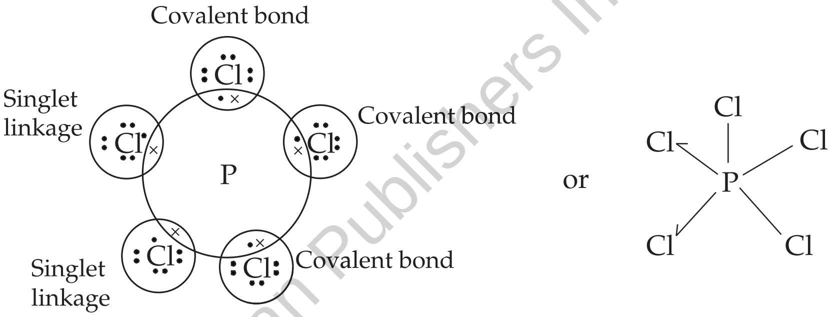
In the molecule of OsF_8, the central atom Os shares eight electrons with eight fluorine atoms. Thus, osmium is surrounded by 2 × 8 = 16 electrons.

3.11.1 Explanation of the Failure of Octet Rule Chemical Bonding

The failure of octet rule in the formation of covalent molecules as mentioned above is explained in terms of Sugden's concept of singlet linkage and Sidgwick's concept of maximum covalency.

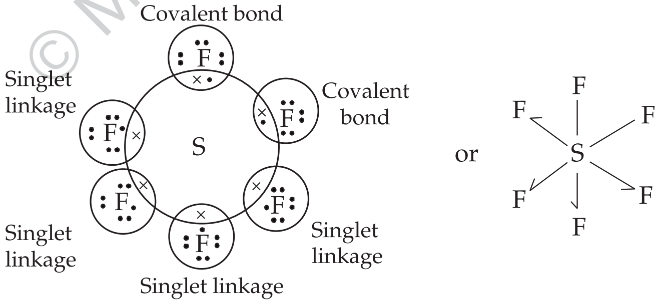
(*i*) **Sugden's Concept of Singlet Linkage.** According to Sugden, the central atom of the molecules like PCl_5, SF_6 etc. maintains its octet. The central atom is linked with some of the combining atoms by *single-electron bonds*, called **singlet linkages** while the remaining atoms are linked by the normal two-electron covalent bonds. The singlet linkage is a special type of bond which is formed by the *one-sided sharing of only one electron* between the central atom and the combining atoms. This bond is also called **single-electron linkage**, **half bond** or simply **singlet**. A singlet-electron linkage is represented by a half arrow (⇀) with its head pointing from the donor towards the acceptor.

On the basis of this concept, we can say that phosphorus atom in PCl_5 molecule is linked with three Cl atoms by three covalent bonds and with each of the remaining two chlorine atoms, it is linked by a singlet linkage. Thus, the structure of PCl_5 can be shown as follows:



Singlet linkage is weaker than a covalent bond and this explains why PCl_5 readily dissociates into PCl_3 and Cl_2.

In SF_6 molecule, sulphur atom is linked with two F-atoms by two covalent bonds and with four F-atoms by four singlet linkages as shown below:



(*ii*) **Sidgwick's concept of maximum covalency.** According to this concept, it is not necessary for an element to have a maximum covalency of four, or to be surrounded by 4 × 2 = 8 electrons for its stability. The covalency of an element may exceed four and the octet can be exceeded. According to Sidgwick, the maximum covalency of an element depends on the period in which the element concerned is located. For hydrogen (first period with $n = 1$) covalency is 2, for the element of 2nd period with $n = 2$ (Li to F) it is 4, for the elements of 3rd ($n = 3$) and 4th ($n = 4$) periods it is equal to 6 and for those in higher periods ($n > 4$) it is equal to 8. Consequently, maximum number of electrons being shared for the elements mentioned above is equal to $2 \times 2 = 4$, $4 \times 2 = 8$, $6 \times 2 = 12$ and $8 \times 2 = 16$ respectively. Thus, we can explain the formation of five covalent bonds by phosphorus in PCl_5, six covalent bonds by sulphur in SF_6 and eight covalent bonds by osmium in OsF_8.

3.12 CHARACTERISTICS OF COVALENT COMPOUNDS

Covalent compounds possess the following general characteristics:

1. **Physical state.** Unlike ionic compounds, the covalent compounds exist in all the three states, *viz.*, solid, liquid and gaseous.
2. **Non-ionic reactions.** Since these compounds are molecular in nature and not ionic, their reactions are molecular and proceed at a much slower rate than those of ionic compounds.
3. **Melting and boiling points.** Covalent compounds have low melting and boiling points because the molecules in covalent compounds are held together less rigidly (by weak van der Waals' forces), than in case of ionic compounds which involve electrostatic forces of attraction.
4. **Crystal structure.** The crystal structure of covalent compounds differs from that of ionic compounds. They usually consist of molecules rather than ions.
5. **Solubility.** Covalent compounds are generally soluble in organic (non-polar or weakly polar) solvents but insoluble in water and other polar solvents.
6. **Isomerism.** As the atoms in covalent compounds are held together by the shared electrons and not by the electrostatic force, it is rigid and directional and hence there is directional type of arrangements, *i.e.*, structural and stereo isomerism in molecules.
7. **Electrical conductivity.** Since there are no free ions in covalent compounds, they are bad conductors of electricity.

3.13 COMPARISON BETWEEN THE PROPERTIES OF ELECTROVALENT AND COVALENT COMPOUNDS

The main points of differences between electrovalent and covalent compounds are summed up in Table 3.3.

Table 3.3: Differences between Electrovalent and Covalent Compounds

Electrovalent or Ionic Compounds	Covalent Compounds
(i) They are formed by the transference of electrons from one atom to another.	(i) They are formed by the sharing of electrons between two atoms.
(ii) These compounds undergo ionic reactions which are very fast, almost instantaneous.	(ii) These compounds undergo molecular reactions which are very slow.
(iii) These compounds are generally solids.	(iii) These compounds may be solids or liquids or gases.
(iv) Ionic compounds are generally soluble in polar solvents such as water and insoluble in organic solvents.	(iv) Covalent compounds are generally soluble in non-polar solvents such as benzene and insoluble in polar solvent such as water.
(v) They are made up of ions with powerful electrostatic forces of attraction.	(v) They are made up of molecules held together by weak Van der Waals' forces of attraction.
(vi) They possess high melting and boiling points.	(vi) They possess low melting and boiling points.
(vii) Ionic bonds are non-directional and these compounds do not show isomerism.	(vii) Covalent bonds are rigid and directional. These compounds show isomerism.
(viii) Ionic compounds conduct electricity in the molten solutions.	(viii) Covalent compounds are generally bad conductors of electricity.

3.14 LIMITATIONS OF LEWIS CONCEPT OF COVALENT BOND

Lewis concept of covalent bond has the following limitations:

(*i*) It can not explain how the atoms are held together in the molecules like H_2, Cl_2, etc., in which there are no ions and hence, no electrostatic force of attraction, *i.e.*, it could not explain the formation of a covalent bond. The idea of sharing of electrons was incomplete.

(*ii*) It can not explain energy changes during the formation of a covalent bond.

(*iii*) It can not explain the formation of molecules like NO, NO_2, etc., having odd number of electrons.

(*iv*) It can not explain the shapes of molecules containing covalent bonds.

Orbital concept as given in the following sections explains these points satisfactorily.

3.15 THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Molecular geometry is the 3-D arrangement of atoms in a molecule which is responsible for physical and chemical properties. Lewis concept is unable to explain the shapes of the molecule. So, new approach to study the molecular geometry or shape was introduced which is known as Valence Shell Electron Pair Repulsion (VSEPR) theory by Sidgwick and Powell in 1940, which is based on the repulsive interaction of the electron pairs present in the valence shell of atoms. This theory was further developed and modified by Nyholm and Gillespie in 1957.

The basic assumptions of the VSEPR theory are as follows:

(a) The shapes of a molecule depend on the number of valence shell electron pairs (bonded or non-bonded) around the central atom.

(b) Pairs of electrons in valence shell repel each other since their electron clouds are negatively charged.

(c) The valence shell tend to occupy such positions in space that minimise the repulsion and thus maximise the distance between them.

(d) These valence shell consider as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.

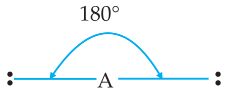
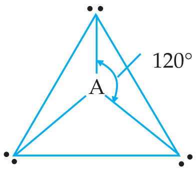
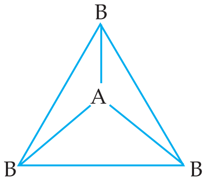
(e) If a molecule has two or more resonating structure, then VSEPR theory is applicable to any resonating structure.

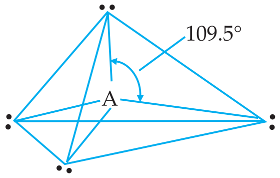
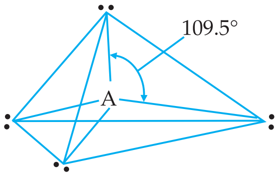
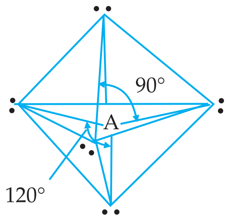
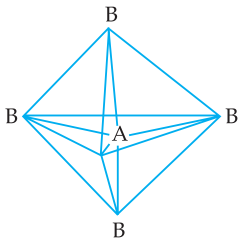
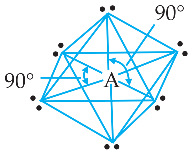
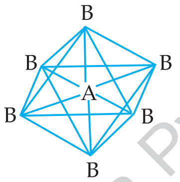
To study the geometrical shape of molecules with help of VSEPR theory, all the molecules are divided into two parts:

(a) Molecules in which central atom has no lone pair

In the given Table 3.4, we show five possible arrangements of electron pairs around the central atom 'A'. As a result of repulsion between them the electron pairs stay as far as possible from each other. Molecules in which the central atom has no lone pair of electrons have one of these five possible arrangements of bonding pairs. In compounds of AB_2, AB_3, AB_4, AB_5 and AB_6 types, the arrangement and geometry are linear, trigonal planar, tetrahedral, trigonal bipyramidal and octahedral respectively. The examples of these arrangements are $BeCl_2$ (AB_2 type), BF_3 (AB_3 type), CH_4 (AB_4 type) and PCl_5 (AB_5 type).

Table 3.4: 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		B — A — B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_2

4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

(b) Molecules in which central atom has one or more lone pairs of electrons

The geometry of those molecules in which the central atom has one or more lone pairs of electrons is more complicated. If the central atom has both types of electron pairs, i.e., bond pair (bp) and lone pair (lp) of electrons, then there are three types of repulsive forces possible, they are:

(*i*) Repulsive force between bonding pairs (bp – bp).

(*ii*) Repulsive force between lone pairs (Ip – Ip).

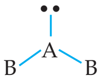
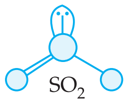
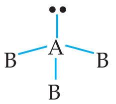
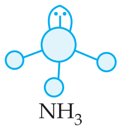
(*iii*) Repulsive force between bond pair and lone pair (bp – lp).

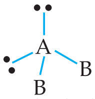
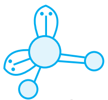
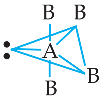
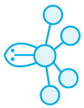
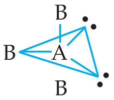
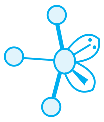
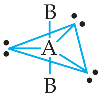
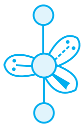
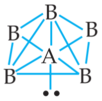
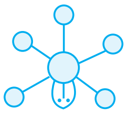
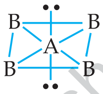
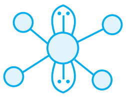
According to VSEPR theory, the decreasing order of strength of these repulsive forces are as:

lp – lp > lp – bp > bp – bp

Due to the presence of number of lone pair and bond pair the shapes of molecules become deviated which is shown in given Table 3.5.

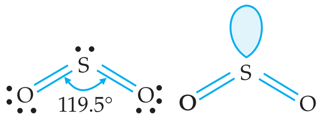
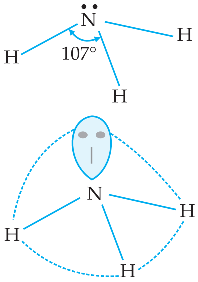
Table 3.5: Geometry of Simple Molecules and Ions in which the Central Atom has One or More Lone Pairs

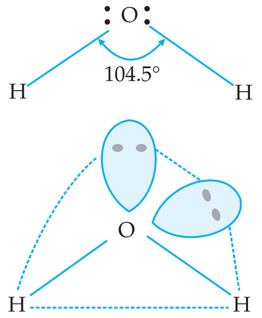
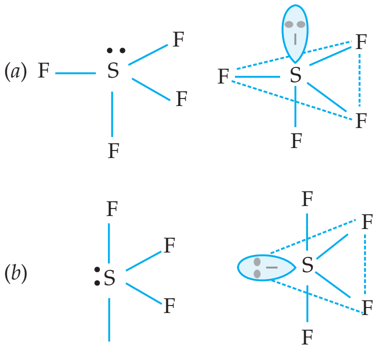
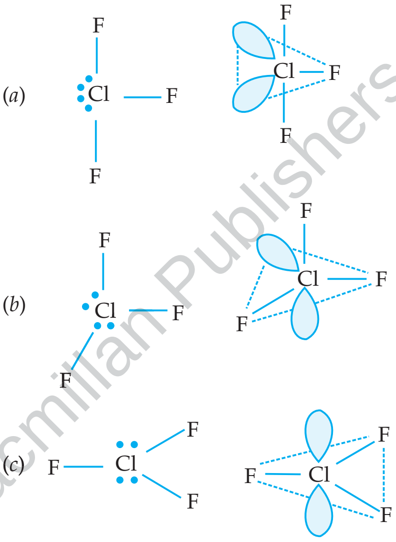
Class of molecules	Total number of electron pairs	Number of bonding pairs	Number of lone pairs	Arrangement of electron pairs	Geometry	Examples
AB_2E	3	2	1	 Trigonal planar	Bent	
AB_3E	4	3	1	 Tetrahedral	Trigonal pyramidal	

AB_2E_2	4	2	2	 Tetrahedral	Bent	 H_2O
AB_4E	5	4	1	 Trigonal bipyramidal	Distorted tetrahedron (or seesaw)	 SF_4
AB_3E_2	5	3	2	 Trigonal bipyramidal	T-shaped	 ClF_3
AB_2E_3	5	2	3	 Trigonal bipyramidal	Linear	 I_3
AB_5E	6	5	1	 Octahedral	Square pyramidal	 BrF_5
AB_4E_2	6	4	2	 Octahedral	Square planar	 XeF_4

Examples of some molecules having both lone pair and bond pair with their deviated shapes and the reasons for their acquiring the shapes are given in the following Table 3.6. These deviations can easily be explained by VSEPR theory.

Table 3.6: Shapes of Molecules containing Bond Pair and Lone Pair

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB_2E	4	1		Bent	Theoretically the shape should have been triangular planar but actually it is found to be bent or V-shaped. The reason being the lone pair-bond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5° from 120°.
AB_3E	3	1		Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° from 109.5°.

AB_2E_2	2	2		Bent	The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°.
AB_4E	4	1	 [More stable]	Seesaw	In (*a*), the lp is present at axial position so there are three lp–bp repulsions at 90°. In (*b*), the lp is in an equatorial position, and there are two lp–bp repulsions. Hence, arrangement (*b*) is more stable. The shape shown in (*b*) is described as a distroted tetrahedron, a folded square or a seesaw.
AB_3E_2	3	2		T-shape	In (*a*), the lp are at equatorial position so there are less lp-bp repulsions as compared to others in which the lp are at axial positions. So structure (*a*) is most stable. (T-shaped).

3.15.1 Valence Bond Theory (VBT)

The VSEPR theory is based on Lewis structure and provides a relatively simple and straightforward method for predicting the geometry of molecules. But Lewis theory cannot explain the property of chemical bond formation as well as give any reason for difference in bond dissociation enthalpies and bond length in molecules.

To overcome the limitations of VSEPR theory, two quantum mechanical theories are used to describe covalent bond formation and the electronic structure of molecules. They are:

1. Valence Bond Theory
2. Molecular Orbital Theory

This theory is based on the knowledge of atomic orbitals, electronic configuration of elements, the overlapping criteria of atomic orbitals, hybridisation and the principles of variation and superpositions.

Let us consider the formation of a hydrogen molecule from two hydrogen atoms. Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and the electrons present in them are represented by e_A and e_B. When these atoms are far from each other, there is no force of attraction between them but when these atoms come closer to each other, the following new forces are developed:

1. *Attractive forces* arise between nucleus of one atom (N_A) and electrons of the second atom (e_B) and same force is developed between N_B and e_A.
2. *Repulsive forces* arises between electrons of both atoms A and B, i.e., $e_A - e_B$ and between the nuclei of atoms A and B, i.e., $N_A - N_B$.

Both these forces are working in opposite directions and experimentally it is found that attractive force strength is more as compared to repulsive forces. So both atoms combine together by decrease of potential energy. Finally, when the net force of attraction becomes equal and balanced by net repulsive force, then the bond is formed between these atoms and a molecule (H_2) is formed which has minimum energy and maximum stability and bond length of this bond is found to be 74 pm.

The energy released during the entire process of formation of a H_2 molecule from two hydrogen atoms is called bond enthalpy and it is 435.8 kJ mol^{-1} for one mole of H_2 molecules.

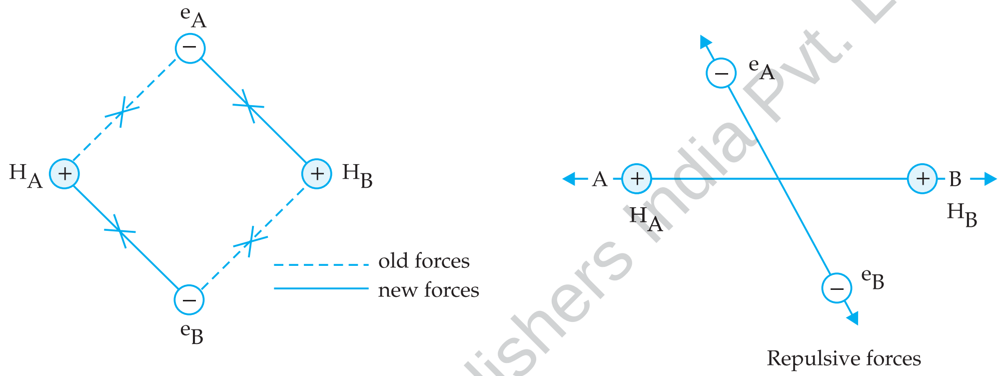


Fig. 3.5: *Forces of attraction and repulsion during formation of H_2 molecule*

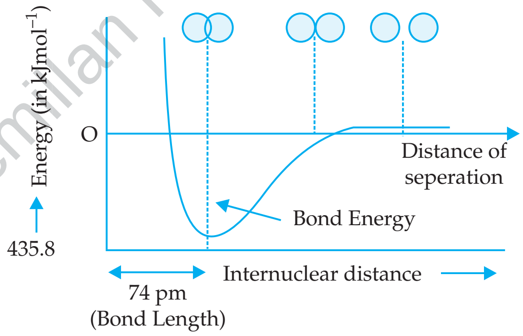


Fig. 3.6: *The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H_2.*

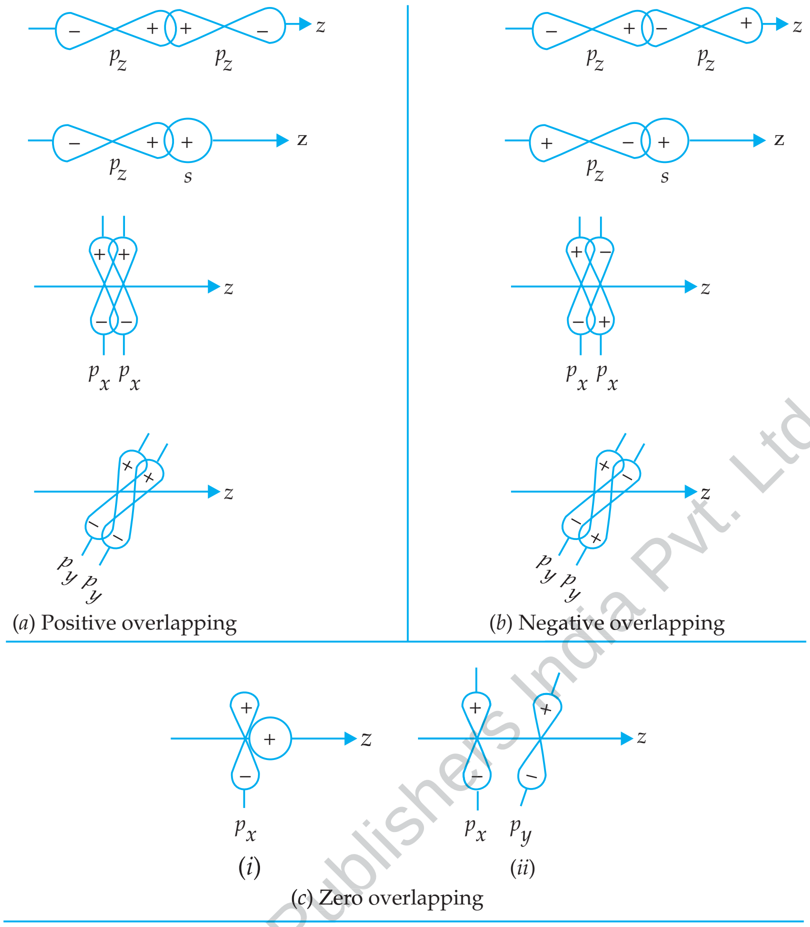
The energy required to break one mole of bonds of same kind is known as **bond dissociation energy**.

The bond dissociation energy of H_2 molecule can be represented as:

$$\text{H—H}(g) \text{ or } H_2(g) + 435.8 \text{ kJ mol}^{-1} \longrightarrow \text{H}(g) + \text{H}(g)$$

Orbital overlapping concept of valence bond theory: According to this concept covalent bond is formed when overlapping of atomic orbitals takes place because during the overlapping of orbital energy is decreased. The strength of bond formed during the overlapping of atomic orbitals depends on the extent of the overlapping of orbitals. More the overlapping, stronger is the bond.

Overlapping of atomic orbitals may be +ve, -ve or zero as shown in the given figures.



(a) Positive overlapping

(b) Negative overlapping

(c) Zero overlapping

Fig. 3.7: *Showing different types of overlapping*

In case of polyatomic molecules like CH_4, NH_3 and H_2O, the valence bond theory says that the shapes of CH_4, NH_3 and H_2O molecules are tetrahedral, pyramidal and bent shaped, respectively. The shape of these molecules can be explained on the basis of valence bond theory.

CH_4 (Methane) molecule: The electronic configuration of carbon in ground state is $1s^2 2s^2 2p^2$ and in excited state it becomes $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$. The energy required for excitation is compensated by the release of energy due to overlapping between the 2*p* orbital of carbon and Is orbital of hydrogen. This will result in the formation of four C—H bonds but the bond angle of H—C—H is not explained by this concept.

Types of overlapping and nature of covalent bond: On the basis of overlapping of orbitals, covalent bonds are divided into the following two types:

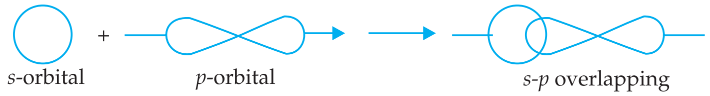
1. Sigma (σ) bond
2. pi (π) bond.

1. Sigma (σ) bond: When overlapping of atomic orbital takes place along the internuclear axis, the sigma (σ) bond is formed. This type of overlapping is also called end-to-end or head-on overlapping. This extent of overlapping in this type of bond is great, so sigma bond is stronger than pi bond.

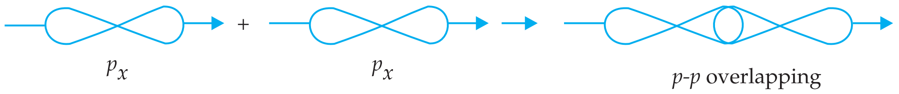
This type of bond can be formed by the following type of overlapping:

(*a*) ***s-s* overlapping:** When two half filled *s*-orbitals overlap along the axis, then sigma bond is formed.

(*b*) ***s-p* overlapping :** When one half filled *s*-orbital and one half filled *p*-orbital overlap with each other, then sigma bond is formed.



(*c*) ***p-p* overlapping :** When two half filled *px* orbitals overlap with each other, then sigma bond is formed.



2. pi (π) bond : When the overlapping of atomic orbitals takes place parallel to the internuclear axis, then π bond is formed. This is also known as sideways overlapping. In this type of bond formation, the extent of overlapping is very less so pi (π) bond is weaker than sigma bond. This is formed by following type of overlapping.

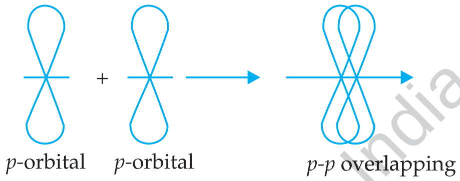


Table 3.7: Differences between Sigma (σ) and Pi (π) bond

Sigma (σ) bond	pi (π) bond
(i) A σ bond is formed by the axial overlapping of atomic orbitals.	(i) A π bond is formed by the sideways overlapping of orbitals.
(ii) σ bond formation involves overlapping of *s-s*, *s-p* and *p-p* orbitals.	(ii) It involves overlapping of *p-p* orbitals.
(iii) σ bond is stronger because of larger extent of overlapping.	(iii) π bond is relatively weaker because of smaller extent of overlapping.
(iv) The molecular orbital is symmetrical about internuclear axis and electron cloud is present on this axis.	(iv) The molecular orbital is discontinuous and consists of two electron clouds below and above the internuclear axis.
(v) Free rotation exists round a σ bond.	(v) Free rotation does not exist round π bond.
(vi) A sigma bond may exist either alone or along with π bonds.	(vi) A π bond is always present along with a sigma bond.
(vii) Hybridised orbitals or unhybridised orbitals are involved in a bond.	(vii) Hybridised orbitals are never involved in π bond.

3.15.2 Molecular Orbital Theory (MOT)

Valence bond theory is one of the two quantum mechanical approaches that explain bonding in molecules. In some cases, valence bond theory cannot explain properties of molecules. For example, in O_2 molecule, according to Lewis, all the electrons in O_2 are paired and oxygen molecule should, therefore, be diamagnetic. But experimentally it is clear that O_2 molecule is paramagnetic due to presence of two unpaired electrons. The molecular orbital theory was given by F. Hund and R.S. Mulliken in 1932. The main features of this theory are:

(*i*) As like atomic orbitals in atom, the electrons are present in molecular orbitals in a molecule.

(*ii*) Molecular orbitals are formed during the formation of molecule when atomic orbitals of combining atoms of comparable energies are combined.

(*iii*) Molecular orbitals are polycentric while atomic orbitals are dicentric in nature.

(*iv*) When molecular orbitals are formed by atomic orbitals, then their number is equal to the number of combining atomic orbitals.

(*v*) When two atomic orbitals combine, then two molecular orbitals are formed, one is known as bonding molecular orbital and the other orbital is antibonding molecular orbital.

The bonding molecular orbital is more stable as compared to the antibonding molecular orbital because the energy of the bonding molecular orbital is lower than that of the antibonding molecular orbital.

(*vi*) Molecular orbital is given by the electron probability distribution around the group of nuclei of molecule same as in atomic orbitals.

(*vii*) The shapes of the molecular orbitals depend upon the type of the combining atomic orbitals.

(*viii*) The filling of electrons in molecular orbitals takes place according to the same rules used in filling of atomic orbitals, i.e., Hund, Pauli, Aufbau etc.

Differences between atomic and molecular orbitals: The differences in atomic and molecular orbitals are given in the following Table 3.8:

Table 3.8: Differences between Atomic orbitals and Molecular orbitals

Atomic orbitals	Molecular orbitals
1. They are monocentric because electron cloud is present around one nucleus only.	1. They are polycentric because molecule has more than one nucleus.
2. They are less stable.	2. They are more stable.
3. They are represented by *s*, *p*, *d* and *f* etc.	3. They are represented by σ, π, δ etc.

Linear Combination of Atomic Orbitals (LCAO) or Formation of Molecular Orbitals

The formation of molecular orbitals can be explained by LCAO. According to it each atomic orbital is an wave function.

When atomic orbitals combine, then their wave also combines which has the following two possibilities :

(*a*) When the two waves of atomic orbitals are in the same phase, their amplitude is added, bonding molecular orbital is formed.

$$\sigma = \psi_A + \psi_B,$$

ψ_A and ψ_B = wave function of atomic orbital A and B.

(*b*) When two waves of atomic orbitals are not the same, the molecular orbital formed is antibonding and their wave functions are subtracted from each other.

$$\sigma^* = \psi_A + \psi_B$$

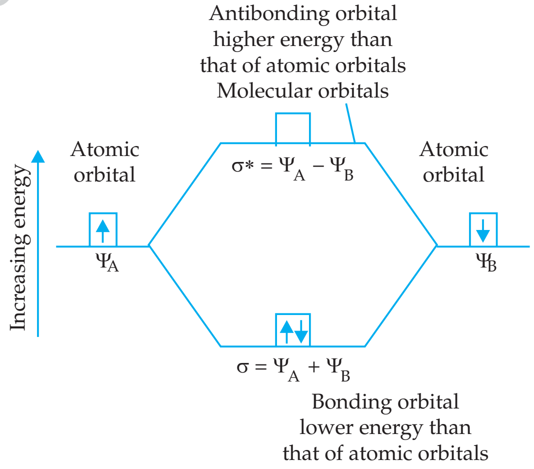


Fig. 3.8: *Formation of bonding (σ) and antibonding (σ*) molecular orbitals by the linear combination of atomic orbitals* ψ_A *and* ψ_B *centred on two atoms A and B, respectively.*

Conditions for Combination of Atomic Orbital to form Molecular Orbitals

1. The combining atomic orbitals must have approximately same energies.
2. The combining atomic orbitals have the same symmetry about the molecular axis.
3. The combining atomic orbitals must overlap each other to the maximum extent.

Energy Level Diagrams of Molecular Orbitals

We know that two atomic orbitals combine to form two molecular orbitals. So, the following types of molecular orbitals are formed up to the second shell:

Bonding molecular orbitals – $\sigma\ 2s\ \sigma\ 2p_z\ \pi\ 2p_x\ \pi\ 2p_y$

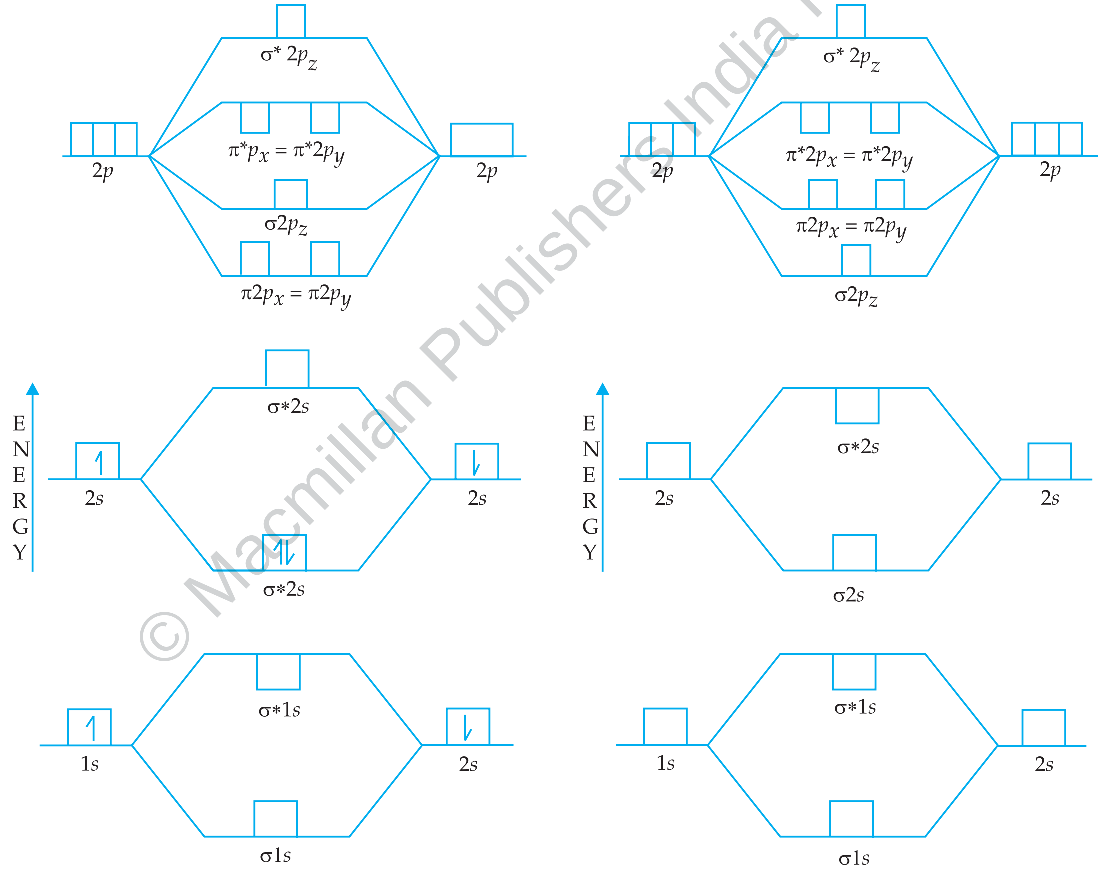
Antibonding molecular orbitals – $\sigma^*\ 2s\ \sigma^*\ 2p_z\ \pi^*\ 2p_x\ \pi^*\ 2p_y$

The increasing order of molecular orbitals for molecules O_2 and F_2 are given below :

$$\sigma^*\ 1s < \sigma^*\ 1s < \sigma\ 2s < \sigma^*\ 2s < \sigma\ 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^*\ 2p_z$$

But for molecules lower than O_2, i.e., Li_2, Be_2, B_2, C_2, N_2, etc. the increasing energy order of different atomic orbital is different and it is given as

$$\sigma 1s < \sigma^*\ 1s < \sigma 2s < \sigma^*\ 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^*\ 2p_z$$



(*a*) Representation of different molecular orbital in increasing order of energy for Li_2, Be_2, B_2, C_2, N_2

(*b*) For molecules O_2 and F_2

Electronic Configuration and Molecular Behaviour

The distribution of electrons in increasing order of molecular orbitals is called the electronic configuration of molecules. By knowing the electronic configuration of a molecule we can get some important information about them. They are given below:

Stability of a molecule: Stability of a molecule is measured by the bond order of the molecule, which indirectly depends on number of electrons in different molecular orbitals.

Bond order can be defined as "It is equal to the half of the difference of electrons present in bonding molecular orbitals (N_b) and electrons present in antibonding molecular orbitals (N_a)."

$$\text{Bond order} = \frac{1}{2}[N_b - N_a]$$

- If bond order is +ve, then molecule is stable ($N_b > N_a$).
- If bond order is –ve, then molecule is unstable ($N_b < N_a$).
- If bond order is zero, then molecule is unstable ($N_b = N_a$).

Nature of bond: In diatomic molecules 1, 2 and 3, value of bond order represents the presence of single, double and triple bond, respectively, between atoms.

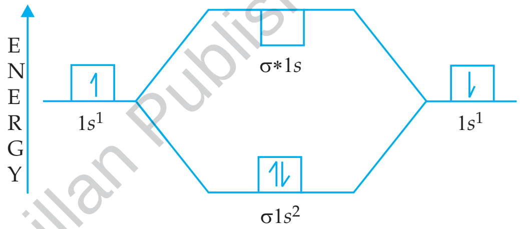
Bond length: Bond length of a molecule is inversely proportional to the bond order.

Magnetic nature: If all the molecular orbitals are doubly occupied by the electrons, then the molecule is diamagnetic in nature and repelled by magnetic field. But, if one or more molecular orbitals have a single electron, then the molecule is paramagnetic and is attracted by magnetic field.

Bonding in Some Homonuclear Diatomic Molecules

1. **Hydrogen molecule (H_2)**

   The molecular orbital electronic configuration of $H_2 = \sigma 1s^2$

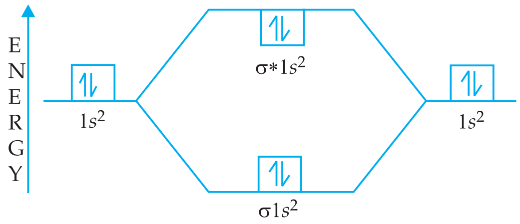


$$\text{Bond order} = \frac{1}{2}[2 - 0] = 1$$

So it is not clear that single bond is present between two hydrogen atoms and it is diamagnetic in nature.

2. **Helium molecule (He_2)**

   The molecular orbital electronic configuration of $He_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2$

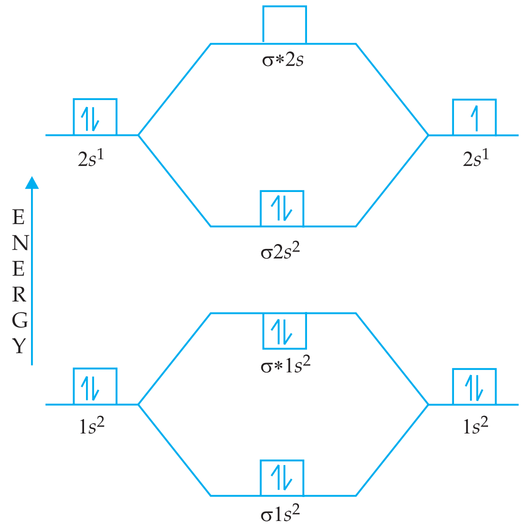


$$\text{Bond order} = \frac{1}{2}[2 - 2] = 0$$

So helium molecule is not possible because bond order is zero. In the same way, Be_2 molecule also does not exist.

3. Lethium molecule (Li_2)

The molecular orbital electronic configuration of $Li_2 = (\sigma 1s)^2, \sigma^* 1s^2 , \sigma 2s^2$

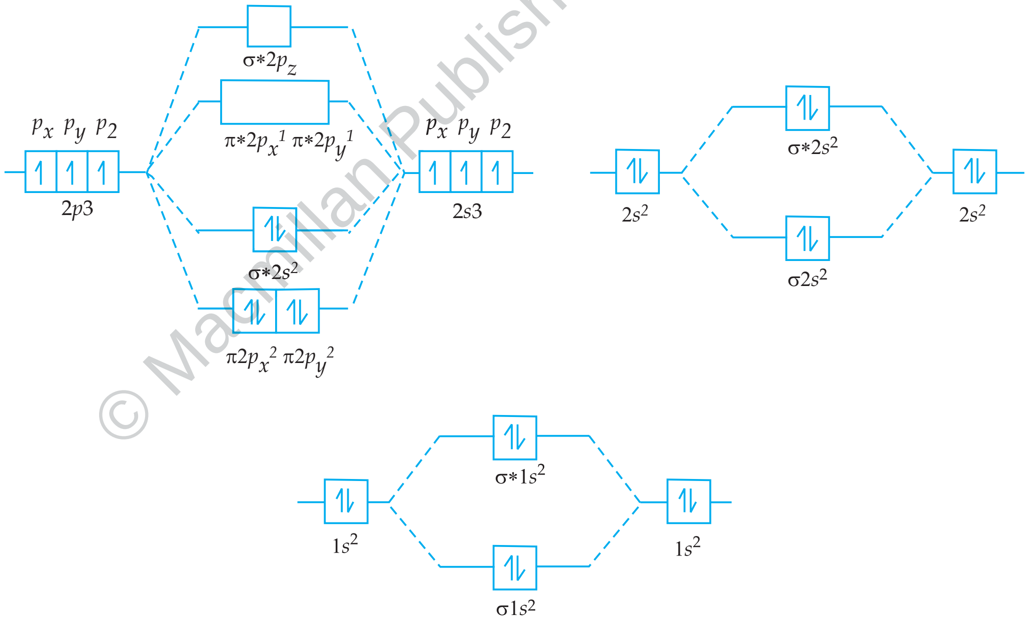


$$\text{Bond order} = \frac{1}{2}[4 - 2] = 1$$

So Li_2 molecule is stable and diamagnetic (no unpaired electron).

4. Carbon molecule (C_2)

The molecular orbital electronic configuration of $C_2 = \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p^2_x = \pi 2s^2_y$

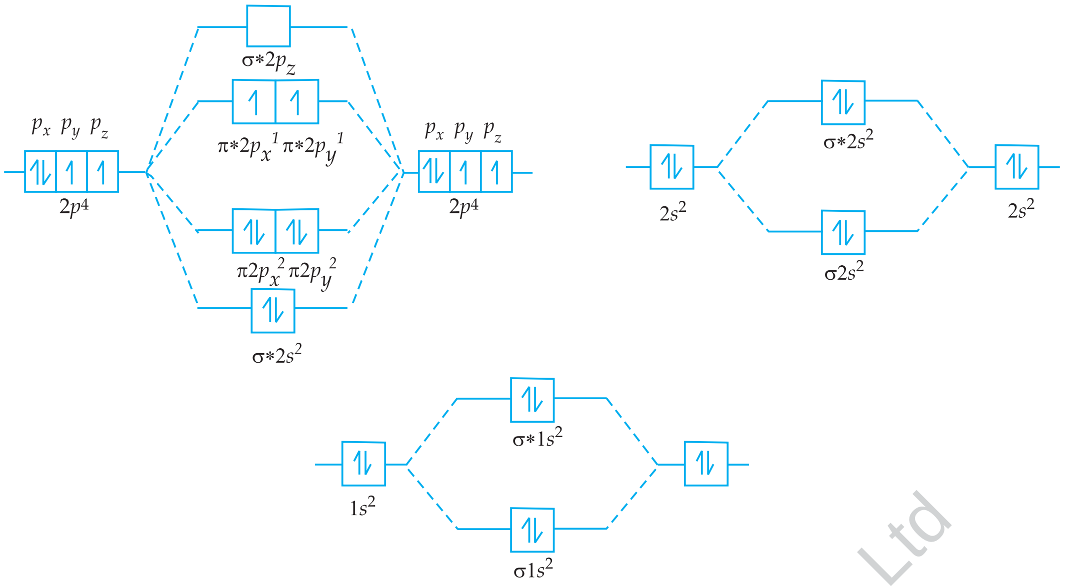


$$\text{Bond order} = \frac{1}{2}[8 - 4] = 2$$

So C_2 molecule is possible as it is found in vapour phase.

5. Oxygen molecule (O_2)

The molecular orbital electronic configuration of $O_2 = \sigma 1s^2\ \sigma^* 1s^2, \sigma 2s^2\ \sigma^* 2s^2, \sigma 2p^2_z$, $\pi 2p^2_x = \pi 2p^2_y$ $\pi^* 2p^1_x = \pi^* 2p^1_y$



$$\text{Bond order} = \frac{1}{2}\,[N_b - N_a] = \frac{1}{2}\,[10 - 6] = 2$$

So O_2 molecule is possible and is paramagnetic in nature due to the presence of two unpaired electrons. It is also clear that double bond is present between oxygen atom as bond order is 2.

3.15.3 Hydrogen Bonding

When highly electronegative elements like N, O and F are attached to the hydrogen atom in a molecule by a covalent bond, then polarity is developed due to the difference in their electronegativities and hydrogen gets partial positive charge (δ+) and other atoms get partial negative charge (δ–). Then the partially positive charged hydrogen atom of one molecule forms a bond with the partially negative charged electronegative atom of the other molecule. This type of bond is called hydrogen bond. It is a weak bond in nature and is represented by (-----) dotted line as follows:

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

So hydrogen bond is defined as, “that force of attraction which develops between the hydrogen atom of one molecule and electronegative atom of the other molecule in a compound”. The magnitude of hydrogen bond depends on the physical state of a compound, i.e., it is maximum in solid state and minimum in vapour (gas) state.

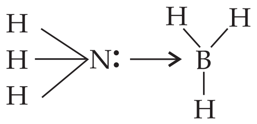
Effect of Hydrogen Bond

Hydrogen bond can be explained with many abnormal behaviours of compounds. Some of them are:

1. In aqueous solutions of HF, HF_2^- ions are produced instead of F^- ion.
2. Carboxylic acid (acetic acid) exists as a dimer.

3.16 COORDINATE OR DATIVE BOND

This is the third type of bond in the molecules. This bond is formed in molecules when an atom having completed its octet links with another atom which contains one or more lone pair of electrons. These electrons can be donated to some other atom to complete its octet and form a bond. Let us say we have a hypothetical compound ABC. Let B be the central atom. Suppose B forms a double bond with A and the octets of both are complete. Further suppose that B contains a lone pair of electrons and C contains six electrons in its outermost orbit, then B will donate the electrons to C to complete the octet of C and form a coordinate bond between B and C. In such a case B is called the *donor* and C the *acceptor.* A coordinate bond is represented by an arrow pointing from the donor to the acceptor.



This bond is proposed to strictly adhere to *the octet theory of chemical bonding.* If we form a normal double bond between B and C, then B would possess 10 electrons instead of 8. It may be pointed that in considering bonding on the basis of overlapping of orbitals, the octet rule is sometimes disobeyed. For example, in the case of SO_2, studied in the last section, sulphur possesses 10 electrons instead of 8. The main difference between a covalent bond and a coordinate bond lies in the fact that electrons are contributed equally in the sharing of electrons by the atoms in a covalent bond and that electrons are contributed by one atom only in the coordinate bond. The other atom simply accepts them. However, this donated pair of electrons acts towards the stability of both and it count towards both.

A **coordinate bond** *may be defined as a bond between two atoms formed with the help of an electron pair donated by one atom only.*

This bond is also known as a **dative bond** because there is some polarity in such a bond, the donor being slightly positive and the acceptor slightly negative.

3.17 SOME EXAMPLES OF COORDINATE MOLECULES

1. **Formation of Hydrogen Peroxide Molecule.** Hydrogen peroxide is obtained by combining an oxygen atom to the oxygen atom in a molecule of water. In the water molecule, the octet of oxygen and duplets of hydrogen atoms are completed by forming two covalent bonds between oxygen and hydrogen. Now oxygen contains two lone pair of electrons. It can donate one pair to another oxygen atom to form a coordinate bond between oxygen and oxygen (Fig. 3.9).

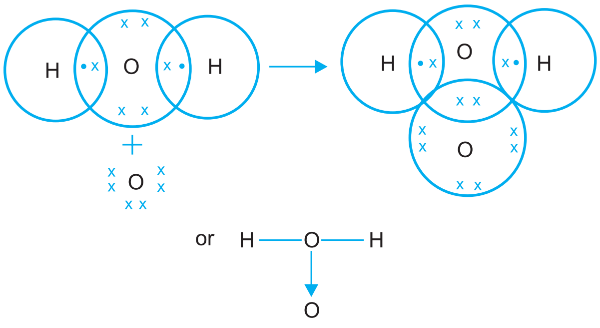


Fig. 3.9: *Coordinate bond in H_2O_2*

2. **Formation of Ozone Molecule.** Oxygen molecule is formed by a double bond between two oxygen atoms. The octets of both are completed. Now the lone pair of electrons on one of the oxygen atoms are donated to the third oxygen atom to complete its octet and form a coordinate bond with the third oxygen as shown in Fig. 3.10.

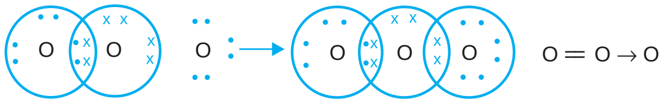
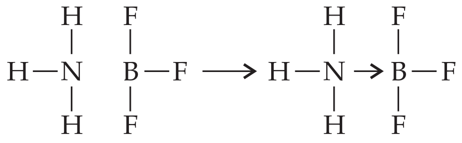


Fig. 3.10: *Coordinate bond in ozone molecule*

3. **Formation of Addition Compounds.** A coordinate bond is formed between two molecules, one of which contains a lone pair of electrons, and the other contains an electron-deficient atom. Ammonia and boron trifluoride form an addition compound with the help of coordination bond. Nitrogen of ammonia contains a lone pair of electrons which are donated to electron-deficient boron atom of boron trifluoride.



$$H_3N + BF_3 \longrightarrow H_3N \rightarrow BF_3$$

Addition compound

Octets of all atoms are completed.

4. **Formation of Nitric Acid Molecule.** Nitric acid is a monobasic acid. Therefore, one —OH group is directly linked to nitrogen. One oxygen is linked by a double bond and the other oxygen by a coordinate bond to the nitrogen atom to complete the octets of all atoms (Fig. 3.11).

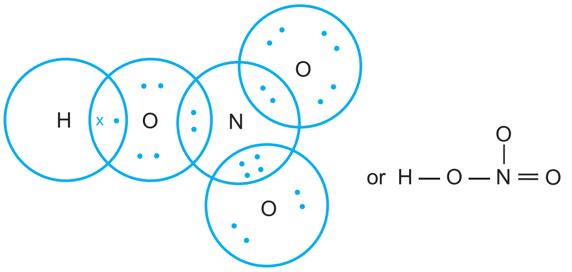


Fig. 3.11: *Coordinate bond in nitric acid*

5. **Formation of Ammonium Ion.** In the molecule of ammonia, nitrogen forms three bonds with three hydrogen atoms. There is a lone pair of electrons on nitrogen which is donated to a proton to complete its duplet and a coordinate bond is formed between nitrogen and hydrogen (Fig. 3.12).

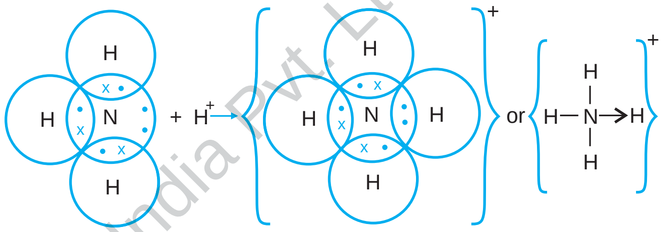


Fig. 3.12: *Ammonium ion*

6. **Formation of Sulphur Dioxide Molecule.** Sulphur forms a double bond with oxygen by equal sharing of two electrons each. As sulphur contains lone pairs of electrons, it donates one pair to oxygen to complete its octet. In the molecule of SO_2, there is one sulphur-oxygen double bond and one sulphur-oxygen coordinate bond (Fig. 3.13).

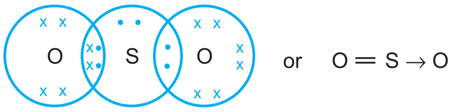


Fig. 3.13: *Sulphur dioxide molecule*

7. **Formation of Sulphuric Acid.** In the molecule of sulphuric acid, the central sulphur atom is linked to two —OH groups by covalent bonds and to two oxygen atoms by coordinate bonds (Fig. 3.14).

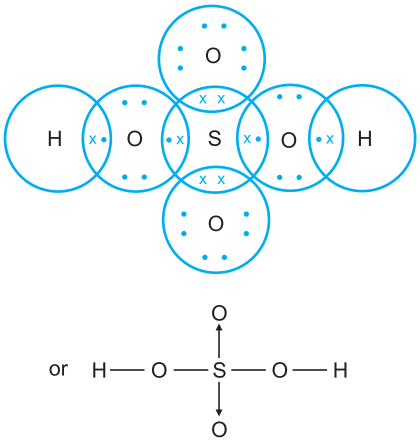


Fig. 3.14: *Coordinate bond in H_2SO_4 molecule*

Dative or coordinate bond is found in the oxides and oxy-acids of nitrogen, phosphorus and sulphur. Transition metals form a number of coordinate compounds with ligands (groups containing lone pairs of electrons or negatively charged ions) like water, ammonia and a number of organic molecules. These ligands are accommodated in the vacant *d*-orbitals of the transition metals.

8. **Formation of H_3PO_4 Molecule.** It is a tribasic acid and hence three —OH groups are directly attached to the P-atom. One oxygen is linked with the help of coordinate bond. There are five electrons in the outer orbit of phosphorus (Fig. 3.15).

9. Formation of Oxy-acids of Chlorine. Chlorine forms four oxy-acids, as given below:

- (*i*) Hypochlorous acid ($HClO$)
- (*ii*) Chlorous acid ($HClO_2$)
- (*iii*) Chloric acid ($HClO_3$)
- (*iv*) Perchloric acid ($HClO_4$).

Each has one —OH group which is directly attached to the chlorine. The remaining O-atoms can be attached either by covalent or coordinate bonds.

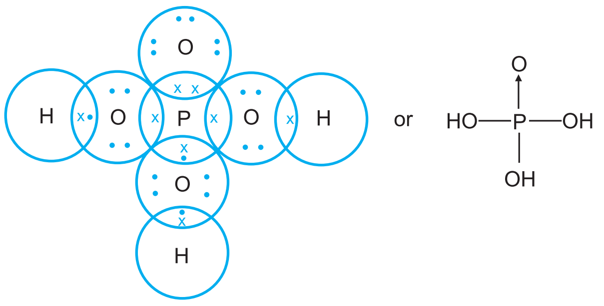


Fig. 3.15: *Coordinate bond in phosphoric acid*

3.18 PROPERTIES OF COORDINATE COMPOUNDS

Properties of the coordinate compounds are found to be intermediate between those of ionic and covalent compounds.

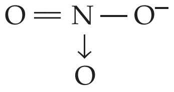
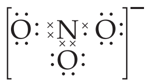
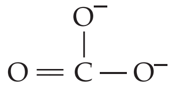
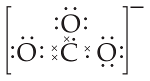
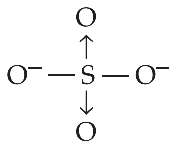
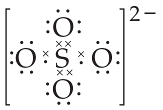
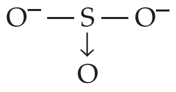
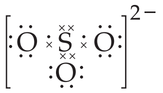
1. **Melting and Boiling Points.** Coordinate compounds exhibit higher melting points and boiling points than covalent compounds and lower than ionic compounds.
2. **Solubility.** These compounds are soluble in organic solvents just like covalent compounds and are insoluble in water.
3. **Poor Conductor of Electricity.** As these compounds are not much ionised in water, the solutions do not conduct electricity.
4. **Isomerism.** Like a covalent bond, coordinate bond is also rigid and directional, hence, the coordinate compounds show isomerism.

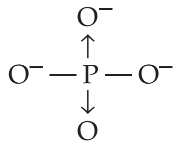
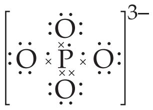
PROBLEM FOR PRACTICE

Name the types of bonds present and draw the electron dot or equivalent structure of $HClO_4$.

3.18.1 Lewis Structures of Some Ions

In the structures given below, the symbol $\longrightarrow$ represent a coordinate bond. The electrons belonging to oxygen are represented by dots (•) and those belonging to the second atom (N, S, P) are represented by cross (x).

Name of the ion	*Formula*	*Structural formula*	*Lewis structure*
Nitrite ion	NO_2^-	$O=N-O^-$	
Nitrate ion	NO_3^-	 $\begin{array}{c} O=N-O^- \\ \downarrow \\ O \end{array}$	
Carbonate ion	CO_3^{2-}	 $\begin{array}{c} O^- \\ \vert \\ O=C-O^- \end{array}$	
Sulphate ion	SO_4^{2-}	 $\begin{array}{c} O \\ \uparrow \\ O^- - S - O^- \\ \downarrow \\ O \end{array}$	
Sulphite ion	SO_3^{2-}	 $\begin{array}{c} O^- - S - O^- \\ \downarrow \\ O \end{array}$	

Phosphate ion	PO_4^{3-}		

3.19 THE SHAPES OF MOLECULES AND IONS

3.19.1 Hybridisation of Orbitals

The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$ as its atomic number is 6. As the bonds are formed by unpaired electrons, carbon should show a valency of 2. But, we observe that carbon shows tetravalency in its compounds like methane or carbon dioxide. This was explained by saying that the above mentioned configuration is the configuration in ground state. During the formation of bonds with other atoms, some of the electrons in lower energy levels are excited to higher levels. Thus, in the case of carbon, one electron from 2*s* level is excited to empty $2p_z$ level (Fig. 3.16).

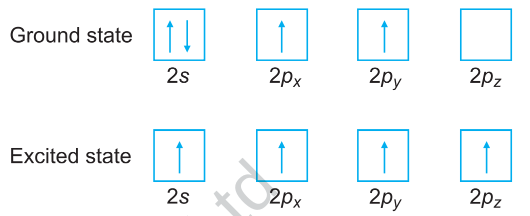


Fig. 3.16: *Ground and excited state configuration of carbon*

Now there are 4 electrons which are unpaired. These four electrons will form four bonds by overlapping with the orbitals of other atoms. For example, they combine with four hydrogen atoms to form methane (CH_4).

However, there is one thing which is surprising. We find that in methane, all the C—H bond have the same bond energy and all the angles H—C—H are the same, *i.e.*, 109° 28´. Looking back at the orbitals, which participate in bonding, *i.e.*, one *s*-orbital and three *p*-orbitals which have different shapes and energies, we expect one of the bonds formed by *s*-orbital to be different from the three bonds formed by *p*-orbitals. Moreover, as the *p*-orbitals are inclined at an angle of 90° to each other, we expect the bond angles of 90° in methane also. But this actually is not so. Thus to explain this anomaly, the concept of *hybridisation* was introduced.

It is assumed that the 2*s*-orbital and three 2*p*-orbitals which are associated with different shapes and energies mix with each other and produce four equivalent types of orbitals with the same shape and energy and are oriented symmetrically in space. These are called **hybrid** or **hybridised** orbitals and this phenomenon is called **hybridisation.** These hybridised orbitals then overlap with the orbitals of other atoms to form bonds.

Thus, **hybridisation** *is the process of mixing of orbitals of different shapes and energies, to produce orbitals of equivalent shape and energy oriented symmetrically with respect to one another.*

This phenomenon explains satisfactorily why the bond energies and bond angles are equal in the case of methane and many other molecules.

3.19.2 Necessary Conditions for Hybridisation

There are certain conditions which must be satisfied before the orbitals hybridise to produce equivalent type of orbitals. These are:

1. The orbitals taking part in hybridisation should not differ too much in their energies. For example, 1*s* and 2*p* orbitals can not hybridise. The participating orbitals must possess almost similar energies.
2. Number of hybrid orbitals formed will be equal to the number of orbitals combining together.
3. Whereas the paired electrons do not take part in bonding, they can take part in hybridisation. In such a case one of the positions in the geometrical shape is occupied by the lone pair of electrons. This happens in the case of ammonia and water molecules.
4. It is not essential for all the unpaired electrons to participate in hybridisation. Those unpaired electrons which don't take part in hybridisation form π-bonds by lateral overlapping.

3.19.3 Types of Hybridisation

Depending upon which atomic orbitals are combining together, we have different types of hybridisation, which are given below:

1. ***sp* or Diagonal Hybridisation.** This type of hybridisation occurs when one *s*-orbital and one *p*-orbital combine together to give two hybridised orbitals known as *sp* hybridised orbitals which have equal energies and they are oriented along the same line in opposite direction at an angle of 180°. Since the orbitals are negatively charged, they repel each other. Hence, they orient themselves in such a way that they are as far apart as possible from each other. Two orbitals can orient themselves along the same line in opposite directions to have minimum repulsive interactions. The shapes of the hybridised orbitals in *sp* hybridisation is given in Fig. 3.17.

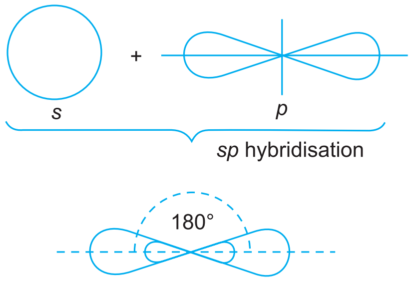


Fig. 3.17: *sp hybridisation*

2. **sp^2 or Trigonal Hybridisation.** This type of hybridisation takes place when one *s*-orbital and two 2*p*-orbitals combine together to give three sp^2 hybridised orbitals of equal energies.
   These hybrid orbitals are oriented at an angle of 120° in the same plane. The three orbitals point towards the corners of an equilateral triangle with the nucleus occupying the centre of the triangle. This is illustrated in Fig. 3.18.

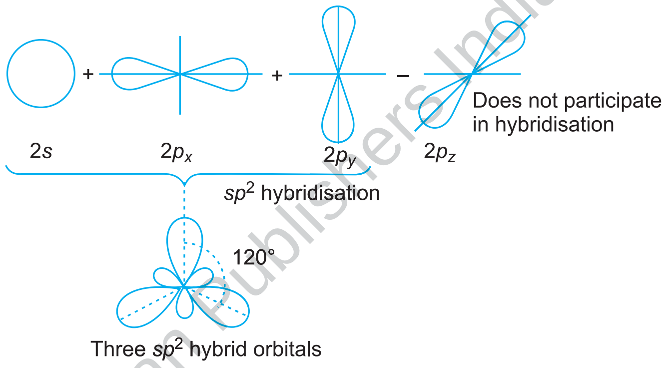


Fig. 3.18: *sp^2 hybridisation*

3. **sp^3 or Tetrahedral Hybridisation.** When one *s*-orbital and three *p*-orbitals combine together to produce equivalent type of orbitals, sp^3 hybridisation takes place. Four sp^3 hybridised orbitals are produced which have the same energy and shape and are oriented at an angle of 109° 28´ to one another. This is also known as *tetrahedral* hybridisation because the hybridised orbitals are pointing towards four corners of a tetrahedron with the nucleus occupying the centre of the tetrahedron. In this position, the hybridised orbitals experience minimum repulsive forces. This is illustrated in Fig. 3.19.

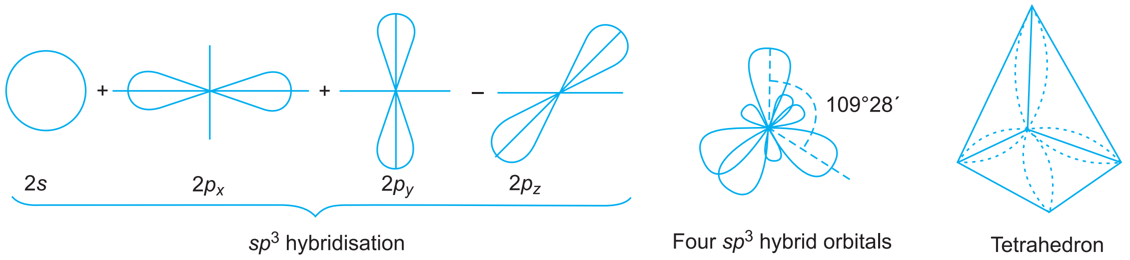


Fig. 3.19: *sp^3 hybridisation*

The geometry and shape of molecules associated with different types of hybridisation is summarised in Table 3.9.

Table 3.9

S. No.	Type of Hybridisation	Combination of Orbitals	Bond Angle (degrees)	Geometry
1.	sp	$s + p_x$	180	Linear
2.	sp^2	$s + p_x + p_y$	120	Trigonal
3.	sp^3	$s + p_x + p_y + p_z$	109º – 28´	Tetrahedral
4.	dsp^2	$d + s + p_x + p_y$	90º	Square planar
5.	$sp^3\,d$	$s + p_x + p_y + p_z + d$	90º, 120º	Trigonal bipyramidal
6.	$sp^3\,d^2$	$s + p_x + p_y + p_z + (2 \times d)$	90º	Octahedral

Trigonal bipyramidal and planer shapes of molecules are discussed under shapes of PCl_5 and $[Ni(CN)_4]^{2-}$.

3.20 FACTORS INFLUENCING SHAPES OF MOLECULES

Molecules having covalent bonds possess definite geometrical shapes. The shape of the molecule depends upon the following factors:

1. **Type of Hybridisation.** Type of hybridisation decides the shape of the molecules. If *sp* hybridisation is taking place and the molecule is of the type AB_2 where the atom A is the central atom and is surrounded by two B atoms, then the molecule will have a linear shape B—A—B with the ∠ BAB equal to 180º. Similarly, if the molecule is of the type AB_3 with sp^2 hybridisation then the atom A will lie in the centre of an equilateral triangle and the three B atoms will occupy the vertices of the triangle. If, however, the molecule is of the type AB_4 with sp^3 hybridisation taking place, the atom A occupies the centre of a tetrahedron and the vertices of the tetrahedron is occupied by B. This is based on the fact that the hybridised orbitals repel each other due to similar charge and occupy positions in which there are minimum repulsive forces.
2. **Lone Pair of Electrons. VSEPR or Valence Shell Electron Pair Repulsion Theory.** Another factor which decides the geometry of a molecule is the lone pair of electrons on the central atom. Certain elements like nitrogen and oxygen contain lone pair or pairs of electrons on them, which repel the shared pair of electrons away from them. In such a case, the bond angle changes from the expected angle. The order of repulsion between the electron is as follows:

   Lone-pair – Lone-pair > Lone-pair – Shared-pair > Shared pair – Shared pair.

   Repulsion between the two lone-pairs is maximum followed by that between a lone pair and a shared pair followed by the repulsion between two shared pairs of electrons.

   Greater the number of lone-pair of electrons on the central atom, greater is the distortion produced in the normal angle or shape.

3.21 SHAPES OF CERTAIN MOLECULES

1. **Shape of Methane (CH_4) Molecule:** At. no. of carbon = 6. Electronic configuration of C in ground state = $1s^2\,2s^2\,2p_x^1\,2p_y^1$. Electronic configuration of C in excited state = $1s^2\,2s^1\,2p_x^1\,2p_y^1\,2p_z^1$.

   There are four orbitals having unpaired electrons. These are $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals. They will first hybridise. So it is a case of sp^3 hybridisation. Four hybridised orbitals are oriented tetrahedrally as shown in Fig. 3.20.

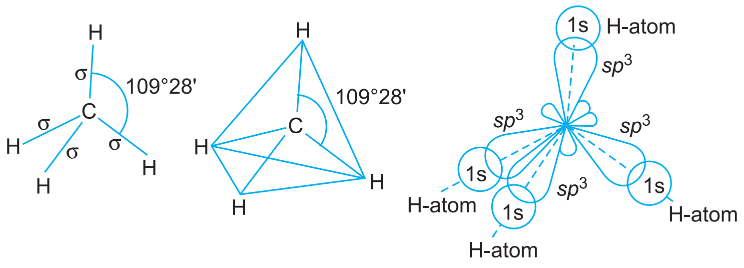


Fig. 3.20: *Shape of methane molecule*

All the four hybridised orbitals overlap with the 1*s*-orbital of four hydrogen atoms. All these overlappings take place along the internuclear axes. Hence, four carbon-hydrogen σ-bonds are formed. The angle ∠HCH is 109° 28´.

2. **Shape of Ammonia (NH_3) Molecule:** Atomic number of nitrogen = 7

Electronic configuration of nitrogen = $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

Here there is no possibility of shifting of the electron from 2*s* level to 2*p* level as there is no empty 2*p*-orbital. 2*s*-orbital although incapable of overlapping or forming the bond, participates in hybridisation. Hence, it is a case of sp^3 hybridisation. This will give rise to tetrahedral shape. The hybridised orbitals are oriented to the corners of a tetrahedron with one corner occupied by the lone pair of electrons from 2*s*-orbital. Three sp^3 hybridised orbitals overlap with the 1*s*-orbitals of three hydrogen atoms. We expect an angle of 109° 28´ between H—N—H in the tetrahedral geometry. Actually this angle is 107°. This contraction in angle takes place because the lone pair of electrons repels the shared pair or bonded pair of electrons with a greater force (see Fig. 3.21). Thus, it is of pyramidal shape.

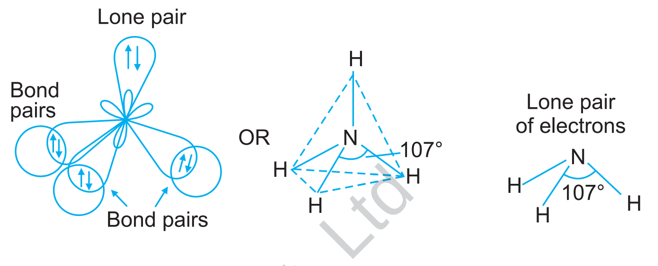


Fig. 3.21: *Shape of ammonia molecule*

3. **Shape of Water (H_2O) Molecule:** Atomic number of oxygen = 8. Electronic configuration = $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

In the 2nd orbit, there are four orbitals, *viz.*, 2*s*, $2p_x$, $2p_y$ and $2p_z$. Out of these 2*s* and $2p_x$ cannot form the bonds as they are paired. But they can participate in hybridisation. Hence, it is a case of sp^3 hybridisation. The hybridised orbitals are oriented along the corners of a tetrahedron. Two of the positions on the tetrahedron are occupied by lone pair of electrons from 2*s* and $2p_x$ orbitals. The other two hybridised orbitals will overlap with the 1*s* orbitals of two hydrogen atoms to form a water molecule as shown in Fig. 3.22. We expect an angle of 109° 28´ in HOH. Actually the angle is 105°. This is due to stronger repulsion of two lone pairs of electrons with the shared pairs of electrons. Thus, it is of V shape.

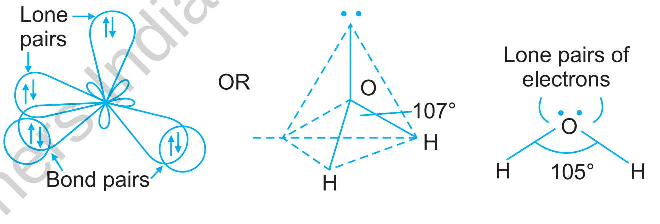


Fig. 3.22: *Shape of water molecule*

4. **Shape of Ethane (C_2H_6) Molecule:** In the molecule of ethane, two carbon atoms are linked to each other by a σ-bond and each carbon is linked to three hydrogen atoms by σ-bonds (Fig. 3.23). Both the carbon atoms are sp^3 hybridised. Out of the four sp^3 hybridised orbitals of one carbon, one orbital overlaps with one of the hybridised orbitals of the second carbon making a C—C bond. The other three hybridised orbitals overlap with the 1*s*-orbitals of three hydrogen atoms. Similarly, one hybridised orbital of the second carbon overlaps with one of the orbitals of the first carbon and three orbitals overlap with three 1*s*-orbitals of three hydrogen atoms. In other words three hybridised orbitals of each carbon overlap with three hydrogens and the fourth orbital of each overlaps with each other.

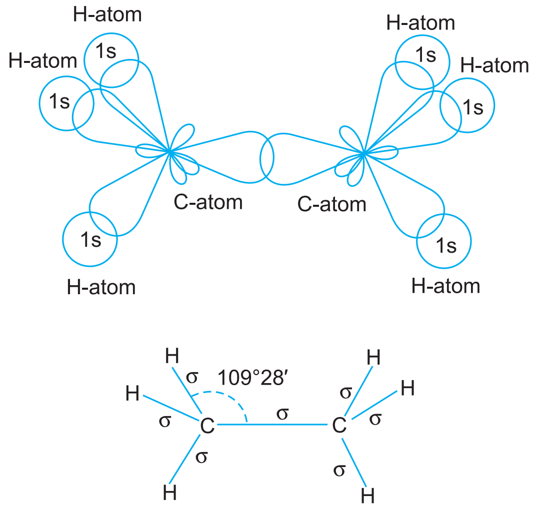


Fig. 3.23: *Shape of ethane molecule*

The C—C bond length in a molecule of ethane is 1.54 Å whereas C—H bond length is 1.10 Å. The dissociation energy of C—C bond is 348 kJ/mole.

5. **Shape of Ethylene (C_2H_4) Molecule:** The electronic configuration of C in excited state is:
$1s^2\ 2s^1\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$

Here all the four unpaired orbitals do not participate in hybridization. Out of four, only three orbitals say 2*s*, $2p_x$ and $2p_y$ hybridise. The fourth one $2p_z$ remains unhybridised. Hence, it is a case of sp^2 hybridisation. The hybridised orbitals are oriented in the same plane at an angle of 120°. We have two such carbons. One orbital of each carbon overlap with each other to form a σ-bond. Two orbitals of each carbon overlap with two 1*s* orbitals of hydrogen to form four C—H bonds. We are left with 2 unhybridised orbitals of two carbons which are oriented perpendicular to the plane of the rest of the molecule. They will overlap laterally giving rise to a weak π-bond between carbon-carbon. Hence, there will be a double bond, one σ-bond and one π-bond between carbon-carbon (Fig. 3.24).

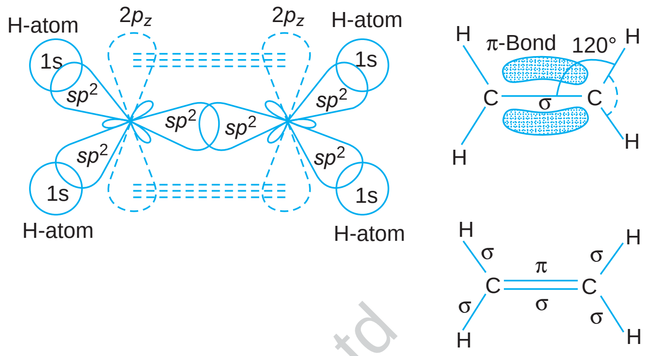


Fig. 3.24: *Shape of ethylene molecule*

A double bond brings the carbon atoms together. Hence, the C═C bond length in C_2H_4 is shortened to 1.34 Å. The angle ∠ HCH or ∠ HCC is 120°, the trigonal angle bond dissociation energy of C═C bond is 614 kJ/mole.

6. **Shape of Ethyne (acetylene) (C_2H_2) Molecule:** Coming again to the electronic configuration of carbon $1s^2\ 2s^1\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$ (Excited state).

Here only 2*s* and $2p_x$ orbitals take part in hybridisation. $2p_y$ and $2p_z$ orbitals remain unhybridised. Hence, it is a case of *sp* hybridisation. We have seen earlier that *sp* hybridised orbitals are oriented along the same axis at an angle of 180°. One *sp* hybridised orbital of each carbon overlaps with the 1*s*-orbital of hydrogen atom on the two sides. One *sp* hybridised orbital of each carbon overlaps with each other forming a C—C σ-bond. The unhybridised $2p_y$ orbital of one carbon overlaps laterally with the $2p_y$ orbital of the other carbon forming a π-bond. Similarly, $2p_z$ orbital of one carbon overlaps with the $2p_z$ orbital of the other carbon laterally forming another π-bond. The molecule of acetylene has a linear shape (Fig. 3.25). There is a cylinder of negative charge around C≡C bond.

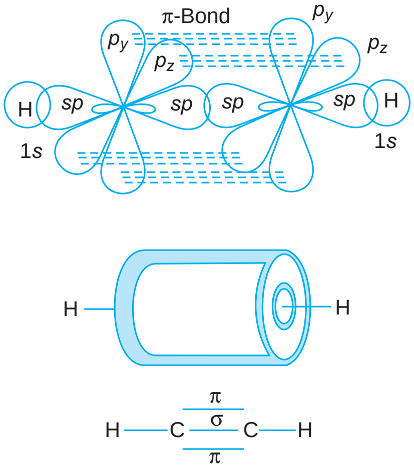


Fig. 3.25: *Shape of ethyne molecule (Linear shape)*

A triple bond is formed between carbon-carbon. But of the three bonds, one is a σ-bond and two are π-bonds. Triple bond brings carbon atoms still nearer. The bond length C≡C is 1.20 Å. Acetylene being a linear molecule, angle H — C — C is 180°. Bond dissociation energy of the C≡C bond is 811 kJ/mole.

7. **Shape of Carbon Dioxide (CO_2) Molecule:** At. No. of carbon is 6 and its electronic configuration in the excited state is: $1s^2\, 2s^1\, 2p_x^1\, 2p_y^1\, 2p_z^1$. Here, *sp* hybridisation takes place. The hybridised orbitals are oriented along the same time at an angle of 180°. $2p_y$ and $2p_z$ orbitals do not participate in hybridisation.

Coming to oxygen, its electronic configuration is:

$$1s^2\, 2s^1\, 2p_x^1\, 2p_y^1\, 2p_z^1$$

There are two such oxygen atoms in the molecule of CO_2. Two *sp* hybridised orbitals of carbon overlap with one unpaired 2*p*-orbital of each oxygen on the two sides forming two σ-bonds. And then, one unhybridised 2*p*-orbital of carbon overlaps with the other unpaired orbital of one oxygen laterally forming a π-bond. Similarly, the second unhybridised 2*p*-orbital of carbon overlaps with the other unpaired 2*p*-orbital of second oxygen atom (Fig. 3.26).

The molecule of carbon dioxide has a linear shape.

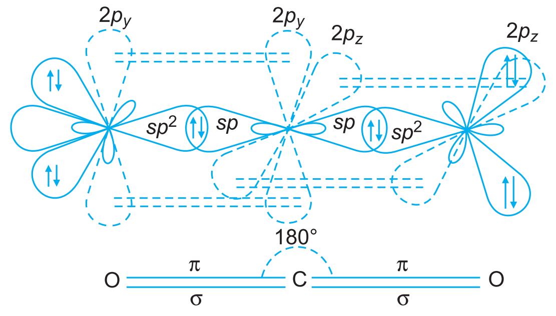


Fig. 3.26: *Shape of CO_2 molecule*

8. **Shape of Sulphur Dioxide (SO_2) Molecule:** The atomic number of sulphur is 16 and it has the electronic configuration $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p_x^2\, 3p_y^1\, 3p_z^1$ in the ground state. In the excited state, one electron from $3p_x$ orbital is shifted to 3*d* orbital so that its configuration becomes:

$$1s^2\, 2s^2\, 2p^6\, \underbrace{3s^2\, 3p_x^1\, 3p_y^1}_{\text{Hybridised}}\ \underbrace{3p_z^1\, 3d^1}_{\text{Unhybridised}}$$

Here, sp^2 hybridisation takes place. The hybridised orbitals are oriented along the corners of a triangle at an angle of 120°. One of the positions is occupied by the lone pair of electrons of 3*s*-orbital. $3p_z$ and 3*d* orbitals remain unhybridised. Sulphur is the central atom in the molecule of SO_2.

Oxygen has electronic configuration $1s^2\, 2s^2\, 2p_x^2\, 2p_y^1\, 2p_z^1$. It has two unpaired electrons which can form the bonds. Two hybridised orbitals of sulphur overlap with one 2*p* orbital of each oxygen forming a σ-bond. The other unpaired orbital of each oxygen overlaps with the unhybridised orbitals of sulphur laterally to form π-bonds as shown in Fig. 3.27.

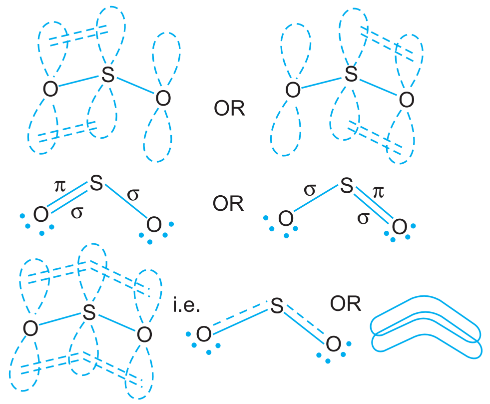


Fig. 3.27: *Shape of SO_2 molecule*

Sulphur dioxide has a bent structure or V-shape structure with an angle ∠OSO = 119.5°. This is quite close to the angle of 120° expected from sp^2 hybridisation.

9. **Shape of Phosphorus Pentachloride (PCl_5) Molecule (Trigonal Bipyramidal of sp^3d Hybridisation):** Consider the bond formation in a molecule of PCl_5. The electronic configuration of a phosphorus atom in the last orbit is $3s^2\, 3p_x^1\, 3p_y^1\, 3p_z^1$.

There are three orbitals with single electrons. This would allow the formation of only three bonds. But phosphorus forms five bonds with chlorine atoms in PCl_5. This can be explained by assuming that one electron from 3*s*-orbital is excited to 3*d* level as follows:

$$3s^1\, 3p_x^1\, 3p_y^1\, 3p_z^1\, 3d^1$$

Now there are five orbitals with single electrons which can form the bonds. But before bond formation, they will hybridise and produce equivalent orbitals. This type of hybridisation is known as sp^3d hybridisation. It is also called trigonal-bipyramidal hybridisation because out of the 5 hybridised orbitals, 3 are oriented along the corners of a regular triangle, one above the triangle and one below the triangle. Then each of the hybridised orbitals of phosphorus overlaps with a *p*-orbital of chlorine to give the molecule of PCl_5 (see Fig. 3.28 and Fig. 3.29).

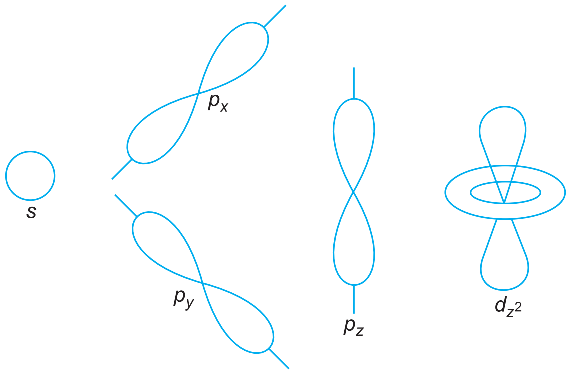


Fig. 3.28: *Formation of five sp^3d hybrid orbitals*

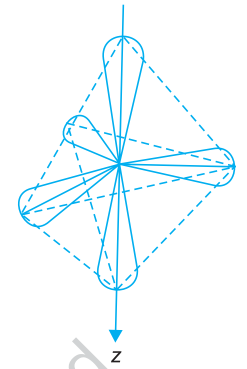


Fig. 3.29: *Orientation of sp^3d hybrid orbitals*

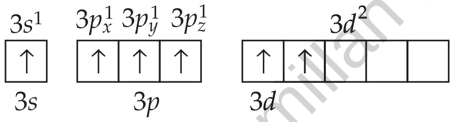
The orbitals after hybridisation are not symmetrically oriented. The three orbitals lying along the triangle form an angle of 120° with another. The orbitals above and below the plane form an angle of 90° with the orbitals in the plane. This is the reason for instability of PCl_5 molecule. This molecule has a tendency to decompose as

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

10. **Shape of Sulphur Hexafluoride (SF_6) Molecule (*sp^3d^2* or octahedral hybridisation):** Consider the molecule of SF_6. The configuration of an atom of sulphur in the outer orbit is

$$3s^2\ 3p_x^{\ 2}\ 3p_y^{\ 1}\ 3p_z^{\ 1}$$

One electron from 3*s* and one from $3p_x$ orbital are excited to *d*-orbitals to give the following configuration:



These six orbitals containing single electrons hybridise. This is known as sp^3d^2 or octahedral hybridisation because the hybridised orbitals are oriented along the corners of a octahedron as shown below in Fig. 3.30.

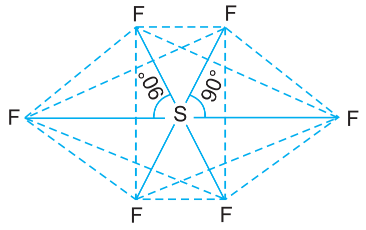


Fig. 3.30: *Arrangement of sp^3d^2 hybrid orbitals*

11. **Shape of $[Ni(CN)_4]^{2-}$ (*dsp^2* or Square Planar Hybridisation):** In certain compounds of nickel and platinum, one *d*, one *s* and two *p* orbitals hybridise. The hybridised orbitals are oriented along the corners of square (Fig. 3.31).

This is called square-planar hybridisation, $Ni(CN)_4^{2-}$ and $(PtCl_4)^{2-}$ are examples of this type of hybridisation.

Table 3.10 lists various types of hybridisations, the shapes of molecules with examples.

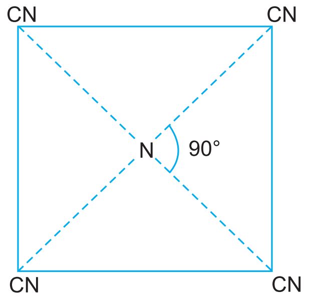


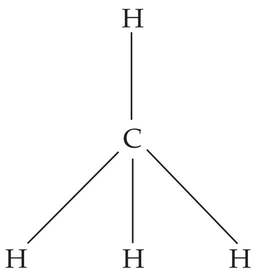
Fig. 3.31: *Orientation of dsp^2 hybrid orbitals*

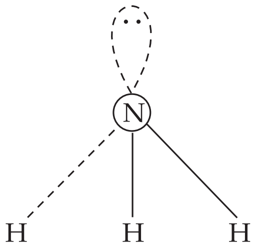
3.21.1 Formula for Predicting Type of Hybridisation and Shapes of Molecules

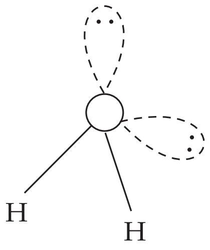
Let us represent the central atom in the molecule by A. The bonding groups may be represented by the letter

B and non-bonding groups (lone pairs of electrons) may be represented as E. We shall consider the following three examples.

AB_4 AB_3E AB_2E_2







CH_4 NH_3 H_2O

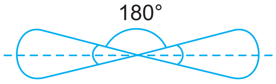
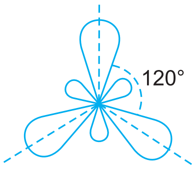
The three compounds represent the structures of the type AB_4, AB_3E and AB_2E_2 respectively.

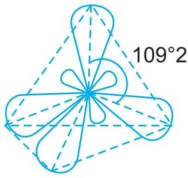
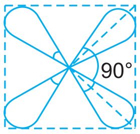
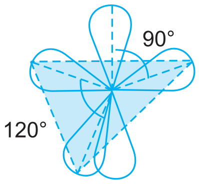
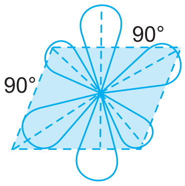
For CH_4		For NH_3		For H_2O	
No. of bonding groups	= 4	No. of bonding groups	= 3	No of bonding groups	= 2
No. of non-bonding groups	= 0	No. of non-bonding groups	= 1	No. of non-bonding groups	= 2
Total groups	= 4	Total	= 4	Total	= 4

All the three molecules considered above have the total number of bonding groups and non-bonding groups (lone pairs of electrons) equal to 4. Thus, they show sp^3 hybridisation of the central atom and the shape of the molecule is tetrahedral. Similarly, we can predict the type of hydridisation and shape of the molecule on the basis of the following table.

No. of bonding and non-bonding groups in the molecule	*Type of hybridisation*	*Shape of the molecule*
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
5	sp^3d	Trigonal pyramidal
6	sp^3d^2	Octahedral

Table 3.10: Various Types of Hybridisations and Shapes

Type of hybridisation and atomic orbitals involved	**Orientation of hybrid orbitals formed along with bond angles**	**Shape of the molecule**	**Examples**
1. *sp* (one *s* + one *p*)		Linear	$BeCl_2$, C_2H_2 and $HgCl_2$
2. sp^2 (one *s* + two *p*)		Triangular-planar	BF_3, C_2H_4 and NO_3^-

3. sp^3 (one s + three p)		Tetrahedral	CH_4, CCl_4 and $SnCl_4$
4. dsp^2 (one d + one s + two p)		Square planar	$[Ni(CN)_4]^{2-}$ and $[PtCl_4]^{2-}$
5. sp^3d (one s + three p + one d)		Trigonal bipyramidal	PF_5 and PCl_5
6. sp^3d^2 (one s + three p + two d)		Octahedral	SF_6 and $[Co(NH_3)_6]^{3+}$

3.22 POLAR MOLECULES

3.22.1 Electronegativity

One of the parameters deciding about the nature of bonds in a molecule is electronegativity.

Electronegativity *of an element is the tendency of its atom to attract the shared pair of electrons towards itself in a covalent bond.*

Consider two atoms which are not identical, *e.g.*, hydrogen and chlorine forming the covalent compound HCl. Since the electronegativity of chlorine is greater than that of hydrogen, the former attracts shared pair of electrons towards itself more than the latter. So, chlorine part of the molecule becomes slightly negative and the hydrogen part becomes slightly positive. Thus, HCl is a polar molecule which may be represented as:

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

Table 3.11 gives relative electronegativities of the elements on the Pauling's scale:

Table 3.11: Electronegativity Values of Representative Elements

Group *1*	Group *2*	Group *13*	Group *14*	Group *15*	Group *16*	Group *17*
H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl

0.9	1.2	1.5^{-}	1	2.1	2.5	3.0
K	Ca	Ga	Ge	As	Se	Br
0.8	1.0	1.8	2.0	2.0	2.4	2.8
Rb	Sr	In	Sn	Sb	Te	I
0.8	1.0	1.5	1.7	1.9	2.1	2.4
Cs	Ba	Tl	Pb	Bi	Po	At
0.7	0.9	1.4	1.6	1.9	2.0	2.2
Fr	Ra					
0.7	0.9					

3.23 POLARITY IN COVALENT BONDS

1. **Non-polar Covalent Bonds.** If two similar atoms form a bond by sharing their electrons, the shared electrons are equally attracted by the two atoms as the electronegativity of the atoms is same. In other words, the shared electrons are not displaced towards any one atom. Hence, no poles are developed. This leads to the formation of completely non-polar bond. For example, if two hydrogen atoms form a bond the electron pair lies exactly in the middle and the resultant bond is non-polar (Fig. 3.32).

   The examples of some non-polar molecules are Cl_2, O_2, N_2, etc.

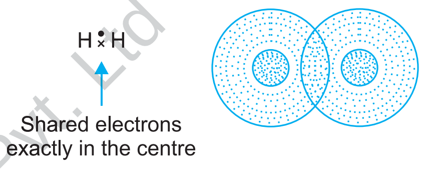


Fig. 3.32: *Non-polar covalent bond between H-atoms*

2. **Polar Covalent Bonds.** When two different atoms, having different electronegativities combine together to form a covalent bond, the shared pair of electrons does not lie at the centre but shifts towards the atom having greater electronegativity. Since the more electronegative atom attracts the electrons more strongly, the electron cloud is displaced more towards the more electronegative atom. As a result, one part of the molecule, having more electronegative atom becomes slightly negatively charged while the other part acquires slightly positive charge. Thus, positive and negative poles are developed and this type of bond is called **polar covalent bond**.

   Consider the case of hydrogen chloride molecule. Chlorine is more electronegative than hydrogen. Hence, the shared pair of electrons will be shifted towards chlorine, *i.e.*, electron density of the electron cloud is more concentrated on chlorine side than on the hydrogen side. Consequently, chlorine becomes slightly negatively charged and hydrogen becomes slightly positively charged as shown in Fig. 3.33.

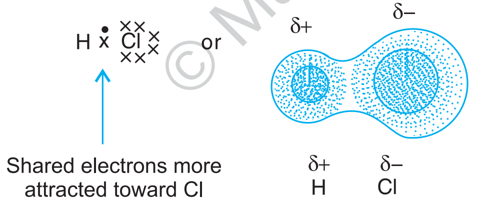


Fig. 3.33: *Polar covalent bond in HCl*

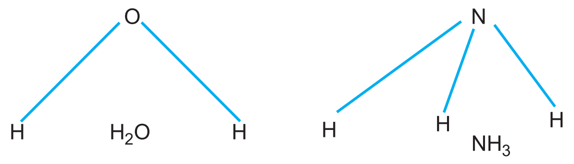


Fig. 3.34: *Polar molecules containing more than one polar bond*

Examples of some other molecules containing more than one polar bond are shown in Fig. 3.34.

It may be noted that in case of symmetrical molecules like CO_2, CCl_4 there are a number of polar bonds present yet the molecules on the whole are non-polar. This is because the polar bonds cancel the effect of one another.

3.23.1 Partial Ionic Character of Covalent Bond

If two atoms linked together have different electronegativities, the bond formed is polar. In other words, the bond is said to possess **partial ionic character**.

The extent of partial ionic character is determined by the difference in electronegativities of the combining atoms. Greater the difference in electronegativities, greater will be the ionic character. The following generalizations have been observed in this matter:

(*i*) If the electronegativity difference between two atoms is 1.9, the bond has 50% ionic character and 50% covalent character.

(*ii*) If the electronegativity difference between the two atoms is more than 1.9, the partial ionic character of the bond is more than 50% and the bond is taken as predominantly ionic.

(*iii*) If the electronegativity difference between two atoms is less than 1.9, the bond is predominantly covalent.

The following relationship between electronegativity difference and percentage ionic character has been observed:

Electronegativity difference:	0.2	0.6	0.8	1.2	1.9	2.2	2.8	3.2
Percent ionic character:	1	10	15	30	50	70	86	92

3.24 DIPOLE MOMENT

In a polar molecule, one end of the molecule is negative and the other is positive. In other words, there are two poles present in the molecule. Hence, the molecule is said to possess an electric dipole. Further, since the molecule as a whole is electrically neutral, the negative charge is always equal in magnitude to the positive charge. Such a molecule possesses dipole moment, an important property of the molecules.

The product of magnitude of negative or positive charge (q) *and the distance* (d) *between the centres of positive and negative charges is called* **dipole moment.** It is usually denoted by μ. Mathematically,

$$\mu = q \times d$$

The charge 'q' is of the order of 10^{-10} e.s.u. and the internuclear distance 'd' is of the order of 10^{-8} cm (Å), therefore, the dipole moment 'μ' is of the order of $10^{-10} \times 10^{-18}$ e.s.u. cm (Fig. 3.35). This quantity is known as one Debye and is denoted by the symbol D. Thus,

$$1 \text{ Debye (D)} = 1 \times 10^{-18} \text{ e.s.u. cm}$$

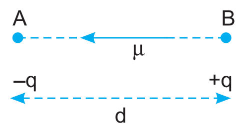


Fig. 3.35: *Dipole moment*

Dipole moment is a vector quantity and is represented by an arrow with its head pointing towards negative centre (Fig. 3.35), *e.g.*,

$$\overset{\delta+ \longrightarrow \delta-}{\text{H — F}}$$

The net dipole moment of a molecule is called molecular dipole moment and the compounds which have a definite value of molecular dipole moment are called **polar compounds**. There may be more than one polar bond in a molecule. Since dipole moment is a vector quantity, the molecular dipole moment will be the resultant of the individual bond dipole moments. Thus, whether a molecule possesses dipole moment or not, depends upon the bond dipoles. This leads to some useful informations about the geometry of molecules. For example:

In *beryllium fluoride*, Be—F bond is polar but molecular dipole moment of BeF_2 is found to be zero. This can be explained only when the two Be—F bonds are oriented in such a way that their individual bond dipoles cancel each other. Therefore, BeF_2 must be a linear molecule.

$$\delta- \longleftarrow \delta+ \longrightarrow \delta-$$
$$\text{F ——— Be ——— F}$$

Net dipole moment = 0

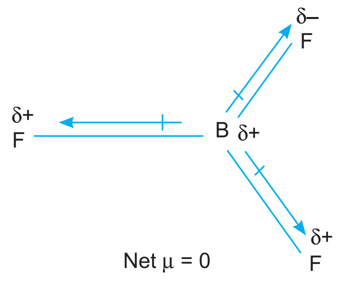


Fig. 3.36: *Dipole moments in BF_3 molecule*

Similarly, $\mathbf{BF_3}$ has a zero dipole moment, but B—F bond is polar. This indicates that the three fluorine atoms should be at the vertices of an equilateral triangle with the boron atom at the centre. In this arrangement, the bond dipole of one B—F bond will cancel the resultant of the other two (Fig. 3.36).

Water molecule is a triatomic molecule with two polar O—H bonds. It has a dipole moment which shows that it cannot be a linear molecule and must be angular (Fig. 3.37).

In a similar way, the non-polar nature of carbon dioxide and carbon tetrachloride, and polar nature of ammonia can be explained (Fig. 3.38).

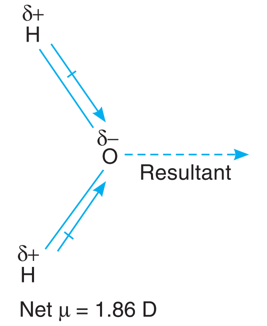


Fig. 3.37: *Dipole moments in H_2O molecule*

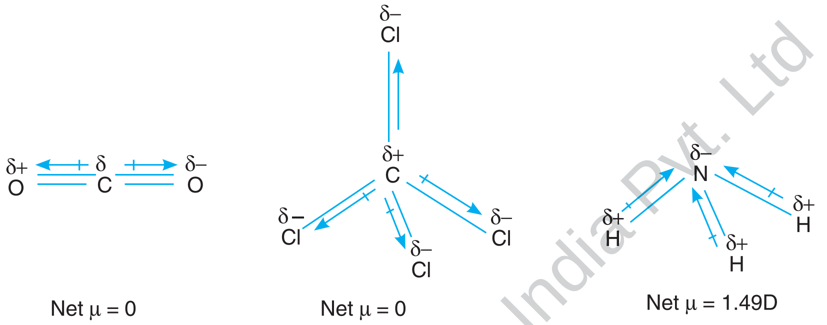


Fig. 3.38: *Dipole moments in CO_2, CCl_4 and NH_3 molecules*

3.24.1 Applications of Dipole Moment

1. **In determining the symmetry (or shape) of the molecules.** Dipole moment is an important factor in determining the shape of the molecules containing three or more atoms. For instance, if a molecule possesses two or more polar bonds, it will not be symmetrical as it possesses some molecular dipole moment. For example, in case of water (μ = 1.84 D) and ammonia (μ = 1.49 D). But if a molecule contains a number of similar atoms and the overall dipole moment of the molecule is found to be zero, this will imply that the molecule is symmetrical. For example, in case of CH_4, CCl_4, BF_3, etc. (Fig. 3.39).

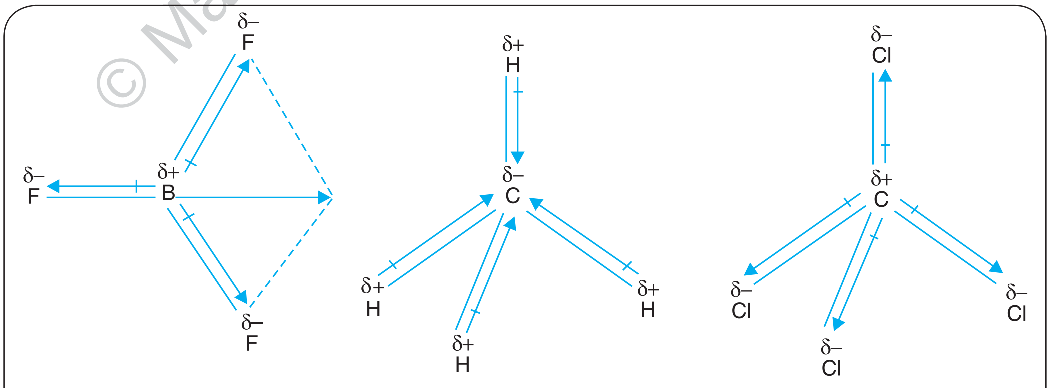


Fig. 3.39: *Zero dipole moment for symmetrical molecules*

2. **In determining the polarity of the bonds.** Dipole moment is given by the relation $\mu = q \times d$. Obviously, greater is the magnitude of dipole moment, higher will be the polarity of the bond. But in a strict sense, this concept is applicable to molecules containing only one polar bond. Dipole moment can also be used to distinguish between polar and non-polar molecules.
3. **In the calculation of percentage ionic character.** Taking the example of HCl, its dipole moment is 1.03 D. If HCl were 100% ionic, each end would carry charge equal to one unit, *viz.*, 4.8×10^{-10} e.s.u. As bond length of HCl is 1.275 Å, its dipole moment for 100% ionic character would be:

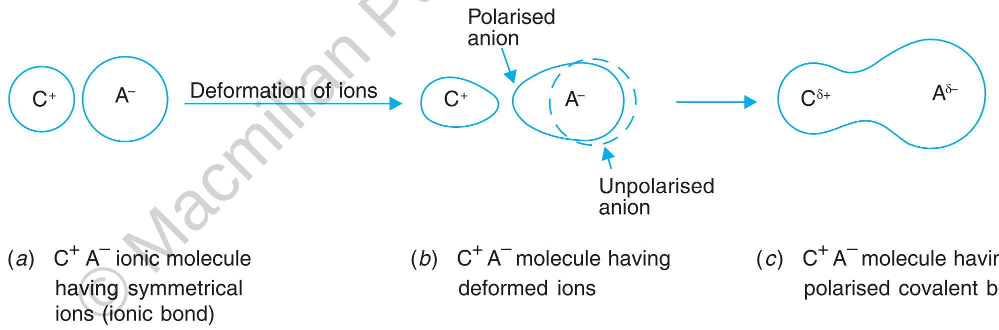
$$\begin{aligned}\mu_{\text{ionic}} &= q \times d\\ &= 4.8 \times 10^{-10} \text{ e.s.u} \times 1.275 \times 10^{-8} \text{ cm}\\ &= 6.12 \times 10^{-18} \text{ e.s.u. cm}\\ &= 6.12 \text{ D.}\end{aligned}$$

$$\therefore \quad \%\text{ ionic character} = \frac{\mu_{\text{observed}}}{\mu_{\text{ionic}}} \times 100$$

$$= \frac{1.03}{6.12} \times 100 = 16.83\%$$

3.25 PARTIAL COVALENT CHARACTER IN IONIC COMPOUNDS

When the ions C^+ and A^- of an ionic molecule, C^+A^- [Fig. 3.40(*a*)] come closer to each other, each of the ions gets distorted or polarised by the other ion. But the polarisation produced by C^+ cation in A^- anion is *appreciable* while that produced by A^- anion in C^+ cation is *negligible, i.e.*, C^+ cation is distorted by A^- anion to a smaller extent while A^- anion is distorted by C^+ cation to a larger extent [Fig. 3.40(*b*)]. This is because electrons are firmly attached to the nucleus in a cation and loosely attached in an anion. There are more protons than electrons in a cation. Reverse is the case with anions. Now C^+A^- molecule had distorted ions. *The ability of a cation to polarise a nearby anion is called its polarising power or polarising ability and the tendency of an anion to get distorted or polarised by a given cation is called its polarisability.*



(*a*) C^+A^- ionic molecule having symmetrical ions (ionic bond)

(*b*) C^+A^- molecule having deformed ions

(*c*) C^+A^- molecule having polarised covalent bond

Fig. 3.40: *Conversion of ionic bond into covalent bond*

In the polarisation process, the electrons of the anion are withdrawn by the cation towards itself. As the electrons withdrawn by the cation from the anion approach closer to the cation, the positive charge on the cation is somewhat reduced. Similarly, as the electrons of anion move towards the cation, the negative charge on the anion is also somewhat reduced. Thus, we see that due to the polarisation effect, the charges on both the ions of C^+A^- ionic molecule are reduced and there occurs a sort of sharing of electrons between C^+ and A^- ions and, consequently, the ionic bond existing between C^+ and A^- ions develop some covalent character, *i.e.*, at stage C^+A^- molecule has partial ionic bond and partial covalent bond character or in other words, C^+A^- molecule has *polarised covalent bond* [Fig. 3.40(*c*)].

Greater the amount of polarisation of A by C^+ *ion, greater is the amount of covalent character produced in* C^+—A^- ionic bond of C^+A^- ionic molecule.

3.26 FAJAN'S RULE

The conditions which bring about the maximum polarisation of anions by a given cation given by Fajan's Rules are mentioned below:

(*i*) *Charge either on cation or on anion should be large.*

(*ii*) *Cation should be small in size.*

(*iii*) *Anion should be large in size.*

(*iv*) *A cation with 18-valence-shell configuration* ($ns^2p^6d^{10}$ *configuration) like* Ag^+ *gives covalent compound while that with 8-valence-shell configuration* (ns^2p^6 *configuration) like* Na^+ *gives ionic compounds. Consider the iodides of silver and sodium AgI is covalent while NaI is ionic (Fig. 3.41). Covalent character of AgI is explained on the basis of the fact that* Ag^+ *ion, due to its 18-electron configuration* ($4s^2p^6d^{10}$) *has greater polarising power to polarise* I^- *ion than* Na^+ *ion having 8-electron configuration* ($2s^2p^6$). *The polarisation power of* Ag^+ *ion is so great that it gives covalent AgI molecule while polarising power of* Na^+ *ion is so small that it gives ionic NaI molecule.*

Fajan

Fig. 3.41: *Fajan's rule*

PROBLEMS FOR PRACTICE

1. Dipole moments are generally measured in debyes, where 1 D = 10^{-18} e.s.u. cm and 1 e.s.u. of charge is defined by 1 C = 2.998×10^9 e.s.u. What is the value of 1 debye in SI units.
   [**Ans.** 3.336×10^{-30} cm]
2. Which out of the two is more polar?
   (*i*) NH_3 (*ii*) NF_3
   [**Ans.** NH_3, because dipole moments of three N–H bonds and the lone pair add up whereas the dipole moments of three N–F bonds and the lone pair partly cancel out.]
3. The molecule of SO_2 has a dipole moment. Is the molecule linear or bent? [**Ans.** Bent]
4. Arrange the following in decreasing order of their (*i*) polarity, (*ii*) solubility in water:
   NaF, NaCl, NaBr, NaI
   [**Ans.** (*i*) NaF > NaCl > NaBr > NaI; (*ii*) NaI > NaBr > NaCl > NaF]
5. Which has greater ionic character — HF or HCl? [**Ans.** HF]
6. Which of the compounds $SnCl_2$, $SnCl_4$, SnF_2, SnF_4 and $SiCl_4$ is least covalent? [**Ans.** SnF_2]
7. The dipole moment of LiH is 1.964×10^{-29} cm and the interatomic distance between Li and H in this molecule is 1.596 Å. What is the percent ionic character in LiH? [**Ans.** 76.8%]
8. The observed dipole moment for a molecule AB is 1.45 D and its bond length is 1.654 Å. Calculate the percentage of ionic character in the bond. [**Ans.** 18.3%]

3.27 HYDROGEN BOND

A weak bond that is formed between hydrogen having a slight positive charge and an electronegative atom having a slight negative charge is called a **hydrogen bond.**

Consider the case of hydrogen fluoride H—F. There is a big electronegativity difference in hydrogen and fluorine. As a result, the shared pair of electrons is displaced towards fluorine, thus giving a slight negative charge to fluorine and a slight positive charge to hydrogen. The positive charge on hydrogen of one molecule is attracted by the negative pole of the other molecule. This effect continues indefinitely as shown below resulting in the association of hydrogen fluoride molecule.

$$.....\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}\;.....\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}\;.....\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}\;.....\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}.....$$

3.27.1 Requirements for a Hydrogen Bond

The following conditions must be satisfied in order that hydrogen forms hydrogen bond with another atoms:

1. **Electronegativity.** The other atom forming a hydrogen bond with hydrogen must be highly electronegative. Only than polarisation of the molecule is possible. It is found that fluorine which has the maximum value for electronegativity forms the hydrogen bond readily. It is followed by oxygen and nitrogen. These elements form hydrogen bond in HF, H_2O and NH_3.
2. **Size of the atom.** Electronegative atom forming a bond with hydrogen should be small in size. It is found that bigger atoms don't form hydrogen bond effectively. Thus, chlorine has an electronegativity equal to that of nitrogen, but nitrogen being smaller in size forms hydrogen bond whereas chlorine being larger in size does not form the hydrogen bond.

3.27.2 Types of Hydrogen Bonding

There are two types of hydrogen bonding:

1. **Intermolecular Hydrogen Bonding.** Intermolecular means between different molecules. When a bond is formed between different molecules of the same substance or different substances, intermolecular hydrogen bonding is said to be formed. For example in the case of hydrogen fluoride molecules, it is intermolecular hydrogen bonding. Similarly is the case of water, ammonia or alcohols, intermolecular hydrogen bonding takes place.

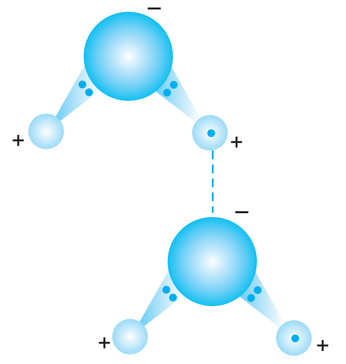
   Some Examples of Hydrogen Bonds

   1. **Hydrogen fluoride.** Hydrogen fluoride exists as shown below. The negative fluorine form a bond with positive hydrogen.

$$.....\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}\;.....\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}\;.....\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}\;.....\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{F}}\;.....$$

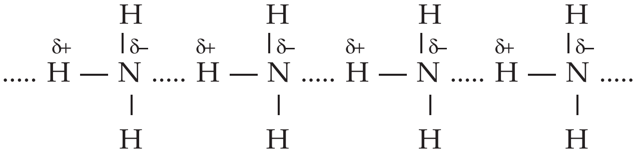
   2. **Water.** In the molecule of water, there is a slight negative charge on oxygen and slight positive charge on the hydrogen atoms. The negative oxygen forms a hydrogen bond with the positive hydrogen of the other molecule and this continues indefinitely as shown below:

$$.....\overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\delta-}{\mathrm{O}}}\;.....\overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\delta-}{\mathrm{O}}}\;.....\overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\delta-}{\mathrm{O}}}\;.....\overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\delta-}{\mathrm{O}}}.....$$



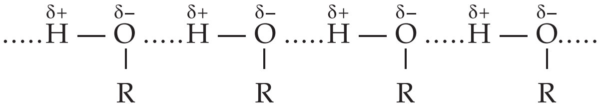
Hydrogen bonds in water molecule

3. **Ammonia.** In ammonia, the nitrogen although not highly electronegative forms a hydrogen bond because of its small size. The negative nitrogen of an ammonia molecule forms a hydrogen bond with hydrogen of another ammonia molecule as shown below:



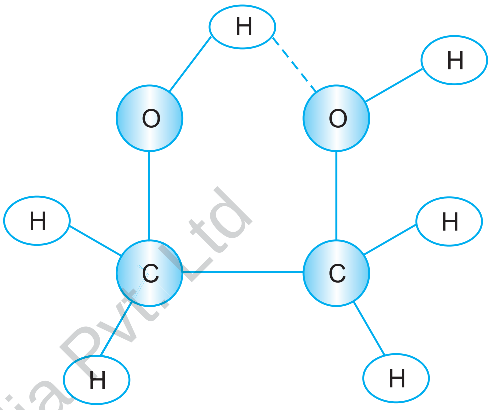
$$\cdots\cdots\ \overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}\,\delta-}{\mathrm{N}}}\ \cdots\cdots\ \overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}\,\delta-}{\mathrm{N}}}\ \cdots\cdots\ \overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}\,\delta-}{\mathrm{N}}}\ \cdots\cdots\ \overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}\,\delta-}{\mathrm{N}}}\ \cdots\cdots$$

4. **Alcohols.** The electronegative oxygen of the alcohol molecule forms a hydrogen bond with hydrogen of another alcohol molecule. This is, however, limited to lower alcohols.



$$\cdots\cdots\overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{R}}{|}}{\overset{\delta-}{\mathrm{O}}}\cdots\cdots\overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{R}}{|}}{\overset{\delta-}{\mathrm{O}}}\cdots\cdots\overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{R}}{|}}{\overset{\delta-}{\mathrm{O}}}\cdots\cdots\overset{\delta+}{\mathrm{H}}-\underset{\underset{\mathrm{R}}{|}}{\overset{\delta-}{\mathrm{O}}}\cdots\cdots$$

5. **Carboxylic Acid.** Carboxylic acids differ from the above mentioned examples in the respect that only two molecules combine together by means of hydrogen bonding forming dimers.



Intramolecular H-bonding in Ethylene Glycol molecule

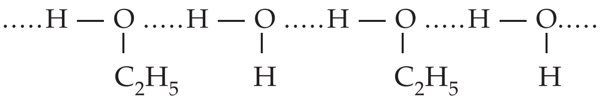
2. **Intramolecular Hydrogen Bonding.** Intramolecular means within the same molecule. Here the bonding takes place between hydrogen and some electronegative element within the same molecules. Some aromatic compounds containing two functional groups like nitrophenol, nitro-benzaldehyde and salicylic acid form intramolecular hydrogen bonding. The necessary requirement here is that the two groups should be present in ortho groups so that there is not much distance between hydrogen and the negative element.

3.27.3 Some Consequences of Hydrogen Bonding

1. **High Melting and Boiling points.** Hydrogen bond links together a number of molecules. We must spend extra energy to break these bonds. Hence, compounds having hydrogen bonding in them melt and boil at higher temperatures than expected. This accounts for the abnormally high boiling points of HF, H_2S and NH_3. Consider the hydrides of sixth group of the periodic table, *viz.*, H_2O, H_2S, H_2Se, H_2Te where all other hydrides are gases at room temperature, the hydride of oxygen, *i.e.*, H_2O is a liquid at room temperature due to hydrogen bonding. This is because of the high electronegativity and small size of oxygen.

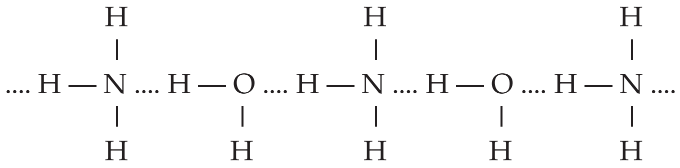
   Ethanol has a higher boiling point compared to diethyl ether although both have the same molecular mass. This is because of the reason that there is hydrogen bonding in the former and no hydrogen bonding in the latter.

2. **Solubility.** A substance will be soluble in water if it can form a hydrogen bond with water. Lower alcohols are soluble in water because they can form hydrogen bonds with water as shown below:



$$\cdots\cdots\mathrm{H}-\underset{\underset{\mathrm{C_2H_5}}{|}}{\mathrm{O}}\cdots\cdots\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{O}}\cdots\cdots\mathrm{H}-\underset{\underset{\mathrm{C_2H_5}}{|}}{\mathrm{O}}\cdots\cdots\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{O}}\cdots\cdots$$

Similarly, ammonia is soluble in water due to hydrogen bonding with water.



$$\cdots\ \mathrm{H-\underset{\displaystyle H}{\overset{\displaystyle H}{N}}}\ \cdots\ \mathrm{H-\underset{\displaystyle H}{O}}\ \cdots\ \mathrm{H-\underset{\displaystyle H}{\overset{\displaystyle H}{N}}}\ \cdots\ \mathrm{H-\underset{\displaystyle H}{O}}\ \cdots\ \mathrm{H-\underset{\displaystyle H}{\overset{\displaystyle H}{N}}}\ \cdots$$

3. **Viscosity and Surface Tension.** Substance which have hydrogen bonding in them are associated molecules. Association brings about increase in viscosity and surface tension.

   This decreases the tendency of liquids to flow. For example, glycerol ($CH_2OH—CHOH—CH_2OH$) has a greater viscosity than ethyl alcohol ($CH_3—CH_2—OH$). This is because there are three alcoholic groups in glycerol and only one alcoholic group in ethyl alcohol. Therefore, glycerol forms more hydrogen bonds than ethyl alcohol and hence, has greater viscosity. Similarly, we can explain why water is more viscous than ethyl alcohol. In alcohol molecule, the bigger C_2H_5 groups prevent formation of a strong hydrogen bond compared to water molecule. Concentrated sulphuric acid is a viscous liquid because of the formation of several hydrogen bonds.

4. **Maximum Density of Water at 277 K.** At sub-zero temperatures, water has a cage-like structure with empty spaces (Fig. 3.42). As the temperature is increased, hydrogen bonds are broken, the empty space starts filling and the density increases. This trend however, is noticed up to 277 K. Above this temperature, although the volume contraction takes place as a result of breaking of hydrogen bonds, volume expansion also takes place as a result of rise in temperature. So density starts falling, hence water has the maximum density at 277 K.

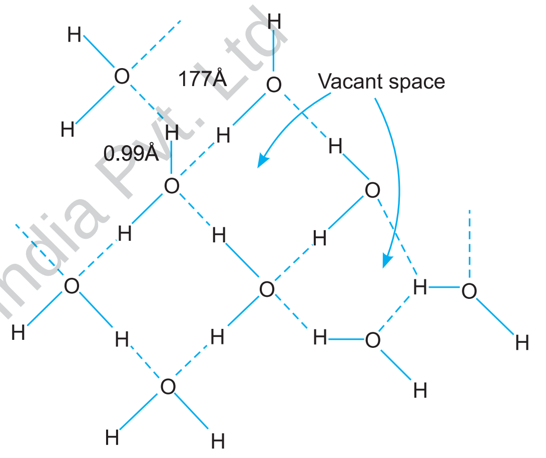
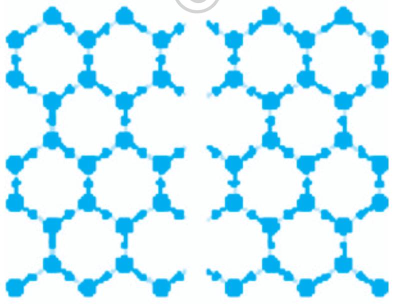


Fig. 3.42: *Cage-like structure of ice*

5. **Intramolecular Hydrogen Bonding** has the reverse effect of that of intermolecular hydrogen bonding. Whereas intermolecular bonding increases the size of the molecules, intramolecular hydrogen bonding results in the decrease of the size of the molecules. This results in lowering of m.p. and b.p. and decrease of solubility, surface tension and viscosity. There is intramolecular hydrogen bonding in the case of *o*-nitrophenol and salicylic acid (Fig. 3.43).



Structure of ice involves H-bonds

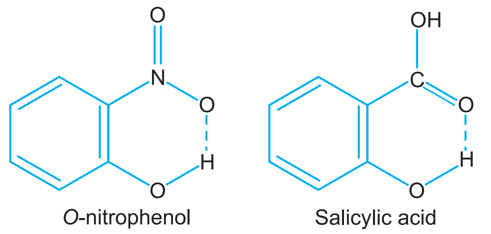
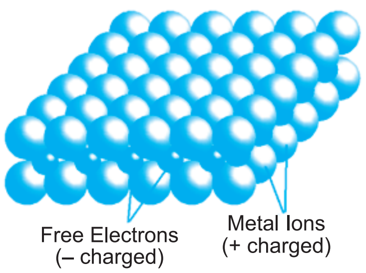


Fig. 3.43: *Intramolecular hydrogen bonding*

3.28 METALLIC BOND

The bonding between atoms in a metal is found to be different from ionic or covalent linkages. Metals generally have a low value of ionisation energy. Hence, the outer electrons, *i.e.*, electrons in the outer shell are loosely bound.These electrons are mobile and are in a state of constant motion. The **kernels,** *i.e.*, the atoms without the last orbits arrange themselves in a definite pattern called lattice with the electrons moving around them. The identity of the electrons is lost because the electrons become the common property of all the atoms. It is not possible to tell which electron belongs to which atom. This is called **electron-sea model** of the metal. The kernels are floating in a sea of electrons.



Structure of metallic copper

These electrons which are in a state of motion bind the various atoms of the metal and give rise to *metallic bond.* A metallic bond may be defined as a bond which is formed between the metal atoms with the help of the outer mobile electrons. Electron-sea model of the metals is shown in Fig. 3.44.

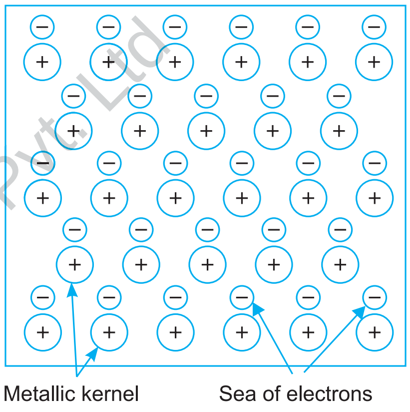


Fig. 3.44: *Electron-sea model*

The metallic bond is different from the ionic bond as the latter involves transference of electrons from one atom to the other.

Metallic bond is also different from covalent bond because the latter involves sharing of electrons between the atoms. Whereas covalent bond is directional in nature, no such property is associated with the metallic bond. Some of the properties exhibited by metals can be well explained in terms of the electron-sea model.

1. **Thermal Conductivity.** Metals are good conductor of heat. When a metal is heated from one end, the electrons present there get some extra kinetic energy. This energy is passed on to the next electron in neighbourhood which in turn passes on to the next electron. This process continues till the other end becomes hot.
2. **Electrical Conductivity.** Metals are good conductors of electricity, too. On creating a potential difference between the two ends of a metal, the free electrons move towards the positively charged end. This results in the flow of electrons through the metal (Fig. 3.45).

   Electron-sea model also explains that the electrical conductivity of the metal increases up to a certain temperature and decreases thereafter. The K.E. of the electrons increases with the increase of temperature up to a certain limit. After that the kernels are also excited to higher energy levels. As a consequence, they start vibrating and offer resistance to the flow of the electrons.

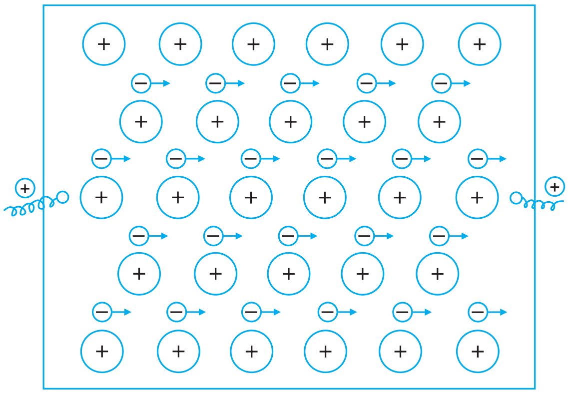


Fig. 3.45: *Electron conductivity of metals*

3. **Metallic Lustre.** Metals particularly when freshly prepared or cut reflect light, *i.e.*, they give a shine. This is called metallic lustre. This lustre is given by the metals because the surface electrons absorb the incident light and later transmit it because of which they shine.

4. **Mechanical Properties.** Metals can be beaten into thin sheets. This property is called **malleability.** They can also be drawn into thin wires. This property is called **ductility.** Both these properties can be explained on the electron-sea model of the metals (see Fig. 3.46). The positively charged kernels which are held together by weak forces can be displaced from their positions and with the help of a suitable force, these layers of kernels can be transformed into sheets or wires.

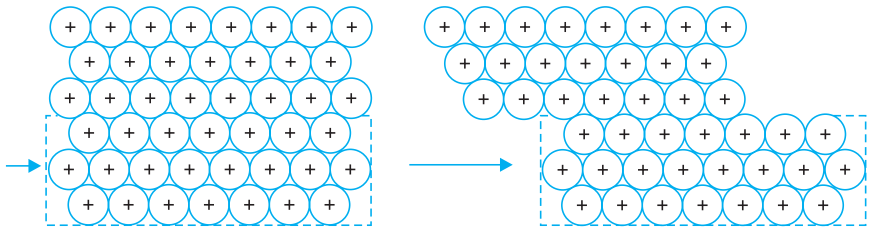


Fig. 3.46: *Mechanical properties of metals*

5. **Elasticity.** Metals can be deformed by the application of force, they come back to their original position when that force is removed. This property is called *Elasticity.* On applying in a force, the layers of kernels are displaced leading to deformation of the metals. These layers regain their position when the force is removed.
6. **Tensile Strength.** Metals have high tensile strength. They resist stretching without breaking. This is explained by strong electrostatic attraction between the positively charged kernels and the sea of electrons surrounding them. Substances which have covalent bonds do not possess high tensile strength. This is because, due to the absence of electrostatic force of attraction in the crystal, there is no oppositely charged units in the lattice in covalent compounds.

   Limitations of electron-sea model

   It cannot explain vast variation in physical properties of metals.

   For example, while mercury melts at –39ºC, tungsten melts at 3300ºC.

   Copper is fifty times better conductor of electricity than bismuth.

   Sodium and potassium are so soft that they can be cut with a knife, whereas osmium is so hard that it can scratch even glass. These observations remain unexplained by the electron-sea model of metallic bond.

   Band Model: Conductivity of metals can be better explained with the help of band model of metallic bonds.

   A conductor may conduct electricity through the movement of electrons or ions. Metallic conductors belong to the former category while the electrolytes like sodium chloride, potassium nitrate, etc. belong to the latter category.

Metals conduct electricity in solid as well as molten states. The conductivity of a metal depends upon the number of valence electrons available per atom. Clearly, greater the number of valence electrons, greater will be the conductivity. The atomic orbitals of metal atoms combine to form molecular orbitals which are so close in energy to each other that they form a kind of **band**.

If this band is partly filled or it is in continuity with a higher energy unoccupied conduction band, then the flow of electrons under an applied electric field takes place easily. Thus, the metal shows conductivity see Fig. 3.47(*a*).

If the gap between the filled valence band and next higher unoccupied band (conduction band) is large, electrons cannot jump to it. Such a substance behaves as **insulator** Fig. 3.47(*b*). There is a category of substances which exhibit a small magnitude of conductivity. Such substances are called semiconductors. In semiconductors, the gap between the valence band and conduction band is small. Therefore, some electrons jump to the conduction band and show some conductivity Fig. 3.47(*c*).

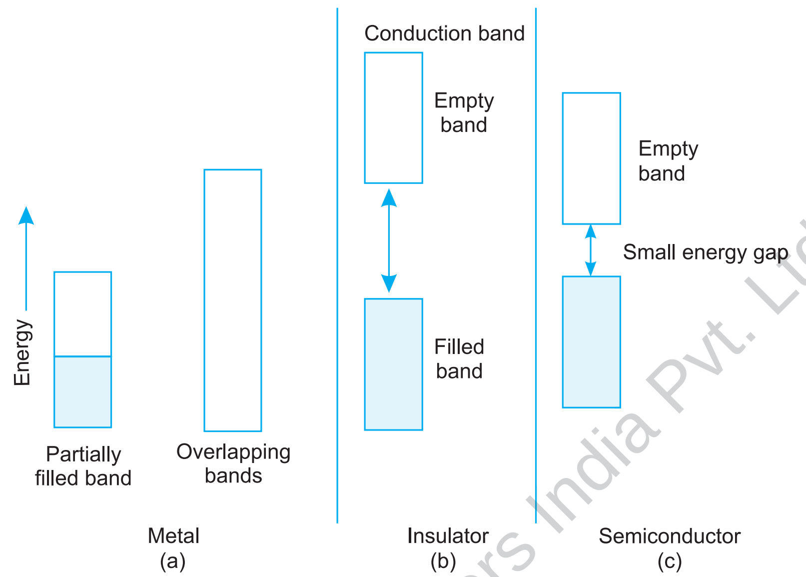
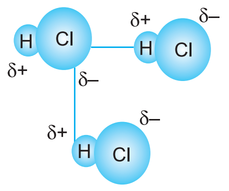


Fig. 3.47: *Distinction among (a) metals, (b) insulators and (c) semiconductors. In each case, an unshaded area represents a conduction band.*

3.29 VAN DER WAALS' FORCES

Forces of attraction exist between *neutral molecules* as well. The magnitude of these forces is maximum in case of solids and decreases on passing from solid to liquid and from liquid to gaseous states. The forces existing between the molecules of a substance are known as **intermolecular forces.** These are also designated as **van der Waals' forces.** The attractive forces which keep the molecules in position in a molecular crystal are van der Waals' forces.



van der Waal's force

The question arises, how can there be electrical attraction between neutral molecules lying close to one another? The existence of electrical repulsion between such molecules, on the other hand, can be more readily understood as these may arise from the interaction of the electron clouds of the molecules when they are in close proximity to each other.

Thus, what could be the cause of **physical forces** or **molecular attraction?** The answer is as follows:

Dipole-Dipole Interaction. In the case of **polar molecules** which have permanent dipoles, the van der Waals' forces are mainly due to electrical interaction between the dipoles known as **dipole-dipole interaction.** For instance, gases such as ammonia, sulphur dioxide, hydrogen fluoride, hydrogen chloride, etc., have permanent dipoles, as a result of which there is appreciable dipole-dipole interaction between the molecules of these gases. The magnitude of this type of interaction depends upon the dipole moment of the molecule concerned. The greater the dipole moment, the greater is the dipole-dipole interaction. Because of the attractive interaction, these gases can be easily liquefied.

Ion-Dipole Interaction. If an ionic solid is to dissolve, some energy is needed to overcome the force of inner-ionic attraction. If water is the solvent, this energy is supplied by the *interaction of water molecules with the ions.* This is known as **ion-dipole interaction.** The positive pole of the water molecules reacts with the negative ion while the negative pole reacts with the positive ion. The ion-dipole interaction results in the release of a considerable amount of energy which becomes available for the separation of the oppositely charged ions. This results in the dissolution of the solute.

But van der Waals' forces exist even in non-polar molecules such as F_2, O_2 and N_2 and even in non-polar mono-atomic molecules such as He, Ne, Ar, etc. This attraction is evident from the condensation of these gases into liquids at sufficiently high pressures and low temperatures. This is explained by London forces.

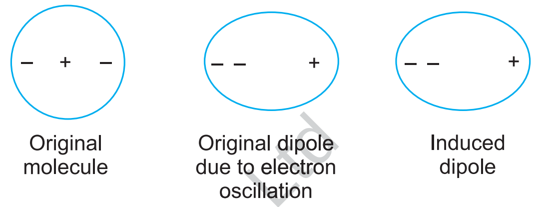


Fig. 3.48: *Origin of cohesive forces in non-polar molecules*

London Forces. In 1930, F. London provided an explanation for the existence of forces of attraction between *non-polar* molecules, based on quantum mechanics. According to this view, *electrons of a neutral molecule keep on oscillating with respect to the nuclei of the atoms. As a result of this, at a given instant, positive charge may be concentrated in one region and negative charge in another region of the same molecule. Thus, a non-polar molecule may become momentarily self-polarised.* This polarised molecule may induce a dipole moment in a neighbouring molecule, as shown in Fig. 3.48.

The electrostatic forces of attraction between induced dipoles and the original dipoles (due to electron oscillation) are known as **London forces.** These forces are also called **dispersive forces** because the well known phenomenon of dispersion of light is also connected with these dipoles. For a pair of adjacent molecules, London forces vary inversely as the *seventh power* of the distance between them, *i.e.*, $F \mu 1/r^7$. The magnitude of these forces, evidently, would be very small.

The van der Waals' attraction in *non-polar molecules* is thus *exclusively* due to London forces. In the case of polar molecules having permanent dipoles, however, other electrostatic forces due to dipole-dipole interaction also contribute towards the van der Waals' attraction.

Factors determining van der Waals' forces. van der Waals' forces depend largely on the following factors:

1. **The Number of Electrons present in a Molecule.** van der Waals' forces increase with increase in the number of electrons in the molecule. Thus, boiling points (T_b) of the halogens increase as we move from fluorine to chlorine, bromine and iodine. Similarly, boiling points of noble gases increase as we move from helium to radon, as shown below:

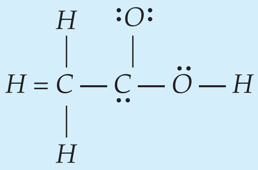
Noble gas	He	Ne	Ar	Kr	Xe	Rn
Boiling point (K)	4.1	27	67.2	121	165	211.2

2. **Molecular Size.** The larger the molecular size (or roughly the larger the molar mass), the stronger the van der Waals' forces. Thus, the boiling point of ethane, C_2H_6 (185 K) is higher than that of methane, CH_4 (112 K). In compounds having similar structures, *viz.*, CH_4, SiH_4 and GeH_4, the boiling points increase with increase in the number of electrons and the size of the molecule, as shown below:

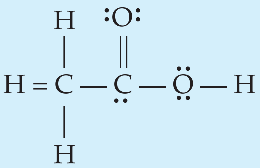
Substance	CH_4	SiH_4	GeH_4
No. of electrons	10	18	36
Boiling point (K)	112	161	183

MISCELLANEOUS SOLVED QUESTIONS

1. *The skeletal structure of CH_3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid.*

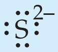
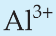


Solution.



2. *Write Lewis symbols for the following atoms and ions: S and S^{2-}, Al and Al^{3+}, H and H^-*

Solution.

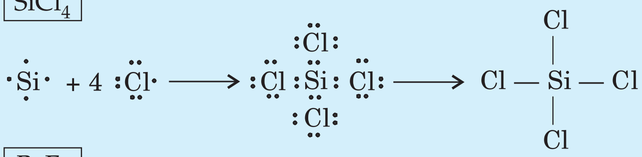
Atoms/Ions	Lewis dot symbol
S	
S^{2-}	
Al	
Al^{3+}	
H	
H^-	

3. *Draw the Lewis structures for the following molecules and ions:*
H_2S, $SiCl_4$, BeF_2, CO_3^{2-}, HCOOH

Solution. Lewis dot structure of:

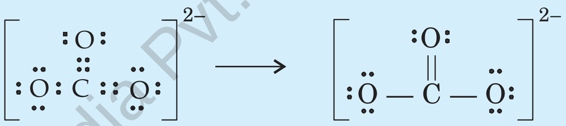
$\boxed{H_2S}$

$\boxed{SiCl_4}$

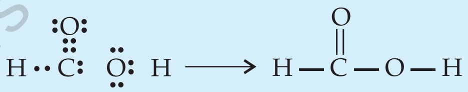


$\boxed{BeF_2}$

$\boxed{CO_3^{2-}}$

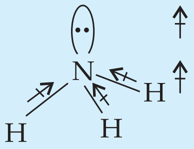


$\boxed{HCOOH}$

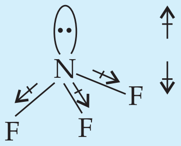


4. *Which out of NH_3 and NF_3 has higher dipole moment and why?*

Solution. NH_3 has higher dipole moment



(They are added up)



(They cancel the net effect)

QUICK SCAN (FOR REVISION)

1. Atoms of different elements combine with each other to complete their octets (duplet in case of H, Li).
2. The common valency of an element is equal to the number of electrons in the valency shell (if it is ≤ 4) or 8 minus this number (if it is > 4).
3. The electrovalency of an element is the number of electrons lost or gained during the formation of electrovalent/ionic compound.
4. A difference of 1.9 in electronegativities of the atoms is necessary for the formation of ionic bond.
5. An ionic compound is formed between an element having low ionization energy and an element having high electron affinity provided further that the lattice energy of the compound formed is high.
6. Ionic compound is formed if: Lattice energy + Electron affinity > Ionization energy.
7. Most predominant ionic bond is formed by Cs and F in CsF (lowest I.E. and highest E.A.).
8. Greater the charge and smaller is the size of ions, greater is the lattice energy.
9. Ionic compounds do not contain molecules but are made up of ions whereas covalent compounds are molecular.

10. Ionic compounds are solids whereas covalent compounds are solid, liquid or gaseous.
11. Ionic compounds have high melting and boiling points due to strong electrostatic forces of attraction among the ions. Covalent compounds have low melting and boiling points.
12. The energy released when required number of oppositely charged ions in the gaseous state form one mole of ionic solid is called lattice energy.

    The energy required to break one mole of ionic solid into gaseous ions separated at infinite distance is called lattice energy.
13. Ionic compounds are soluble in water or any polar solvent whereas covalent compounds are insoluble in water but soluble in non-polar solvents like benzene, CCl_4, ether, etc.
14. Ionic bond has no direction, hence, ionic compounds do not show space isomerism.
15. Covalent compounds have directional characteristic but ionic compounds are non-directional.
16. Some electron deficient compounds, *i.e.*, in which the central atom has less than 8 electrons are $BeCl_2$, BF_3 and $AlCl_3$.
17. Some compounds in which central atom has expanded octet, *i.e.*, more than 8 electrons are PCl_5, SF_6 and IF_7.
18. A covalent bond is formed by the overlap of half-filled atomic orbitals containing electrons with opposite spin.
19. Maximum no. of covalent bonds formed between two atoms never exceeds three.
20. No covalent bond is formed by two helium atoms because they have fully filled orbitals and when they approach each other, the forces of repulsion are greater than the forces of attraction.
21. Covalent bond is directional, therefore, covalent compounds exhibit space isomerism.
22. Due to unequal sharing of electron pair, covalent bond develops partial ionic character.
23. Generally, covalent bond is weaker than ionic bond.
24. Order of repulsion between various electron pairs are: lone pair – lone pair > lone pair – bond pair > bond pair – bond pair.
25. If electronegativity difference between two combining atoms is 1.9, bond has 50% ionic and 50% covalent character. If it > 1.9, ionic character > 50% and bond is taken as ionic. If it is < 1.9, ionic character < 50% and the bond is taken as covalent (*e.g.*, bond between Li and F is ionic but between Li and Cl or Br or I, it is covalent).
26. The units of dipole moment are Debye:

    ($1D = 10^{-18}$ e.s.u. cm)
27. Dipole moment/polar character is in the order:

    $H - F > H - Cl > H - Br > H - I$.
28. Unsymmetrical molecules like H_2O and NH_3 have some resultant dipole moment (*e.g.*, μ for $H_2O = 1.84$ D, μ for $NH_3 = 1.49$ D).
29. Linear molecules like CO_2, CS_2 and BeF_2 have net dipole moment = 0. Similarly, symmetrical molecules like BF_3, CH_4, CCl_4, etc., have net dipole moment = 0.
30. From the value of dipole moment, % ionic character of a covalent bond can be calculated.

    $$\text{Percentage ionic character} = \frac{\mu_{\text{obs.}}}{\mu_{\text{theo.}}} \times 100$$
31. CO molecule is linear. Its μ value is greater than expected because of the presence of a dative bond.
32. Bond angles: $$\underset{104.5^\circ}{H_2O} > \underset{92.1^\circ}{H_2S} > \underset{91^\circ}{H_2Se} > \underset{90^\circ}{H_2Te}$$

    Reason: Size of O < S < Se < Te;

    Electronegativity: O > S > Se > Te.
33. The shape of BF_3, C_2H_4, NO_3^- ion and CO_3^{2-} ion is triangular-planar.
34. The shape of $SnCl_4$ and NH_4^+ is tetrahedral.
35. The *d*-orbital taking part in dsp^2 hybridisation is, $d_{x^2-y^2}$ that in sp^3d hybridisation it is d_{z^2} and sp^3d^2, the *d*-orbitals involved are d_{z^2} and $d_{x^2-y^2}$.

EXERCISES

Very Short Answer Type Questions

1. What is a covalent bond?
2. What are the shapes of BCl_3 and NH_3?
3. What is a chemical bond?
4. Indicate the type of bonding in CaO, CO_2 and NH_3.
5. Is the bond formation exothermic or endothermic?
6. What is octet rule?
7. Why each molecule has a definite geometry?
8. What is meant by geometry of a molecule?
9. Why water molecules remain associated in liquid water?
10. Define electronegativity.
11. Name the type of overlapping and type of bond in forming HF molecule.
12. What is dipole moment? Give its units.
13. Give the number of electrons which occupy the bonding orbitals in H_2 and O_2 molecules.
14. What type of hybridisation is involved in SF_6?
15. Write the state of hybridisation of nitrogen in NO_3^- ion.

16. Write the state of hybridisation of boron in BF_3.
17. Write the number of unpaired electron(s) present is an atom of an element with atomic number 21.
18. On being passed through water, PH_3 forms bubbles but NH_3 dissolves. Why is it so?
19. Explain why H_2S is a gas while H_2O is a liquid even though both S and O belong to the same group in the periodic table.
20. How do you explain the electrical conductivity of metals based on electron-sea model?
21. Explain why concentrated H_2SO_4 is a thick viscous liquid.
22. Explain the lustre in metals.
23. What are van der Waals forces between atoms?
24. Write the shape of NH_4^+.

Short Answer Type Questions

1. What is octet rule? What are its limitations?
2. Explain as to why two hydrogen atoms form H_2 molecule but not the molecules such as H_3, H_4, etc.
3. Explain the terms electrovalency and covalency.
4. What are the necessary conditions for the formation of a covalent bond?
5. What is meant by the term geometry of a molecule? Explain why each molecule has a definite geometry.
6. Explain why He_2 is not formed.
7. Explain giving reasons, which of the following molecules have electric dipoles?
   (*a*) CF_4
   (*b*) CHF_3
   (*c*) CH_2F_2
   (*d*) CH_3F
   (*e*) CH_4
8. Write the differences between σ and π bond.
9. Explain the formation of H_2 molecule on the basis of valence bond theory.
10. If N, C and O all employ sp^3 hybrid orbitals in NH_3, CH_4 and H_2O, what reasons can you advance for NH_3 and H_2O being polar while CH_4 being non-polar?
11. (*a*) Define dipole moment. How does this help to predict the geometries of H_2O and CO_2?
    (*b*) Is it possible for the non-polar molecules to have polar bonds?
    (*c*) Name two molecules that have dipole moment.
12. Carbon has electronic configuration $1s^2\ 2s^2\ 2p^2$. How will you justify its tetravalency in methane?
13. What is meant by electronegativity? How does electronegativity help in predicting the polar and non-polar character of a covalent bond? Illustrate your answer with examples.
14. What important characteristics should M and X have so that they form a predominantly ionic compound MX?
15. Define an electrovalent linkage. What are the necessary conditions for the formation of ionic bond? Give two examples of ionic compounds.
16. HCl gas is a covalent compound but its water solution conducts electricity. Why?
17. Electrovalent compounds are soluble in water whereas covalent compounds are mostly insoluble in water. Why?
18. The melting points of electrovalent compounds are higher than the melting points of covalent compounds. Why?
19. Account for the difference in boiling point (ºC) of LiF: 1717; Li_2O: 2563; MgO: 3260.
20. How will you account for the fact that in metals the atoms are held neither by ionic bonds nor by covalent bonds?
21. Explain why NaCl is a better conductor in the molten state than in the solid state?
22. Draw electron dot representation of (*i*) acetylene and (*ii*) carbon tetrachloride.
23. Arrange the following in order of increasing strength of hydrogen bonding: O, F, S, Cl and N.
24. Which hybridisation is presumed for P in PF_5 and S in SF_6? Give reasons for your answer.
25. Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals.
26. Use molecular orbital theory to explain why Be_2 molecule does not exist.

Long Answer Type Questions

1. Discuss the shapes of BeF_2, H_2O, NH_3, O_2 and CH_4 on the basis of orbital overlap.
2. What do you understand by tetrahedral, pyramidal, trigonal bipyramidal and octahedral structures? Explain giving suitable examples.
3. Explain the formation of hydrogen molecule on the basis of electrostatic interactions. Explain why He_2 is not formed.
4. What is hydrogen bond? What are the conditions for hydrogen bonding? Give two examples each of intermolecular and intramolecular hydrogen bonding.

5. What is electron gas model for metallic bonding? On the basis of electron gas model, how will you account for the following:
   (*i*) Metals are good conductors of heat and electricity.
   (*ii*) Metals are malleable and ductile.
6. What are Van der Waals' forces? What is the origin of these forces? What are the factors on which the magnitude of Van der Waals' forces depend?
7. Define hybridisation. Describe the geometry of sp^3, sp^2 and sp hybrid orbitals of carbon atom and give at least one example of a molecule in each case having different types of orbitals in it.
8. Represent the bonding of the atoms in hydrochloric acid, hypochlorous acid (HClO), chloric acid ($HClO_3$) and perchloric acid ($HClO_4$).
9. (*a*) Which among the following compounds are expected to have fairly high dipole moments?
   Benzene, chlorobenzene, methane and methyl chloride.
   (*b*) N_2O is a linear molecule and has permanent dipole. Draw the electron dot structure of the molecule distinguishing the electrons of each atom.
10. When an element in the first group of the periodic table reacts with an element in the seventh group, what is the type of bond that is likely to be formed?
11. NaCl and urea (H_2NCONH_2) are soluble in water. NaCl solution is a conductor of electricity while urea is not. Explain.
12. Calcium chloride and calcium fluoride are both ionic compounds. Why is calcium fluoride sparingly soluble in water while calcium chloride is very soluble?
13. Among the following, NaCl, CCl_4, HCl and CH_4, which is a polar compound?
14. Give one example each of a planar, tetrahedral, pyramidal and trigonal bipyramidal molecule.
15. Methane, ammonia and water have same hybridisation, sp^3 but the bond angles in methane (109.5°), ammonia (107°) and water (104.5°) are different. Give a suitable reason for this.
16. Draw the electron dot diagram or any other suitable representation of chloric acid and hypochlorous acid.
17. (*a*) Mention the hybridisation of the central atom in ammonia, water and methane molecules. Arrange them in the order of increasing bond angle. Give reason.
    (*b*) Arrange the following in bond order of increasing stability:
    O_2, O_2^-, O_2^{++}, O_2^+, O_2^{--}
18. (*a*) The density of ice is less than that of water. Explain.
    (*b*) Draw the structure of sulphur hexafluoride molecule. Mention the hybridisation of central atom and the shape of the molecule.
19. Calculate the bond order of Li_2, C_2, N_2 and O_2.

ANSWERS TO SELECTED QUESTIONS

Very Short Answers Type Questions

2. Trigonal and Pyramidal
4. CaO : Ionic, CO_2 : Covalent, NH_3 : Covalent.
5. Exothermic
11. Axial overlapping (*s-p*), σ-bond
13. 2 and 10.
14. sp^3d^2.
17. At. no. 21, configuration $4s^2\ 3d^1$, unpaired electrons = 1.
18. NH_3 forms hydrogen bonds with water and, hence, dissolves. PH_3 does not form hydrogen bonds.
19. There is intermolecular hydrogen bonding between water molecules which raises the boiling point of water.
20. Electric charge is passed on from one end to the other with the help of mobile electrons.
21. There is hydrogen bonding between the molecules of H_2SO_4 and between water and H_2SO_4 molecules which makes it viscous.
22. The surface electrons on the metal surface absorb the incident light and later transmit it because of which the metal shines.

SUBJECTIVE PROBLEMS

Problem 1. *Out of NaCl and MgO, which has higher lattice energy and why?*

Solution. MgO has higher lattice energy because each ion carries two unit charge, whereas in NaCl, each ion carries one unit charge.

Problem 2. *Which bond do you expect to be stronger in each of the following cases and why?*

(*i*) H_2, Cl_2 (*ii*) O_2, N_2 (*iii*) F_2, Cl_2

Solution.

(*i*) H–H is stronger because of smaller size of H-atoms.

(*ii*) $N \equiv N$ is stronger because it contains a triple bond while O_2 contains a double bond (O = O).

(*iii*) Cl – Cl is stronger because repulsions between the two F-atoms in F_2 are stronger as compared to those between two Cl-atoms in Cl_2. The electron density in F-atom is greater due to smaller size and, hence, greater repulsion between the two F-atoms.

Problem 3. *Arrange the following compounds in the order of increasing melting points:*

(*i*) *LiF, LiCl, LiBr and LiI.*

(*ii*) *LiCl, NaCl, KCl, RbCl and CsCl.*

Solution.

(*i*) Greater the electronegativity difference between the two concerned atoms, greater would be ionic character and higher the melting points.

LiF > LiCl > LiBr > LiI

(*ii*) Due to covalent character, LiCl has lower melting point. Therefore, LiCl > NaCl > KCl > RbCl > CsCl.

Problem 4. *Two equal and opposite charges* ($\pm q = 1.6 \times 10^{-19}$ C) *are separated by a distance of 0.15 nm. Compute the dipole moment in SI as well as debye units.*

Solution.

$$\begin{aligned} \text{Dipole moment } \mu &= \text{Charge } (q) \times \text{Distance } (r) \\ &= (1.6 \times 10^{-19}\text{ C}) \times (0.15 \times 10^{-9}\text{ m}) \\ &= 2.40 \times 10^{-29}\text{ cm} \\ \because \quad \text{I.D.} &= 3.335 \times 10^{-30}\text{ cm} \\ \mu &= 2.40 \times 10^{-29} \div 3.335 \times 10^{-30} \\ &= 7.196\text{ D.} \end{aligned}$$

Problem 5. *The H – Cl bond is covalent polar and its dipole moment is 1.0 debye. From this information compute the ionic character of H – Cl bond, if H – Cl bond length is 127 pm.*

Solution. Dipole moment is the measure of the ionic character of a compound. The ionic character is related to dipole moment as under:

$$\text{Ionic character} = \frac{\mu\,(\text{Actual})}{\mu\,(\text{Theoretical})}$$

Now, in case of complete transfer of electron the charge on each end of the dipole should be unity.

$$\begin{aligned} \text{A unit charge} &= 1.602 \times 10^{-19}\text{ coulomb. Thus:} \\ \mu\text{ (Theoretical)} &= \text{Theoretical charge} \times \text{Bond length} \\ &= 1.602 \times 10^{-19}\text{ C} \times 127 \times 10^{-12}\text{ m} \\ &= 2.03 \times 10^{-29}\text{ cm} = 6.08\text{ D.} \end{aligned}$$

$$\therefore \quad \text{Ionic character} = \frac{\mu\,(\text{Actual})}{\mu\,(\text{Theoretical})}$$

$$= \; = 0.164.$$

The percentage ionic character of H–Cl bond

$$= 0.164 \times 100 = 16.4.$$

Problem 6. *Arrange the following in the increasing order of their covalent character:*

(*i*) *NaCl, $MgCl_2$ and $AlCl_3$.*

(*ii*) *LiCl, LiBr and LiI.*

Solution.

(*i*) The covalent character increases in a period. The smaller the size of the cation, the higher would be the covalent character. Thus, covalent character increases in the order : NaCl < $MgCl_2$ < $AlCl_3$.

(*ii*) The covalent character increases in a group due to increase in the size of the anion. Thus, variation of covalent character shows the order: LiCl > LiBr > LiI.

Problem 7. *The effect of increase in temperature on the conductance of metallic conductors is opposite to that of electrolytic conductors. Discuss giving reasons for this behaviour.*

Solution. The metallic conductance decreases while electrolytic conductance increases with the increase of temperature. It is because increase in temperature, increases the mobility of ions of the molten electrolyte or the ions in a solution. Moreover, the viscosity of the solution is decreased with the increase in temperature, thus the ions in the solution experience less resistance and conduct more current at higher temperature. On the other hand, the increase of temperature increases the movement of the kernels in the metals which offers more resistance to the flow of electrons, thereby reducing metallic conduction.

Problem 8. *Which of the following have net dipole moment?*

(*i*) H_2O (*ii*) CO_2 (*iii*) CH_4

(*iv*) $CHCl_3$ (*v*) CCl_4 (*vi*) BHF_3

(*vii*) SO_2 (*viii*) CH_2Cl_2

Solution. (*i*), (*iv*), (*vii*) and (*viii*).

Problem 9. *Which of the following sets of molecules have regular geometry?*

(*i*) CCl_4, CH_4, CF_4 (*ii*) NH_3, PH_3, AsH_3

(*iii*) SF_6, SiF_4, BF_3 (*iv*) PCl_5, PF_5, PCl_3

Solution. (*i*) and (*iii*).

Problem 10. *Differentiate between metallic bond and covalent bond.*

Solution.

Metallic bond	*Covalent bond*
1. This bond is due to attractive interactions between the mobile electrons and cores (or kernels) in a metallic crystal.	1. This bond is formed by the mutual sharing of electrons between two atoms of same or different elements.
2. Metals are generally solids with the exception of mercury which is a liquid.	2. Covalent compounds are solids, liquids or gases.
3. It is a weaker bond due to weak interactions between the mobile electrons and cores.	3. It is a stronger bond as shared pair of electrons are firmly held by the nuclei of bonded atoms.
4. Metallic bond is non-directional in nature.	4. Covalent bond is directional in nature.
5. Metals are good conductors of electricity.	5. Compounds containing covalent bonds are poor conductors of electricity.

Problem 11. *Differentiate between metallic bond and ionic bond.*

Solution.

Metallic bond	*Ionic bond*
1. This bond is due to simultaneous attractive interactions between the mobile electrons and cores (or kernels) in a metal crystal.	1. This bond is formed by the complete transference of valence electrons of one atom to the other atom.
2. It is a weaker bond.	2. It is a stronger bond.
3. Metals are malleable due to metallic bond.	3. Ionic compounds are brittle in nature due to ionic bond.
4. Metallic bond is responsible for making the metals conducting in the solid state.	4. Compounds containing ionic bonds are bad conductors of electricity in the solid state.

Problem 12. *Why glucose, fructose, sucrose, etc., are soluble in water though they are covalent compounds?*

Solution. These compounds contain –OH groups which can form H-bonds with water.

Problem 13. *What type of interparticle forces are present in the following?*

(*i*) *Diamond*	(*ii*) *Rock salt*
(*iii*) *Brass*	(*iv*) *Dry ice (solid* CO_2*)*
(*v*) *Mercury*	(*vi*) *Ice.*

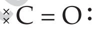
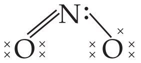
Solution.

(*i*) Covalent bonds
(*ii*) Electrostatic bonds (ionic bonds)
(*iii*) Metallic bonds
(*iv*) van der Waals' forces
(*v*) Metallic bonds
(*vi*) H-bonds.

Problem 14. *Identify the atoms in each of the following compounds which do not obey the octet rule:*

(*i*) *NO* (*ii*) *CO* (*iii*) NO_2 (*iv*) O_2^-

Solution. The structures of these molecules show that these are odd electron molecules. The atoms not obeying octet rule are given against each formula.

(*i*) Nitric oxide (NO):		(N and)
(*ii*) Carbon monoxide (CO):		(C)
(*iii*) Nitrogen dioxide (NO_2):		(N and O)
(*iv*) Superoxide ion (O_2^-):		(O)

Problem 15. *Out of P–F, F–F, S–F and Cl–F bonds, which bond is the least ionic?*

Solution. The ionic character of any bond depends upon the difference in electronegativity between the two atoms. Knowing that electronegativity of F, Cl, S and P is in the order F > Cl > S > P, the least ionic bond would be F–F.

Problem 16. *Explain the following :*

(*i*) AlF_3 *is a high melting solid whereas* SiF_4 *is a gas.*
(*ii*) H_2S *having high molecular weight is a gas whereas* H_2O *is a liquid.*

Solution.

(*i*) AlF_3 is an ionic solid due to large difference in electronegativities of Al and F, whereas SiF_4 is a covalent compound and, hence, there are only weak van der Waals' forces among their molecules.

(*ii*) There is hydrogen bonding in H_2O but no hydrogen bonding H_2S.

Problem 17. *Indicate whether the following statement is true or false. Justify your answer in not more than three lines:*

The dipole moment of CH_3F *is greater than that of* CH_3Cl*.*

Solution. This is because C–F bond is more polar than C–Cl bond due to greater electronegativity of F and Cl.

Problem 18. *Give reason for the following:*

The molecule of $MgCl_2$ *is linear while that of stannous chloride is angular.*

Solution. E.C. of $_{12}Mg$ is $1s^2\ 2s^2\ 2p^6\ 3s^2$ in the ground state. Hence, in the excited state, it is $1s^2\ 2s^2\ 2p^6\ 3s^1\ 3p^1_x$. It undergoes sp^2-hybridisation. The two half-filled hybrid orbitals form bonds with Cl-atoms while the third is occupied by a lone pair. Hence, $SnCl_2$ is bent or V-shaped.

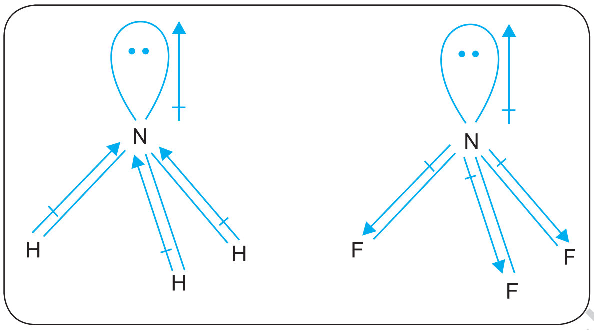
Problem 19. *Account for the following:*

The experimentally determined N–F bond length in NF_3 is greater than the sum of the single covalent radii of N and F.

Solution. This is because both N and F are small and hence have high electron density. So they repel the bond pairs thereby making the N–F bond length larger.

Problem 20. *Explain why the dipole moment of NH_3 is more than that of NF_3?*

Solution. The electronegativity difference between N and H (3.0 – 2.1 = 0.9) and between N and F (4.0 – 3.0 = 1.0) is nearly the same, but the dipole moment of NH_3 is much larger than that of NF_3. This is because of different directions of the bond moments of N–H and N–F bonds. In case of NH_3, N is more electronegative but in case of NF_3, F is more electronegative. Thus, in NH_3, the dipole moments of N–H bonds are in the same direction as that of the lone pair but in NF_3, the dipole moments of N–F bonds oppose that of the lone pair.



OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. Amongst H_2O, H_2S, H_2Se and H_2Te, the one with the highest boiling point is
   (*a*) H_2O because of hydrogen bonding.
   (*b*) H_2Te because of higher molecular weight.
   (*c*) H_2S because of hydrogen bonding.
   (*d*) H_2Se because of lower molecular weight.
2. Maximum dipole moment will be of
   (*a*) $C_2H_2Cl_2$ (*b*) $CHCl_3$
   (*c*) CH_3Cl (*d*) CCl_4
3. Number of lone pair(s) in $XeOF_4$ is/are
   (*a*) 0 (*b*) 1
   (*c*) 2 (*d*) 3
4. The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5 D) is larger than that of NF_3 (0.2 D). This is because
   (*a*) in NH_3 the atomic dipole and bond dipole are in the opposite directions whereas in NF_3 these are in the same direction.
   (*b*) in NH_3 as well as in NF_3 the atomic dipole and bond dipole are in the same direction.
   (*c*) in NH_3 the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in the opposite directions.
   (*d*) in NH_3 as well as in NF_3 the atomic dipole and bond dipole are in the opposite directions.
5. In which of the following molecules/ions are all the bonds not equal?
   (*a*) SF_4 (*b*) SiF_4
   (*c*) XeF_4 (*d*) BF_4^-
6. In which of the following molecules are all the bonds not equal?
   (*a*) NF_3 (*b*) ClF_3
   (*c*) BF_3 (*d*) AlF_3
7. The decreasing values of bond angles from NH_3 (106°) to SbH_3 (101°) down the group-15 of the periodic table is due to
   (*a*) increasing bond-bond pair repulsion.
   (*b*) increasing *p*-orbital character in sp^3.
   (*c*) decreasing lone pair-bond pair repulsion.
   (*d*) decreasing electronegativity.
8. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}?
   (*a*) $Ca^{2+} < Mg^{2+} < Be^{+} < K^{+}$
   (*b*) $Mg^{2+} < Be^{2+} < K^{+} < Ca^{2+}$
   (*c*) $Be^{2+} < K^{+} < Ca^{2+} < Mg^{2+}$
   (*d*) $K^{+} < Ca^{2+} < Mg^{2+} < Be^{2+}$
9. Which of the following hydrogen bonds is the strongest?
   (*a*) O—H.....F (*b*) O—H.....H
   (*c*) F—H.....F (*d*) O—H.....O
10. What is the dominant intermolecular force or bond that must be overcome in converting liquid CH_3OH to a gas?
    (*a*) Dipole-dipole interaction
    (*b*) Covalent bonds
    (*c*) London dispersion force
    (*d*) Hydrogen bonding
11. In which of the following molecules/ions BF_3, NO, NH and H_2O, the central atom is sp^2 hybridised?
    (*a*) NH and H_2O (*b*) NO and H_2O
    (*c*) BF_3 and NO (*d*) NO_2 and NH
12. Which one of the following species does not exist under normal conditions?
    (*a*) Be (*b*) Be_2
    (*c*) B_2 (*d*) Li_2

13. In which of the following pairs of molecules / ions the central atom is *sp*^{2} hybridised?
    (*a*) NO and NH_3 (*b*) BF_3 and NO
    (*c*) NH and H_2O (*d*) BF_3 and NH
14. In which of the following molecules the central atom does not have *sp*^{3} hybridisation?
    (*a*) CH_4 (*b*) SF
    (*c*) BF_4 (*d*) NH
15. The species having pyramidal shape is
    (*a*) SO_3 (*b*) BrF_3
    (*c*) Si O (*d*) OSF_2

(B) Fill in the Blanks

Fill in the blank spaces:

1. The phenomenon of influencing the half-filled orbitals of the two atoms at certain distance apart is known as ___________.
2. The power of attraction that an atom shows for an electron pair situated between two atoms is known as ___________.
3. CCl_4 is a ___________ compound and will not give ___________ with $AgNO_3$ solution.
4. The formation of an anion from a neutral atom is favoured by ___________.
5. Bond angle in water molecule is 104.5° instead of 109°28´ because of ___________ repulsion.
6. For the formation of a hydrogen bond, the electronegativity of the atom attached to hydrogen should be ___________.
7. Solid NaCl is a ___________ conductor of electricity.
8. The shape of $[CH_3]^+$ is ___________.
9. The angle between two covalent bonds is maximum in ___________, (CH_4, H_2O, CO_2)
10. ___________ attractive forces between molecules are called Van der Waals' forces.
11. Glycerol has a high value of ___________ and ___________ due to hydrogen bonding.
12. Boiling point of H_2S is ___________ than that of water due to ___________.
13. Whereas sodium is a soft metal, ___________ can scratch even glass.
14. In coordinate bond, one of the atoms ___________ the electrons and the other ___________ it.
15. Dipole moment of a diatomic molecule is the product of ___________ and ___________.
16. Metals are good conductors of ________ and _________.

(C) True/False Statements

Write T for true and F for false statements:

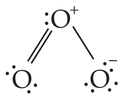
1. The formation of a cation from a neutral atom is favoured by small size of the atom.
2. Covalent bond involves transference of electrons.
3. The shape of methane molecule is tetrahedral.
4. Combination of atoms takes place because they tend to acquire stability by lowering of energy.
5. When two atoms combine to form a molecule, energy is released.
6. Ionic bond involves sharing of electron pair.
7. The shape of SO_2 molecule is planar.
8. Ionic compounds are soluble in non-polar solvents like benzene and ether.
9. The H — N — H bond angle in NH_3 is greater than the H — As — H bond angle in AsH_3.
10. All molecules with polar bonds may or may not have dipole moment.
11. The dipole moment of CHF_3 is greater than that of CH_3Cl.
12. HBr is more acidic than HI because of hydrogen bonding.
13. $SnCl_2$ is a non-linear molecule.
14. The H – N – H bond angle in NH_3 is greater than H – P – H angle in PH_3.
15. A molecule of CO_2 has a bent structure.
16. Glycerol has a lower boiling point than ethyl alcohol.
17. In the formation of a molecule of C_2H_2, *sp*^{2} hybridisation is involved.

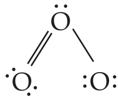
(D) Assertion-Reason Type Questions

*Each question below consists of two parts, **Assertion (A)** and **Reason (R)**. Answer the questions as per instructions below:*

(*a*) If both **A** and **R** are correct, and **R** is the correct reason of **A.**
(*b*) If both **A** and **R** are correct, but **R** is not the correct reason of **A**.
(*c*) If **A** is correct but **R** is wrong.
(*d*) If both **A** and **R** are incorrect.
Mark (*a*), (*b*), (*c*) or (*d*) accordingly.

1. ***Assertion (A)*** : NO_3^- is planer while NH_3 is pyramidal.
   Reason (R) : N in NO_3^- is *sp*^{2} and in NH_3 is *sp*^{3} hybridised.
2. ***Assertion (A)*** : LiCl is predominantly a covalent compound.
   Reason (R) : Electronegativity difference between Li and Cl is too small.
3. ***Assertion (A)*** : The electronic structure of O_3 is



   Reason (R) :  structure is not allowed because octet around O cannot be expanded.

(E) Matching Questions

Match the statements of Column A with those of Column B:

	Column A		Column B
1.	*o*-nitrophenol	*a.*	sp^3d hybridisation
2.	PF_5	*b.*	Intramolecular hydrogen bonding
3.	*p*-nitrophenol	*c.*	Ionic compounds
4.	SF_6	*d.*	Intermolecular
5.	Soluble in polar solvents but insoluble in non-polar solvents.	*e.*	sp^3d^2 hybridisation
6.	Soluble in non-polar solvents but insoluble in polar solvents.	*f.*	Covalent compounds

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. Polarity in a molecule and hence the dipole moment depends primarily on electronegativity of the constituent atoms and shape of the molecule. Which of the following has the highest dipole moment?
   (*a*) CO_2 (*b*) HI
   (*c*) H_2O (*d*) SO_2
2. The types of hybrid orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are expected to be
   (*a*) *sp*, sp^3 and sp^2 (*b*) *sp*, sp^2 and sp^3
   (*c*) sp^2, *sp* and sp^3 (*d*) sp^2, sp^3 and *sp*
3. Hydrogen bonds are formed in many compounds e.g., H_2O, HF, NH_3. The boiling point of such compounds depends to a large extent on the strength of hydrogen bond and the number of hydrogen bonds. The correct decreasing order of the boiling points of above compounds is
   (*a*) HF > H_2O > NH_3 (*b*) H_2O > HF > NH_3
   (*c*) NH_3 > HF > H_2O (*d*) NH_3 > H_2O > HF
4. In PO_4^{3-} ion the formal charge on the oxygen atom of P–O bond is
   (*a*) + 1 (*b*) – 1
   (*c*) – 0.75 (*d*) + 0.75
5. In NO_3^- ion, the number of bond pairs and lone pairs of electrons on nitrogen atom are
   (*a*) 2, 2 (*b*) 3, 1
   (*c*) 1, 3 (*d*) 4, 0
6. Which of the following species has tetrahedral geometry?
   (*a*) BH_4^- (*b*) NH_2^-
   (*c*) CO_3^{2-} (*d*) H_3O^+
7. Which molecule/ion out of the following does not contain unpaired electrons?
   (*a*) N_2^+ (*b*) O_2
   (*c*) O_2^{2-} (*d*) B_2
8. In which of the following molecule/ion all the bonds are not equal?
   (*a*) XeF_4 (*b*) BF_4^-
   (*c*) C_2H_4 (*d*) SiF_4
9. In which of the following substances will hydrogen bond be strongest?
   (*a*) HCl (*b*) H_2O
   (*c*) HI (*d*) H_2S
10. The electronic configuration of an element is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^2$ $4s^2$, the four electrons involved in chemical bond formation will be
    (*a*) $3p^6$ (*b*) $3p^6$, $4s^2$
    (*c*) $3p^6$, $3d^2$ (*d*) $3d^2$, $4s^2$
11. Which of the following angle corresponds to sp^2 hybridisation?
    (*a*) 90° (*b*) 120°
    (*c*) 180° (*d*) 109°

The electronic configurations of three elements, A, B and C are given below. Answer the questions 12 to 15 on the basis of these configurations.

A	$1s^2$	$2s^2$	$2p^6$		
B	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^3$
C	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^5$

12. Stable form of A may be represented by the formula
    (*a*) A (*b*) A_2
    (*c*) A_3 (*d*) A_4
13. Stable form of C may be represented by the formula
    (*a*) C (*b*) C_2
    (*c*) C_3 (*d*) C_4
14. The molecular formula of the compound formed from B and C will be
    (*a*) BC (*b*) B_2C
    (*c*) BC_2 (*d*) BC_3
15. The bond between B and C will be
    (*a*) Ionic (*b*) Covalent
    (*c*) Hydrogen (*d*) Coordinate
16. The electronic configuration of the outermost shell of the most electronegative element is
    (*a*) $2s^22p^5$ (*b*) $3s^23p^5$
    (*c*) $4s^24p^5$ (*d*) $5s^25p^5$
17. Which of the following attain the linear structure?
    (*a*) $BeCl_2$ (*b*) NCO^+
    (*c*) NO_2 (*d*) CS_2

18. Which of the following species have the same shape?
   (*a*) CO_2 (*b*) CCl_4
   (*c*) O_3 (*d*) NO_2^-

19. Which of the following statements are not correct?
   (*a*) NaCl being an ionic compound is a good conductor of electricity in the solid state.
   (*b*) In canonical structures there is a difference in the arrangement of atoms.
   (*c*) Hybrid orbitals form stronger bonds than pure orbitals.
   (*d*) VSEPR theory can explain the square planar geometry of XeF_4.

II. Matching Type Questions

1. Match the species in Column I with the type of hybrid orbitals in Column II.

Column I	**Column II**
(*i*) SF_4	(*a*) sp^3d^2
(*ii*) IF_5	(*b*) d^2sp^3
(*iii*) NO_2^+	(*c*) sp^3d
(*iv*) NH_4^+	(*d*) sp^3
	(*e*) sp

2. Match the species in Column I with the geometry/shape in Column II.

Column I	**Column II**
(*i*) H_3O^+	(*a*) Linear
(*ii*) $HC \equiv CH$	(*b*) Angular
(*iii*) ClO_2^-	(*c*) Tetrahedral
(*iv*) NH_4^+	(*d*) Trigonal bipyramidal
	(*e*) Pyramidal

3. Match the items given in Column I with examples given in Column II.

Column I	**Column II**
(*i*) Hydrogen bond	(*a*) C
(*ii*) Ionic solid	(*b*) LiF
(*iii*) Covalent solid	(*c*) H_2
	(*d*) HF

4. Match the shape of molecules in Column I with the type of hybridisation in Column II.

Column I	**Column II**
(*i*) Tetrahedral	(*a*) sp^2
(*ii*) Trigonal	(*b*) sp
(*iii*) Linear	(*c*) sp^3

III. Assertion-Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below in each question.

1. ***Assertion (A):*** Sodium chloride formed by the action of chlorine gas on sodium metal is a stable compound.

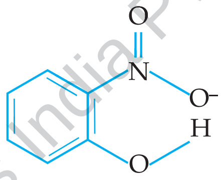
   Reason (R): This is because sodium and chloride ions acquire octet in sodium chloride formation.
   (*i*) A and R both are correct, and R is the correct explanation of A.
   (*ii*) A and R both are correct, but R is not the correct explanation of A.
   (*iii*) A is true but R is false.
   (*iv*) A and R both are false.

2. ***Assertion (A):*** Though the central atom of both NH_3 and H_2O molecules are sp^3 hybridised, yet H–N–H bond angle is greater than that of H–O–H.

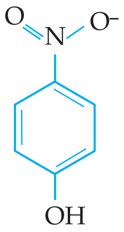
   Reason (R): This is because nitrogen atom has one lone pair and oxygen atom has two lone pairs.
   (*i*) A and R both are correct, and R is the correct explanation of A.
   (*ii*) A and R both are correct, but R is not the correct explanation of A.
   (*iii*) A is true but R is false.
   (*iv*) A and R both are false.

IV. Short Answer Type Questions

1. Explain the shape of BrF_5.
2. Structure of molecules of two compounds are given below:



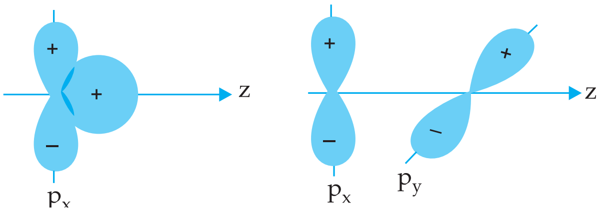
(I)



(II)

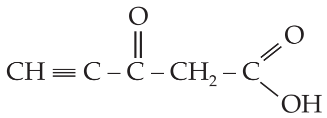
   (*a*) Which of the two compounds will have intermolecular hydrogen bonding and which compound is expected to show intramolecular hydrogen bonding?
   (*b*) The melting point of a compound depends on, among other things, the extent of hydrogen bonding. On this basis explain which of the above two compounds will show higher melting point?
   (*c*) Solubility of compounds in water depends on power to form hydrogen bonds with water. Which of the above compounds will form hydrogen bond with water easily and be more soluble in it?

3. Why does the type of overlap given in the following figure not result in the bond formation?



4. Explain why PCl_5 is trigonal bipyramidal whereas IF_5 is square pyramidal.
5. Write Lewis structure of the following compounds and show formed change on each atom, HNO_3, NO_2, H_2SO_4.

6. Give reasons for the following:
   (*a*) Covalent bonds are directional bonds while ionic bonds are non-directional.
   (*b*) Water molecule has bent structure whereas carbon dioxide molecule is linear.
   (*c*) Ethyne molecule is linear.
7. What is an ionic bond? With two suitable examples explain the difference between an ionic and a covalent bond?
8. Arrange the following bonds in order of increasing ionic character giving reason.
   N—H, F—H, C—H and O—H
9. Explain why CO_3^{2-} ion cannot be represented by a single Lewis structure. How can it be best represented?
10. Predict the hybridisation of each carbon in the molecule of organic compound given below.



$$CH \equiv C - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - C \begin{matrix} \nearrow O \\ \searrow OH \end{matrix}$$

11. Group the following as linear and non-linear molecules:
    H_2O, HOCl, $BeCl_2$, Cl_2O
12. Elements X, Y and Z have 4, 5 and 7 valence electrons respectively. (i) Write the molecular formula of the compounds formed by these elements individually with hydrogen. (ii) Which of these compounds will have the highest dipole moment?
13. Predict the shapes of the following molecules on the basis of hybridisation.
    BCl_3, CH_4, CO_2, NH_3.

ANSWERS

(A) Multiple Choice Questions

1. (*a*) 2. (*c*) 3. (*b*) 4. (*c*) 5. (*a*) 6. (*b*) 7. (*b*) 8. (*d*)
9. (*c*) 10. (*d*) 11. (*c*) 12. (*b*) 13. (*b*) 14. (*b*) 15. (*d*)

(B) Fill in the Blanks

1. overlapping 2. electronegativity 3. covalent 4. high electron affinity
5. lone pair 6. high 7. bad 8. trigonal-planar
9. CO_2 10. weak, nonpolar 11. viscosity, boiling point
12. lower, hydrogen bonding 13. osmium
14. donates, accepts 15. charge and interionic distance $q \times d$ 16. heat, electricity

(C) True/False Statements

1. F 2. F 3. T 4. F 5. T 6. F 7. F 8. F
9. T 10. T 11. T 12. F 13. T 14. F 15. F 16. F
17. F

(D) Assertion-Reason Type Questions

1. (*a*) 2. (*c*) 3. (*a*)

(E) Matching Questions

1. (*b*) 2. (*a*) 3. (*d*) 4. (*e*) 5. (*c*) 6. (*f*)

Some Additional Questions

I. Multiple Choice Questions

1. (*c*) 2. (*b*) 3. (*b*) 4. (*b*) 5. (*d*) 6. (*a*) 7. (*c*) 8. (*c*)
9. (*b*) 10. (*d*) 11. (*b*) 12. (*a*) 13. (*b*) 14. (*d*) 15. (*b*) 16. (*a*)
17. (*a*), (*d*) 18. (*c*), (*d*) 19. (*a*), (*b*)

II. Matching Type Questions

1. (*i*) $\longrightarrow$ (*c*), (*ii*) $\longrightarrow$ (*a*), (*iii*) $\longrightarrow$ (*e*), (*iv*) $\longrightarrow$ (*d*)
2. (*i*) $\longrightarrow$ (*e*), (*ii*) $\longrightarrow$ (*a*), (*iii*) $\longrightarrow$ (*b*), (*iv*) $\longrightarrow$ (*c*)
3. (*i*) $\longrightarrow$ (*d*), (*ii*) $\longrightarrow$ (*b*), (*iii*) $\longrightarrow$ (*a*)
4. (*i*) $\longrightarrow$ (*c*), (*ii*) $\longrightarrow$ (*a*), (*iii*) $\longrightarrow$ (*b*)

III. Assertion-Reason Type Questions

1. (*i*) 2. (*i*)

4

CHAPTER

Oxidation Numbers

LEARNING OBJECTIVES

- Apply the rules for assigning oxidation numbers to atoms in elements, compounds and ions.
- Explain oxidation and reduction in terms of electron transfer and changes in oxidation number.
- Write chemical formulae using oxidation numbers.

4.1 INTRODUCTION

Oxidation and reduction reactions are by far the most important class of reactions and occur in the electrolytic cells, in the human body and in the environment around us. For example, rusting of iron articles, manufacture of chemical compounds, like potassium permanganate, potassium chloride, etc., are associated with oxidation and reduction reactions. Extractions of certain metals like sodium and aluminium are also based upon **oxidation reaction** and **reduction reaction** or **redox reactions**.

These reactions are accompanied by energy changes in the form of heat, light or electricity. In some of these redox reactions, electricity is generated as a result of chemical reactions while in others, electricity is used to bring about a chemical change.

4.2 CLASSICAL CONCEPT OF OXIDATION AND REDUCTION (EARLY VIEW)

1. **Oxidation.** According to classical concept, oxidation may be defined as the chemical process which involves:

   (*a*) *Addition of oxygen or an electronegative element or radical.*

   (*b*) *Removal of hydrogen or an electropositive element or radical.*

   The above definition is illustrated by the following examples:

   (*i*) *Addition of oxygen*

$$C + O_2 \rightarrow CO_2$$

$$2Mg + O_2 \rightarrow 2MgO$$

   (*ii*) *Addition of electronegative radical*

$$\underset{\text{Ferrous chloride}}{2FeCl_2} + Cl_2 \rightarrow \underset{\text{Ferric chloride}}{2FeCl_3}$$

$$\underset{\text{(Dil.)}}{2HNO_3} \rightarrow 2NO + H_2O + 3(O)$$

$$\underline{2FeSO_4 + H_2SO_4 + (O) \rightarrow Fe_2(SO_4)_3 + H_2O] \times 3}$$

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

(*iii*) *Removal of hydrogen*

$$H_2S + Cl_2 \rightarrow S + 2HCl$$

$$4HCl + MnO_2 \rightarrow MnCl_2 + 2H_2O + Cl_2$$

(*iv*) *Removal of electropositive radical*

$$2KI + H_2O_2 \rightarrow I_2 + 2KOH$$

$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

2. **Reduction.** It is just the reverse of oxidation. According to classical concept, reduction may be defined as the process which involves:

(*a*) *Addition of hydrogen or an electropositive element or group.*

(*b*) *Removal of oxygen or an electronegative element or group.*

The above definition is illustrated by the following examples:

(*i*) *Addition of hydrogen*

$$H_2 + S \rightarrow H_2S$$

$$H_2S + Br_2 \rightarrow 2HBr + S$$

(*ii*) *Addition of electropositive element or radical*

$$\underset{\substack{\text{Mercuric}\\ \text{chloride}}}{2HgCl_2} + SnCl_2 \rightarrow \underset{\substack{\text{Mercurous}\\ \text{chloride}}}{Hg_2Cl_2} + SnCl_4$$

$$\underset{\substack{\text{Cupric}\\ \text{chloride}}}{CuCl_2} + Cu \rightarrow \underset{\substack{\text{Cuprous}\\ \text{chloride}}}{Cu_2Cl_2}$$

(*iii*) *Removal of oxygen*

$$ZnO + C \rightarrow Zn + CO$$

$$CuO + C \rightarrow Cu + CO$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

(*iv*) *Removal of electronegative element or radical*

$$2HgCl_2 \rightarrow Hg_2Cl_2 + Cl_2$$

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$$

$$Fe_2(SO_4)_3 + 2(H) \rightarrow 2FeSO_4 + H_2SO_4$$

4.3 ELECTRONIC CONCEPT OF OXIDATION REDUCTION REACTIONS

According to electronic concept, **oxidation** may be defined as *the reaction in which an atom or ion loses electrons.* For this reason *oxidation is usually referred to as de-electronation.*

Oxidation and Reduction as an Electron Transfer Process

Examples. *Sodium loses one electron to become sodium ion. According to definition, this is oxidation.*

$$\underset{\text{Sodium}}{Na} \xrightarrow{\text{Oxidation}} \underset{\text{Sodium ion}}{Na^+} + e^- \qquad (\textit{Loss of 1 electron})$$

Similarly,

$$\underset{\text{Magnesium}}{Mg} \xrightarrow{\text{Oxidation}} \underset{\text{Magnesium ion}}{Mg^{2+}} + 2e^- \qquad (\textit{Loss of 2 electrons})$$

$$Sn^{2+} \xrightarrow{\text{Oxidation}} Sn^{4+} + 2e^-$$

Stannous ion Stannic ion (*Loss of 2 electrons*)

$$Pb^{2+} \xrightarrow{\text{Oxidation}} Pb^{4+} + 2e^-$$

Plumbous ion Plumbic ion (*Loss of 2 electrons*)

$$MnO_4^{2-} \xrightarrow{\text{Oxidation}} MnO^-_4 + 1e^-$$

Manganate ion Permanganate ion (*Loss of 1 electron*)

$$[Fe(CN)_6]^{4-} \xrightarrow{\text{Oxidation}} [Fe(CN)_6]^{3-} + 1e^-$$

Ferrocyanide ion Ferricyanide ion (*Loss of 1 electron*)

It is important to note that in the above examples, during oxidation, there occurs an increase in the positive valency of the atom or ion or a decrease in its negative valency. Hence, *oxidation may also be defined as the process involving increase in positive valency or decrease in negative valency.*

The process of **reduction** is just reverse of oxidation. According to electronic concept, *reduction may be defined as the reaction in which an atom or an ion gains electrons*. For this reason *reduction is usually referred to as electronation*.

Following are some examples of reduction

Chlorine is reduced to chloride ion by gaining an electron.

$$Cl + e^- \xrightarrow{\text{Reduction}} Cl^-$$

Chlorine Chloride (*Gain of 1 electron*)

$$O + 2e^- \xrightarrow{\text{Reduction}} O^{2-}$$

Oxygen Oxide (*Gain of 2 electrons*)

$$Mg^{2+} + 2e^- \xrightarrow{\text{Reduction}} Mg$$

Magnesium ion Magnesium (*Gain of 2 electrons*)

$$Fe^{3+} + 3e^- \xrightarrow{\text{Reduction}} Fe$$

Iron (*Gain of 3 electrons*)

$$MnO_4^- + e^- \xrightarrow{\text{Reduction}} MnO_4^{2-}$$

Permanganate Manganate (*Gain of 1 electron*)

$$[Fe(CN_6)]^{3-} + e^- \xrightarrow{\text{Reduction}} [Fe(CN)_6]^{4-}$$

Ferricyanide Ferrocyanide (*Gain of 1 electron*)

From above it is clear that during *reduction*, there occurs an increase in the negative valency.

4.4 REDOX REACTIONS

A reaction in which one substance is oxidised and the other is reduced is called a **redox reaction**. *Oxidation and reduction occur simultaneously or they go hand in hand.*

Consider the following examples

(*i*) Iron reacts with sulphur to form iron sulphide.

$$Fe + S \rightarrow FeS \quad (i.e.\ Fe^{2+} + S^{2-})$$

In this reaction, Fe changes into Fe^{2+} by losing two electrons due to *oxidation* and S changes into S^{2-} by gaining two electrons due to *reduction* as:

$$Fe - 2e^- \rightarrow Fe^{2+} \qquad (Oxidation)$$

$$S + 2e^- \rightarrow S^{2-} \qquad (Reduction)$$

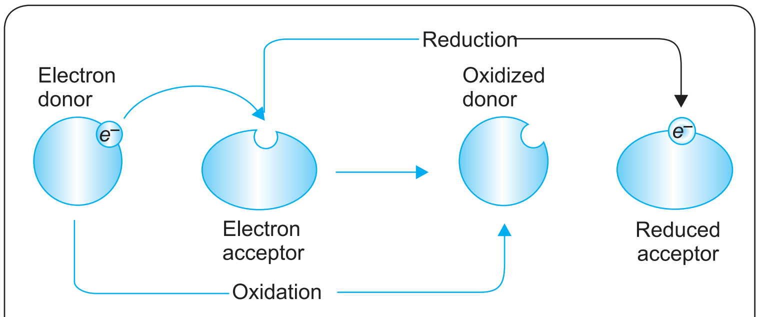


Fig. 4.1: *Representation of oxidation and reduction*

(*ii*) Sodium (solid) and chlorine (gas) react together resulting in the formation of the sodium chloride (solid),

i.e., $2Na\,(s) + Cl_2\,(g) \rightarrow 2NaCl\,(s)$

In this reaction Na changes into Na^+ by losing one electron due to *oxidation* and Cl changes into Cl^- by gaining one electron due to *reduction* as:

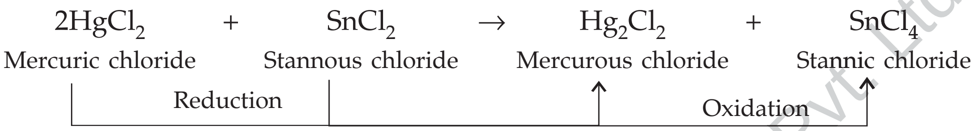
$$2Na\,(s) \rightarrow 2Na^+ + 2e^- \qquad (\textit{Oxidation})$$

$$Cl_2\,(g) + 2e^- \rightarrow 2Cl^- \qquad (\textit{Reduction})$$

Adding the two: $2Na\,(s) + Cl_2\,(g) \rightarrow 2NaCl\,(s)$

The number of electrons lost by sodium is equal to the number of electrons gained by chlorine.

(*iii*) When an aqueous solution of stannous chloride reacts with an aqueous solution of mercuric chloride, stannic chloride along with white precipitate of mercuric chloride are obtained. Here, mercuric chloride is reduced to mercurous chloride and stannous chloride is oxidised to stannic chloride.



$$\underset{\text{Mercuric chloride}}{2HgCl_2} + \underset{\text{Stannous chloride}}{SnCl_2} \rightarrow \underset{\text{Mercurous chloride}}{Hg_2Cl_2} + \underset{\text{Stannic chloride}}{SnCl_4}$$

Here, since Cl^- is common to both the sides, the equation may be written as

$$\underset{(\text{ic})}{2Hg^{2+}} + \underset{(\text{ous})}{Sn^{2+}} \rightarrow \underset{(\text{ous})}{2Hg^+} + \underset{(\text{ic})}{Sn^{4+}}$$

In this reaction, Sn^{2+} changes into Sn^{4+} after losing two electrons, while Hg^{2+} changes to Hg^+ after gaining one electron.

$$Sn^{2+} - 2e^- \rightarrow Sn^{4+} \qquad (\textit{Oxidation})$$

$$Hg^{2+} + e^- \rightarrow Hg^+ \qquad (\textit{Reduction})$$

It is clear from above reactions that an oxidising agent is **reduced** while reducing agent is **oxidised**. Since oxidation involves loss of electrons and reduction involves gain of electrons, it is obvious that a species will lose the electrons only when it is acceptable to the other species, and vice-versa. Hence, reduction and oxidation go side by side or redox reactions are complimentary.

So, from the above reactions it is clear that *oxidation and reduction go hand in hand.*

4.5 OXIDISING AGENT (OXIDANT)

(*i*) **Classical concept.** According to the classical concept, *an oxidising agent is a substance which causes the oxidation of other substances.* Thus, in the reaction,

$$2Mg + O_2 \rightarrow 2MgO$$

Oxygen is the oxidising agent because it causes the oxidation of magnesium.

(*ii*) **Electronic concept.** According to electronic concept, *an oxidising agent is a substance* (*atom, ion or molecule*) *which can gain or accept one or more electrons readily*. To be more clear, an oxidising agent readily removes electrons from other substances which are oxidised and the oxidising agent itself gets reduced. Hence, *oxidising agents or oxidant are electron acceptors.* The oxidising capacities of the above mentioned oxidising agents are due to their tendencies to accept electron/electrons from other substances as illustrated below:

(*a*) $(O) + 2e^- \rightarrow O^{2-}$

(*b*) $O_3 + 2e^- \rightarrow O_2 + O^{2-}$

(*c*) $H_2O_2 + 2e^- \rightarrow H_2O + O^{2-}$

(*d*) $X_2 + 2e^- \rightarrow 2X^-$ (where X = F, Cl, Br or I)

(*e*) $H_2SO_4 + 2e^- \rightarrow H_2O + SO_2 + O^{2-}$

4.6 REDUCING AGENT (REDUCTANT)

(*i*) **Classical concept.** According to the classical concept, *a reducing agent is a substance which causes reduction of other substances.* Thus, in the reaction

$$2Na + Cl_2 \rightarrow 2NaCl$$

Sodium is a reducing agent because it causes the reduction of chlorine.

(*ii*) **Electronic concept.** According to electronic concept, *a reducing agent is a substance (atom, ion, or molecule) which can furnish one or more electrons readily.* To be more clear, a reducing agent readily gives or donates electrons to other substances which are reduced. Hence, *reducing agents or reductants are electron donors.*

The reducing capabilities of the above mentioned reducing agents are due to their tendencies to lose one or more electrons to other substances as shown below:

(*a*) $H_2 \rightarrow 2H^+ + 2e^-$

(*b*) $SO_2 + 2O^{2-} \rightarrow SO_4^{2-} + 2e^-$

(*c*) $S^{2-} \rightarrow S + 2e^-$

(*d*) $2X^- \rightarrow X_2 + 2e^-$ (where, X = Cl, Br, or I)

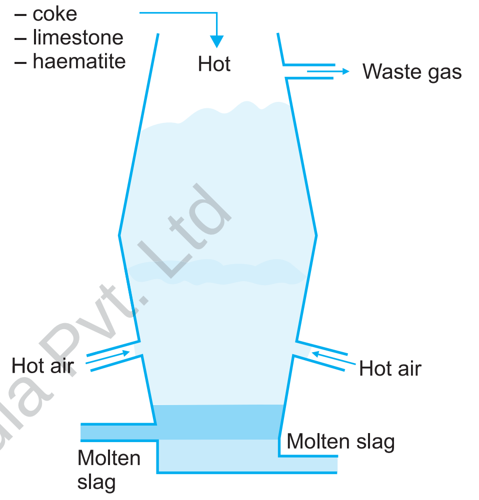


Fig. 4.2: *Coke and CO act as reducing agents in metallurgy*

Remember

In a chemical reaction, oxidising agent is reduced and reducing agent is oxidised.

Some examples of oxidising and reducing agents are given below:

(*i*) Iron reacts with chlorine to give ferrous chloride.

$Fe\ (s)$	+	$Cl_2\ (g)$	→	$FeCl_2\ (s)$
Iron gets oxidised or it is a reducing agent		Chlorine gets reduced or it is an oxidising agent		Ferrous chloride

(*ii*) Cupric oxide reacts with hydrogen to give copper and water.

$CuO\ (s)$	+	$H_2\ (g)$	→	$Cu\ (s)$	+	$H_2O\ (l)$
Cupric oxide is reduced or it is an oxidising agent		Hydrogen is oxidised or it is a reducing agent		Copper		Water

(*iii*)

PbS	+	$4H_2O_2$	→	$PbSO_4$	+	$4H_2O$
Lead sulphide		Hydrogen peroxide		Lead sulphate		Water

Here PbS is oxidised to lead sulphate or PbS is a reducing agent and hydrogen peroxide is reduced, so it is an oxidising agent.

4.7 ACTIVITIES BASED ON OXIDATION–REDUCTION PHENOMENON

Activity 1

Materials required:

250 ml beaker, zinc rods (plate may also be used), sand paper, copper sulphate powder.

Procedure

1. Take 2.5 g copper sulphate powder in a clean 250 ml beaker. Dissolve it in 100 ml distilled water by stirring with a glass rod [Fig. 4.3(a)].
2. Take a zinc rod (or plate). Clean the surface with the help of sand paper.
3. Place the rod in the beaker containing copper sulphate solution. Wait for half an hour. Record the observations in the following table.

Observations

	Colour of the rod	Colour of the solution
Before placing the rod in the solution		
After placing the rod in the solution		

Explanation: The above changes take place because of the oxidation–reduction phenomenon. Copper sulphate ionises in water to form Cu^{2+} and SO_4^{2-} ions. When the zinc rod is dipped into copper sulphate solution, the following reaction takes place.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

or

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

In this reaction, Zn has lost two electrons to change into Zn^{2+}, zinc has thus undergone *oxidation*. On the other hand, Cu^{2+} ions have gained two electrons, Cu^{2+} ions thus have been reduced. This may be written as under:

$$Zn \longrightarrow Zn^{2+} + 2e^- \qquad \text{(Oxidation)}$$

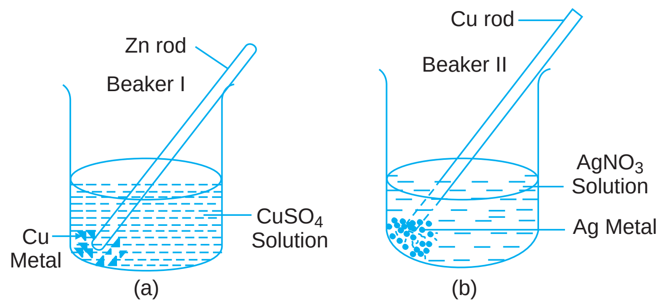
$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad \text{(Reduction)}$$

We shall observe that the blue colour of the solution has been decolourised. This is because copper sulphate solution (blue) has been converted into zinc sulphate (colourless) solution.

Also we shall observe that a reddish brown coating of Cu is deposited on zinc rod. Zinc rod which was grey in colour before dipping into copper sulphate solution appears reddish brown due to deposit of copper on it.

Activity 2

Students may perform a similar activity by taking a combination of copper rod and silver nitrate solution [Fig. 4.3(b)]. Record your observations in the format as used in activity no. 1 and give the appropriate explanation.



(a) (b)

Fig. 4.3: *Redox reactions*

4.8 OXIDATION NUMBER

Redox reacations involve the transfer of electrons from one atomic system to another. The account of the electron transfer in oxidation-reduction reaction is expressed in terms of oxidation number or oxidation state.

Or

Oxidation number of an element may be defined as the charge which an atom of the element has on its ion or appears to have when present in combined state with other atoms.

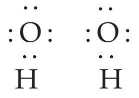
Or

It is defined as the charge which an atom has or appears to have when all other atoms are removed from it as ion.

Rules for determination of oxidation number of an atom:

1. The oxidation number of each element in the free or elementary state is always zero.
   Oxidation number of helium in He = 0
   Oxidation number of oxygen in O_2 = 0
   Oxidation number of chlorine in Cl_2 = 0
   Oxidation number of hydrogen in H_2 = 0
   Oxidation number of phosphorus in P_4 = 0
2. Fluorine, which is the most electronegative element, has oxidation number –1 in all of its compounds.
3. The oxidation number of an element in a monoatomic ion is equal to the charge present on the ion.
   Oxidation number of Na in Na^+ = +1
   Oxidation number of Fe in Fe^{2+} = +2
   Oxidation number of Cl in Cl^- = –1
   Oxidation number of S in S^{2-} = –2
   Oxidation number of Al in $A1^{3+}$ = +3
4. The oxidation number of the alkali metal (Li, Na, K, Rb, Cs and Fr) is +1 in all of their compounds and the oxidation number of the alkaline earth metals (Be, Mg, Ca, Sr, Ba and Ra) is +2 in all of their compounds.
5. In compounds, the oxidation number of oxygen is generally –2 except in F_2O wherein oxidation number of fluorine is –1 and that of oxygen is +2.

   In hydrogen peroxide molecule, the electron pair shared between O and H is counted with O but the other electron pair between two O atoms is equally shared.

   Hydrogen peroxide

   The number of electrons counted with each O is 7 and, therefore, appears to have –1 charge or its oxidation number in H_2O_2 is –1.
6. The oxidation number of hydrogen in all of its compounds except hydride is +1. In hydrides (e.g., KH, CaH_2 etc.), the oxidation number of hydrogen is +1.
7. In case of neutral molecules, the algebraic sum of the oxidation numbers of all the atoms present in the molecule is zero.

   Following examples illustrate this rule:

   (a) In H_2O,
   Oxidation number of H = +1
   Oxidation number of O = –2
   The sum of oxidation numbers = (+1) × 2 – 2 = 0

(b) In H_2SO_4,

Oxidation number of H = +1

Oxidation number of O = –2

Oxidation number of S = +6

The sum of oxidation numbers = (+1) × 2 + (+6) × 1 + (–2) × 4 = 0

8. The oxidation number of an ion is equal to the electrical charge present on it. Following examples illustrate this rule:

(a) In OH^- ion,

Oxidation number of O = –2

Oxidation number of H = +1

∴ The sum of oxidation numbers = –2 + 1

= –1 = charge on the ion

(b) In SO_4^{2-} ion,

Oxidation number of S = +6

Oxidation number of O = –2

The sum of oxidation numbers = +6 + (–2) × 4 = –2

= charge present on the ion

9. In compounds formed by the combination of different elements, the more electronegative atom or the atom possessing higher ionisation potential will have negative oxidation state, whereas, the less electronegative atom or the atom possessing lower ionisation potential will have positive oxidation state.

(a) In interhalogen compounds of Cl, Br, and I, the more electronegative of the two halogen gets the oxidation number –1 .

(b) Oxidation number of N (Nitrogen) is –3 when it is bonded to less electronegative atom as in case of NH_3 and NI_3, but when nitrogen is bonded to more electronegative atoms as in case of NCl_3, then the oxidation number of nitrogen is +3.

By the application of above rules, we can find out the oxidation number of the desired element in a molecule or in an ion. It is clear that the metallic elements have positive oxidation number and non-metallic elements have positive or negative oxidation number.

Redox reactions in terms of oxidation number

Oxidation may be defined as a chemical reaction in which the oxidation number of an atom or atoms increases. On the other hand, reduction may be defined as chemical reaction in which the oxidation number of an atom or atoms decreases. Let us consider the following example:

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$

In ionic form, the reaction can be written as:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Now, the oxidation and reduction processes involved in this reaction are as follow:

$$\underbrace{\overset{0}{Zn}(s) \longrightarrow \overset{2+}{Zn}}_{\text{Increase in oxidation number}}(aq) + 2e^- \qquad \text{(Oxidation)}$$

$$\underbrace{Cu^{2+} + (aq) + 2e^- \rightarrow \overset{0}{Cu}}_{\text{Decrease in oxidation number}}(s) \qquad \text{(Reduction)}$$

During the oxidation of Zn(s) into $Zn^{2+}(aq)$ ions, the oxidation number of Zn is increased from 0 to +2. On the other hand, in the reduction of $Cu^{2+}(aq)$ ion into Cu(s), the oxidation number of Cu is reduced from +2 to 0.

Oxidation Number of Atoms in Compounds and Ions

Example 1. *Calculate the oxidation number of sulphur in* Na_2SO_4 *molecule.*

Solution. Let the oxidation number of S be x. Writing the oxidation numbers of each atom above the symbol of each element.

$$\overset{+1}{Na_2} \qquad \overset{x}{S} \qquad \overset{-2}{O_4}$$

Sum of oxidation numbers of various atoms in $Na_2SO_4 = 2 \times (+1) + x + 4 \times (-2) = 2 + x - 8 = x - 6$

Since the sum of oxidation numbers of all the atoms of a neutral molecule like Na_2SO_4 is zero.

$\therefore \qquad x - 6 = 0$

or $\qquad x = +6.$

Hence, the oxidation number of sulphur in Na_2SO_4 is 6.

Example 2. *Calculate the oxidation number of manganese in* K_2MnO_4 *and* $KMnO_4$.

Solution.

(*i*) **K_2MnO_4.** Let the oxidation number of Mn be x.

Writing the oxidation numbers of each atom above the symbol of each element.

$$\overset{+1}{K_2} \qquad \overset{x}{Mn} \qquad \overset{-2}{O_4}$$

Sum of the oxidation numbers of various atoms in $K_2MnO_4 = 2 \times (+1) + x + 4 \times (-2) = 2 + x - 8 = x - 6$

Since the sum of the oxidation numbers of all the atoms of a neutral molecule is zero.

$\therefore \qquad x - 6 = 0$

or $\qquad x = +6$

Hence, the oxidation number of Mn in K_2MnO_4 is +6.

(*ii*) **$KMnO_4$.** Let oxidation number of Mn be x.

Writing the oxidation numbers of each atom above the symbol of each element.

$$\overset{+1}{K} \qquad \overset{x}{Mn} \qquad \overset{-2}{O_4}$$

Sum of the oxidation numbers of various atoms in $KMnO_4 = +1 + x + 4 \times (-2) = 1 + x - 8.$

Since the sum of oxidation numbers of all the atoms of a neutral molecule is zero.

$\therefore \qquad 1 + x - 8 = 0$

or $\qquad x = +7$

Hence, the oxidation number of Mn in $KMnO_4$ is +7.

Example 3. *What is the oxidation number of carbon in the following compounds.*

(*i*) CH_2Cl_2 (*ii*) $C_{12}H_{22}O_{11}$ (*iii*) $NaHCO_3$ (*iv*) CH_3Cl

Solution.

(*i*) **CH_2Cl_2.** Let the oxidation number of C in CH_2Cl_2 be x. Writing the oxidation numbers of each atom above the symbol of each element.

$$\overset{x}{C} \qquad \overset{+1}{H_2} \qquad \overset{-1}{Cl_2}$$

Sum of the oxidation numbers of all the atoms in CH_2Cl_2

$$= x + 2 \times (+1) + 2 \times (-1) = x$$

Since the sum of oxidation numbers of all the atoms of a neutral molecule is zero.

$\therefore \qquad x = 0$

Hence, the oxidation number of carbon in CH_2Cl_2 is zero.

(*ii*) **$C_{12}H_{22}O_{11}$.** Let the oxidation number of C in $C_{12}H_{22}O_{11}$ be x. Writing the oxidation numbers of each atom above its symbol.

$$\overset{x}{C_{12}} \qquad \overset{+1}{H_{22}} \qquad \overset{-2}{O_{11}}$$

Sum of the oxidation numbers of all the atoms in $C_{12}H_{22}O_{11}$

$$= 12 \times (x) + 22 \times (+1) + 11 \times (-2)$$
$$= 12x + 22 - 22 = 12x$$

Since the sum of oxidation number of all the atoms of a neutral molecule like $C_{12}H_{22}O_{11}$ is zero.

$\therefore \qquad 12x = 0$

or $\qquad x = 0$

Hence, the oxidation number of C in $C_{12}H_{22}O_{11}$ is zero.

(*iii*) **$NaHCO_3$.** Let the oxidation number of C in $NaHCO_3$ be x. Writing the oxidation numbers of each atom above its symbol in $NaHCO_3$.

$$\overset{+1}{Na} \qquad \overset{+1}{H} \qquad \overset{x}{C} \qquad \overset{-2}{O_3}$$

Sum of oxidation numbers of all the atoms in $NaHCO_3$

$$= (+1) + (+1) + x + 3 \times (-2) = x - 4$$

Since the sum of oxidation numbers of all the atoms of a neutral molecule is zero.

$\therefore \qquad x - 4 = 0$

or $\qquad x = +4$

Hence, the oxidation number of C in $NaHCO_3$ is +4.

(*iv*) **CH_3Cl.** Let the oxidation number of C in CH_3Cl be x. Writing the oxidation numbers of each atom on its symbol in CH_3Cl, we get

$$\overset{x}{C} \qquad \overset{+1}{H_3} \qquad \overset{-1}{Cl}$$

Sum of the oxidation numbers of all the atoms in CH_3Cl

$$= x + 3 \times (+1) + 1 \times (-1) = x + 2.$$

Since the sum of oxidation numbers of all the atoms of a neutral molecule like CH_3Cl is zero.

$\therefore \qquad x + 2 = 0$

or $\qquad x = -2$

Hence, the oxidation number of C in CH_3Cl is –2.

PROBLEMS FOR PRACTICE

1. Determine the oxidation number of:
   (*i*) C in HCO_3^- (*ii*) S in $S_2O_3^{2-}$ (*iii*) P in $H_2PO_4^-$ (*iv*) Fe in $[Fe(CN)_6]^{3-}$
   (*v*) U in $U_2O_7^{4-}$ (*vi*) Cr in CrO_4^{2-} (*vii*) Mn in MnO_4^{2-} (*viii*) S in HSO_4^-

   [**Ans.** (*i*) +4 (*ii*) +2 (*iii*) +5 (*iv*) +3 (*v*) +5 (*vi*) +6 (*vii*) +6 (*viii*) +6]

2. Calculate the oxidation number of:
   (*i*) S in $PbSO_4$ (*ii*) B in BF_3 (*iii*) C in CH_4 (*iv*) C in $C_{12}H_{22}O_{11}$
   (*v*) Mn in MnO_2 (*vi*) Si in SiO_2 (*vii*) Cr in $K_2Cr_2O_7$ (*viii*) Fe in Fe_3O_4

   [**Ans.** (*i*) +6 (*ii*) +3 (*iii*) –4 (*iv*) 0 (*v*) +4 (*vi*) +4 (*vii*) +6 (*viii*) 8/3]

3. Calculate the oxidation number of:
   (*i*) P in PO_4^{-3} (*ii*) Mn in MnO_4^- (*iii*) N in NO_3^- (*iv*) N in NH_4^+
   (*v*) Fe in $[Fe(CN)_6]^{-4}$

[**Ans.** (*i*) +5 (*ii*) +7 (*iii*) +5 (*iv*) –3 (*v*) +2]

4. Calculate the oxidation number of:
   (*i*) Cr in $Cr_2O_7^{2-}$ (*ii*) S in $Na_2S_2O_3$ (*iii*) Cr in Na_2CrO_4

[**Ans.** (*i*) +6 (*ii*) +2 (*iii*) +6]

4.8.1 Oxidation Number and Nomenclature

The oxidation number/state of a metal in a compound is sometimes presented according to the notation given by German Chemist, Alfred Stock.

It is popularly known as *stock notation*. Several elements show variable oxidation states and form compounds in more than one oxidation state. For example, copper exists in +1 state (i.e., possesses oxidation number equal to +1) in cuprous salts (e.g., Cu_2O, Cu_2Cl_2 etc.) and exists in +2 state (oxidation number = +2) in cupric salts (e.g., $CuSO_4$, $CuCl_2$ etc.). In order to specify the oxidation state of an atom in such a compound, the oxidation number of the atom is written as roman numeral in parenthesis along with the symbol of the atom in the formula of the compound. This system of nomenclature is known as **stock notation**. Thus, aurous chloride and auric chloride are written as Au (I) Cl and Au (III) Cl_3. Similarly, stannous chloride and stannic chloride are written as Sn (II) Cl_2 and Sn (IV) Cl_4. This change in oxidation number implies change in oxidation state, which in turn helps to identify whether the species is present in oxidised or reduced form.

The stock notation of some compounds are given below :

Formula of the compounds	Central atom and it's oxidation state	Name of the compound in stock notation
Cu_2O	Cu, +1	Copper (I) oxide
CuO	Cu, +2	Copper (II) oxide
$FeSO_4$	Fe, +2	Iron (II) sulphate
$Fe_2(SO_4)_3$	Fe, +3	Iron (III) sulphate
$SnCl_2$	Sn, +2	Tin (II) chloride
$SnCl_4$	Sn, +4	Tin (IV) chloride
Mn_2O_7	Mn, +7	Manganese (VII) oxide
V_2O_5	V, +5	Vanadium (V) oxide
Cr_2O_3	Cr, +3	Chromium (III) oxide
$K_2Cr_2O_7$	Cr, +6	Potassium dichromate (VI)

Normally, we don't use stock notations in case of compounds of non-metals which show variable oxidation states. For example, two halides of phosphorus such as PCl_3 and PCl_5 having phosphorus in oxidation states of +3 and +5, respectively, are distinguished by names only, i.e., phosphorus trichloride and phosphorus pentachloride, respectively.

4.8.2 Types of Redox Reactions

1. **Combination reaction:** A combination reaction may be represented as:

$$X + Y \longrightarrow Z$$

To be a redox reaction either A or B or both A and B must be in the elemental form. A compound is formed by chemical combination of two or more elements. The combination of an element or compound with oxygen is called **combustion**. For example,

$$\overset{0}{C}(s) + \overset{0}{O}_2(g) \xrightarrow{\text{Heat}} \overset{+4}{C}\overset{-2}{O}_2(g)$$

$$\overset{0}{H}_2 + \overset{0}{Cl}_2 \longrightarrow 2\overset{+1}{H}\overset{-1}{Cl}$$

2. **Decomposition reaction:** Decomposition reaction leads to the breakdown of a compound into two or more components, at least one of which must be in the elemental state. For example,

$$2\overset{+1}{Na}\overset{-1}{H}(s) \xrightarrow{\text{Heat}} 2\overset{0}{Na}(s) + \overset{0}{H}_2(g)$$

$$2\overset{+1}{K}\overset{+5}{Cl}\overset{-2}{O}_3(s) \xrightarrow{\text{Heat}} 2\overset{+1}{H}\overset{-1}{Cl} + 3\overset{0}{O}_2(g)$$

It should be noted that the decomposition does not result in changing the oxidation number of each element. In the above example, there is no change in oxidation state of potassium.

3. **Displacement reaction :** In displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as:

$$X + YZ \longrightarrow XZ + Y$$

Displacement reactions are further divided into two categories:

(*i*) Metal displacement

(*ii*) Non-metal displacement

(*i*) Metal displacement: In this reaction, a metal in a combined state can be displaced by another metal in the uncombined state.

It is found that a metal with stronger reducing character can displace the other metal having a weaker reducing character. For example,

$$\overset{+5}{V}_2\overset{-2}{O}_5(s) + 5\overset{0}{Ca}(s) \xrightarrow{\text{Heat}} 2\overset{0}{V}(s) + 5\overset{+2}{Ca}\overset{-2}{O}$$

$$\overset{+4}{Ti}\overset{-1}{Cl}_4(l) + 2\overset{0}{Mg}(s) \xrightarrow{\text{Heat}} \overset{0}{Ti}(s) + 2\overset{+2}{Mg}\overset{-1}{Cl}_2(s)$$

(*ii*) Non-metal displacement: The non-metal displacement redox reactions include displacement of hydrogen and sometimes oxygen.

Alkali and alkaline earth metals are highly electropositive, they displace hydrogen from cold water.

$$2\overset{0}{Na}(s) + 2\overset{+1}{H}_2\overset{-2}{O}(l) \longrightarrow 2\overset{+1}{Na}\overset{-2}{O}\overset{+1}{H}(aq) + \overset{0}{H}_2(g)$$

$$\overset{0}{Ca}(s) + 2\overset{+1}{H}_2\overset{-2}{O}(l) \longrightarrow \overset{+2}{Ca}(\overset{-2}{O}\overset{+1}{H})_2(aq) + \overset{0}{H}_2(g)$$

Less active metals such as Mg and Fe react with steam to produce H_2.

$$\overset{0}{Mg}(s) + 2H_2O(g) \longrightarrow \overset{+2}{Mg}(\overset{-2}{O}\overset{+1}{H})(s) + \overset{0}{H}_2(g)$$

$$2\overset{0}{Fe}(s) + 3\overset{+1}{H}_2\overset{-2}{O}(g) \longrightarrow \overset{+3}{Fe}\overset{-2}{O}_3(s) + 3\overset{0}{H}_2(g)$$

4. **Disproportionation reaction:** Reaction in which a substance undergoes simultaneous oxidation and reduction is called disproportionation and the substance is said to be disproportionate. For example,

(*i*) $2\overset{+1}{H}_2\overset{-1}{O}_2 \longrightarrow 2\overset{+1}{H}_2\overset{-2}{O} + \overset{0}{O}_2$

Disproportionation of oxygen takes place and its oxidation state change from –1 to 0 and –2 state.

(*ii*) Phosphorus undergoes disproportionation in alkaline medium.

$$\overset{0}{P}_4(s) + 3OH\ \ (ag) + 3H_2O(l) \longrightarrow \overset{-3}{P}H_3(g) + 3H_2\overset{0}{P}O_2^-$$

Oxidation state of phosphorus changes from 0 to –3 and +1 state.

4.8.3 Balancing of Redox Reactions

A redox reaction involves the simultaneous occurrence of both oxidation and reduction processes. Two methods are used to balance chemical equations for redox processes. One of these methods is based on the change in the oxidation number of reducing agent and the oxidising agent and the other method is based on splitting the redox reaction into two half reactions – one involving oxidation and the other involving reduction.

Oxidation Number Method

This method is based on the principle that the electrical charge must be conserved in a chemical reaction. The conservation of charge is possible only when any increase in oxidation number is compensated by a decrease in oxidation number. This means that in a balanced equation, total increase in oxidation number must be equal to the decrease in oxidation number.

The balancing of a redox reaction by oxidation number method is carried out systematically in the following steps:

Step 1. Write the skeleton equation for the redox reaction.

Step 2. Assign oxidation numbers to the atoms that change.

Step 3. Choose the proper ratio of oxidising agent to the reducing agent so that the oxidation number change is balanced.

Step 4. Make appropriate change in the coefficient of the products corresponding to the change of coefficient in step (3).

Step 5. Balance the oxygen atoms on both the sides by adding H_2O molecules to the side that is deficient in oxygen.

Step 6. Balance the hydrogen atoms on both the sides by adding H^+ ion to the side that is deficient in hydrogen.

Step 7. The equation is balanced in case the reaction is occurring in acidic solution. If however the reaction takes place in the basic solution, add suitable number of OH^- ion to get rid of H^+ ion in the reaction. Remember to add equal number of OH^- ions on both sides of the reaction.

Half Reaction Method

All the equations based on oxidation-reduction processes taking place in aqueous solution are ionic in nature. In this method, the two half equations, one corresponding to the process of oxidation and the other to the process of reduction are balanced separately and then added together to give balanced equation.

The two half equations are added in such a way that the electrons released in the process of oxidation cancel the electrons captured in the process of reduction.

Rules for balancing chemical equations by ion–electron (half reaction) method are:

Step 1. Write the given equation.

Step 2. Write the oxidation numbers of all atoms involved in the equation and find the species undergoing oxidation and reduction.

Step 3. Split the given reaction into two half reactions, one corresponding to the process of oxidation and the other to the process of reduction.

Step 4. Balance each half reaction in the following sequence:

(*i*) Balance all atoms other than H and O.

(*ii*) **In neutral or acidic solution:**

(*a*) Balance oxygen by adding sufficient number of H_2O molecules on the side deficient in oxygen.

(*b*) Balance hydrogen by adding sufficient number of H^+ ions on the side deficient in hydrogen.

In basic solution:

(*a*) Balance oxygen by adding sufficient number of OH^- ions on the side deficient in oxygen.

(*b*) Balance hydrogen by adding one H_2O molecule for each H atom needed on the side deficient in H atom. Now, add an equal number of OH^- ions to the opposite side.

(*iii*) Balance charge by adding the required number of electrons on the side deficient in negative charge. In the oxidation half equation, electrons are required to be added on the right, whereas in the reduction half equation on the left.

Step 5. Now, the balanced half reactions obtained in the above step are to be added in such a way that the electrons appearing in them get cancelled. For this, multiply the two half reactions by appropriate factors and add them in such a way that electrons appearing on left of one half equation cancel the electrons appearing on the right of the other half equation.

4.8.4 Redox Reactions as the Basis for Titrations

The redox titrations involve the chemical reaction between the oxidising agent and reducing agent in aqueous solutions under suitable conditions.

(*a*) **Potassium permanganate titrations :** In one situation, the reagent itself is intensely coloured, e.g., permanganate ion, MnO_4^- as oxidising agent against the reducing agents such as ferrous salts, oxalic acid or oxalate salts etc. in acidic medium. Here, MnO_4^- acts as the self indicator. The visible end point in this case is achieved after the last trace of the reductant is oxidised and the first lasting tinge of pink colour appears at MnO_4^- concentration as low as 10^{-6} mol dm^{-3}. During the titration a point will come where the reductant and the oxidant are equal in terms of their mole stoichiometry. A few examples are :

(*i*) Oxidation of ferrous salts

$$\underset{\text{Permanganate ion}}{MnO_4^-} + \underset{\text{Ferrous ion}}{5Fe^{2+}} + 8H^+ \longrightarrow Mn^{2+} + \underset{\text{Ferric ion}}{5Fe^{3+}} + 4H_2O$$

(*ii*) Oxidation of oxalates

$$\underset{\text{Permanganate ion}}{2MnO_4^-} + \underset{\text{Oxalate ion}}{5C_2O_4^{2-}} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(*b*) **Iodimetric titrations :** These titrations involve the direct use of iodine as an oxidising agent. It is used for the estimation of reducing agents such as thiosulphates, sulphates, arsenites, tartrates (potassium antimony tartrate) etc. This method relies on the fact that iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate ions ($S_2O_3^{2-}$).

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Similarly, oxidation of arsenite to arsenate is also a redox reaction.

$$I_2 + AsO_3^{3-} + H_2O \longrightarrow 2I^- + AsO_4^{3-} + 2H^+$$

(*c*) **Ceric sulphate titrations:** In these titrations, the oxidising agent employed is ceric sulphate $[Ce(SO_4)_2]$. The reagent is used for the quantitative estimation of ferrous salts, cuprous salts, nitrite, arsenites etc. Some of the examples are:

(*i*) **Oxidation of arsenite (AsO_3^{3-}) to arsenate (AsO_4^{3-}):**

$$\underset{\text{Ceric ion}}{2Ce^{4+}} + \underset{\text{Arsenite ion}}{AsO_3^{3-}} + H_2O \longrightarrow \underset{\text{Cerous ion}}{2Ce^{3+}} + \underset{\text{Arsenate ion}}{AsO_4^{3-}} + 2H^+$$

(*ii*) **Oxidation of ferrous salts:**

$$\underset{\text{Ceric ion}}{Ce^{4+}} + \underset{\text{Ferrous ion}}{Fe^{2+}} \longrightarrow \underset{\text{Cerous ion}}{Ce^{3+}} + \underset{\text{Ferric ion}}{Fe^{3+}}$$

(*d*) **Iodometric titrations:** These titrations involve the indirect use of iodine for estimation of oxidising agents viz. $KMnO_4$, $K_2Cr_2O_7$, CuSO4 etc. Here, the oxidising agent to be estimated is allowed to react with potassium iodide (KI) and iodine liberated by the oxidation of I^- ions is titrated against a standard solution of sodium thiosulphate. For example,

$$CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4$$

$$(2Cu^{2+} + 2I^- \longrightarrow 2Cu^+ + I_2$$

$$I_2 + \underset{\text{Thiosulphate}}{2S_2O_3^{2-}} \longrightarrow 2I^- + \underset{\text{Tetrathionate}}{S_2O_6^{2}}$$

Applications of Redox Reactions in Human Activity

Redox reactions are the basis of many applications of chemistry in industry and in our daily life. Some examples are listed below:

(*i*) Extraction of metals: Many metals are extracted from their oxides by using suitable reducing agents. Iron is obtained by doing reduction of Fe_2O_3 by coke in a blast furnace. Al_2O_3 is reduced to aluminium by cathode reduction in an electrolytic cell.

(*ii*) Photosynthesis: It is a natural process through which green plants convert carbon dioxide and water into carbohydrates in the presence of sunlight.

$$6CO_2(g) + 6H_2O(l) \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_6H_{12}O_6\,(ag) + 6O_2(g)$$

In this process, CO_2 is reduced to carbohydrate and water is oxidised to oxygen. Sunlight provides the energy for the reaction.

(*iii*) Production of energy: Oxidation of fuels (such as wood, coal, petrol, kerosene, diesel, etc.) is the important source of energy which meets our daily needs.

$$\text{Fuel} + O_2 \longrightarrow CO_2 + H_2O + \text{Heat energy}$$

The human body also requires energy which is provided in the form of food. In living cells, glucose is oxidised to CO_2 and water and the released energy is utilised in the human body.

$$\underset{\text{Food component}}{C_6H_{12}O_6(aq)} + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) + \text{Energy}$$

QUICK SCAN (FOR REVISION)

1. **Oxidation number (O.N.)** is the charge which an atom has in its ion or appears to have when present in the combined state.
2. Oxidation number may be a whole number, a fraction, negative, positive or even zero.
3. Valency of nitrogen in NH_3 and NF_3 is three, while its oxidation numbers are –3 and +3 respectively.
4. **Rules for Assigning Oxidation Number**
   (*i*) The O.N. of atoms of all elements in their elementary state is zero.
   (*ii*) The O.N. of hydrogen is normally +1 except in metal hydrides where it is –1.
   (*iii*) The O.N. of oxygen is usually –2 except in case of peroxides where it is –1 and in OF_2 where it is +2.
   (*iv*) For each covalent bond between two different atoms, assign an O.N. of +1 to the less electronegative atom and –1 to the more electronegative atom.
   (*v*) If a coordinate bond is formed between two dissimilar atoms but the donor atom is less electronegative than the acceptor atom, assign an O.N. of +2 to the donor atom and –2 to the acceptor atom. However, if the donor atom is more electronegative than the acceptor atom, neglect the contribution of the coordinate bond.
   (*vi*) In neutral compounds, the sum of the oxidation numbers of all the atoms is zero.
   (*vii*) In monoatomic ions, the O.N. of the atom is equal to its charge.
   (*viii*) In complex ions, the sum of oxidation numbers of all the atoms in the ion is equal to the charge on the ion.
5. The O.N. of metals in amalgams and metal carbonyls, *i.e.* $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, etc., is zero.
6. Increase in valency of an element is oxidation, while decrease is reduction.
7. **Oxidation** is a process which
   (*i*) involves addition of oxygen or any other electronegative element, or removal of hydrogen or any other electropositive element, or
   (*ii*) involves loss of electrons. That is why oxidation is also called **de-electronation**, or
   (*iii*) results in the increase in oxidation number (O.N.) of its atom or atoms.

EXERCISES

Very Short Answer Type Questions

1. What is redox reaction? Give one example.
2. Define oxidation and reduction in terms of electrons.
3. What are oxidation numbers?
4. What are oxidation numbers of:
   (*i*) C in CH_2O
   (*ii*) Pt in $Pt[(C_2H_4)Cl_3]^-$?
5. In the reaction $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$ which species is oxidised?
6. What is the oxidation state of Ni in $Ni(CO)_4$?
7. Show by equation that SO_2 acts both as an oxidant and a reductant.
8. Name one compound each in which oxidation number of:
   (*a*) Oxygen is –1 (*b*) Oxygen is +1
   (*c*) Oxygen is +2 (*d*) Hydrogen is –1
   (*e*) Nitrogen is –2 (*f*) Nitrogen is +3
9. What is the lowest oxidation state of Cl, S and N?
10. What is the highest oxidation state of phosphorus, sulphur and chlorine?
11. Which element shows highest oxidation state in its compounds?
12. What is the valency and oxidation state of
    (*a*) C in CH_2Cl_2, (*b*) C in $C_{12}H_{22}O_{11}$,
    (*c*) P in P_4 molecule, and (*d*) S in S_8 molecule?
13. What is the oxidation number of oxygen on O_3?

Short Answer Type Questions

1. How would you apply the concept of oxidation number to processes involving oxidation and reduction? Give examples.
2. Name the species which are oxidised or reduced and to what extent in the following reactions:
   (*i*) $Zn\ (s) + PbCl_2\ (aq) \rightarrow Pb\ (s) + ZnCl_2\ (aq)$
   (*ii*) $2Fe^{3+}\ (aq) + 2I^-\ (aq) \rightarrow I_2\ (aq) + 2Fe^{2+}\ (aq)$
3. Explain the term oxidation numbers. What rules are used in giving oxidation number to various elements?
4. How does oxidation number differ from valency of an atom? What is the oxidation number of:
   (*i*) N in NH_3 (*ii*) S in K_2SO_4
   (*iii*) Mn in MnO_2 (*iv*) S in $H_2S_2O_7$
   (*v*) N in NO_2?

5. Write the skeleton equations for the following chemical reaction and balance them by oxidation number method. Chloride ions reduce manganese dioxide to manganese (II) ions in acidic medium and get oxidised to chlorine gas.

Long Answer Type Questions

1. Explain the terms with examples:
   (*i*) oxidation (*ii*) reduction
   (*iii*) oxidising agent (*iv*) reducing agent
2. Write the various steps for balancing a chemical equation by oxidation number method.
3. (*i*) Explain the term oxidation number.
   (*ii*) What are the rules for assigning oxidation numbers to elements in chemical compounds?
4. Describe Stock's nomenclature with reference to oxidation number of elements.
5. In each of the following reactions indicate which element is oxidised and which is reduced:
   (*i*) $Mg + 2HCl \rightarrow MgCl_2 + H_2$
   (*ii*) $Cl_2 + 2FeCl_2 \rightarrow 2FeCl_3$
   (*iii*) $2H_2S + SO_2 \rightarrow 3S + 2H_2O$
   (*iv*) $2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3$
6. Balance the following reaction
   (*i*) $Cr^{3+} + Na_2O_2 \longrightarrow CrO_4^- + Na^+$ (basic medium)
   (*ii*) $S^{2-} + NO_3^- \longrightarrow NO + S$ (acidic medium)

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. Oxidation-reduction reactions are called redox reactions.
2. Oxidation involves loss and reduction involves gain of electrons.
3. Oxidation number of an element is the charge which the atom has or appears to have when all other atoms are removed as ions from the molecules.
4. (*i*) zero (*ii*) 2
5. HCl is oxidised to Cl_2
6. zero
7. In SO_2, sulphur exists in an intermediate oxidation state of +4 from which it can either be oxidised into higher (+6) oxidation state or reduced to lower oxidation state (–2). Thus, it can act both as a reducing agent and as an oxidising agent *e.g.*,

   $3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
   In this case oxidation number of S changes from +4 to +6. Hence, it gets oxidised and acts as a reducing agent.

   $$\overset{4+}{SO_2} + 2H_2S \rightarrow \overset{0}{2S} + \overset{0}{S} + 2H_2O$$

   Here SO_2 gets reduced to S and thus acts as an oxidising agent.
8. (*a*) Na_2O_2 (*b*) O_2F_2 (*c*) OF_2
   (*d*) NaH (*e*) NH_3 (*f*) N_2O_3
9. –1, –2 and –3 respectively.
10. +5, +6 and +7 respectively.
11. Osmium (+8 in OsO_4)
12. (*a*) 4, 0 (*b*) 4, 0 (*c*) 3, 0 (*d*) 2, 0
13. Zero

COMPETITION FILE

SUBJECTIVE PROBLEMS

Problem 1. *Arrange the following in order of:*

(*a*) *increasing oxidation number:* $MnCl_2, MnO_2, KMnO_4$
(*b*) *increasing oxidation number:* $NH_3, N_3H, N_2O, NO, N_2O_5$
(*c*) *decreasing oxidation number:* HXO, HXO_2, HXO_3, HXO_4

Solution.

(*a*) $MnCl_2 < MnO_2 < KMnO_4$
(*b*) $NH_3 < N_3H < N_2O < NO < N_2O_5$
(*c*) $HXO_4 > HXO_3 > HXO_2 > HXO$

Problem 2. *Name one compound each in which oxidation number of:*

(*a*) *oxygen is +2* (*b*) *oxygen is –1*
(*c*) *hydrogen is –1* (*d*) *nitrogen is +1*
(*e*) *Cl is +4* (*f*) *oxygen is –2*

Solution.

(*a*) F_2O (*b*) H_2O_2
(*c*) NaH (*d*) N_2O
(*e*) ClO_2 (*f*) H_2O.

Problem 3. *H_2S acts only as reductant, whereas SO_2 acts as oxidant and reductant both. Explain.*

Solution. Sulphur can have maximum oxidation number of +6 because it has 6 electrons in its outermost shell. It can have minimum value of oxidation number as –2. In H_2S, oxidation number of S is –2. The oxidation number of S can be increased from –2 in H_2S to some higher value, so it can act as a reductant. Its oxidation number cannot be decreased further from –2 value, so it cannot act as an oxidant.

But O.N. of sulphur in SO_2 is +4. This value can be increased upto +6 and decreased upto –2. So SO_2 can act as oxidant as well as reductant.

Yes, Cl_2 undergoes disproportionation.

Problem 4. *Write the half reactions corresponding to the complete reaction.*

$$2Fe^{3+}\,(aq) + 2I^-\,(aq) \rightarrow I_2\,(aq) + 2Fe^{2+}\,(aq)$$

Also, mention the species reduced and oxidised.

Solution. In this reaction, Fe^{3+} ion gains electron and is reduced to Fe^{2+} while I^- loses electron and is oxidised to I_2. The two half reactions are:

$$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+} \qquad (Reduction)$$

$$2I^- \longrightarrow I_2 + 2e^- \qquad (Oxidation)$$

Problem 5. *What will be the conjugate base of H_3PO_4?*

Solution. H_3PO_4 can dissociate as under:

$$H_3PO_4 \longrightarrow H_2PO_4^- + H^+$$

Thus, $H_2PO_4^-$ is the conjugate base of H_3PO_4.

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. When $CuSO_4$ reacts with KI the oxidation number of Cu changes by
   (*a*) 1 (*b*) –1
   (*c*) 0 (*d*) 2
2. If HNO_3 changes into N_2O the oxidation number is changed by:
   (*a*) 6 (*b*) +2
   (*c*) 0 (*d*) +4
3. How many faradays are needed to reduce a mole of MnO_4^- to Mn^{2+}?
   (*a*) 4 (*b*) 3
   (*c*) 5 (*d*) 2
4. Oxidation state of Fe in Fe_3O_4 is:
   (*a*) $\frac{3}{2}$ (*b*) $\frac{4}{5}$
   (*c*) $\frac{5}{4}$ (*d*) $\frac{8}{3}$
5. The oxidation numbers of sulphur in S_8, S_2F_2, H_2S respectively, are:
   (*a*) 0, +1 and –2 (*b*) +2, +1 and –2
   (*c*) 0, +1 and +2 (*d*) –2, +1 and –2
6. The pair of compounds having metals in their highest oxidation state is
   (*a*) MnO_2, $FeCl_3$ (*b*) $[MnO_4]$, Cr_2Cl_2
   (*c*) $[Fe(CN)_6]^{3-}$, $[Co(CN)_3]$ (*d*) $[NiCl]^{2-}$, $[CoCl_4]^-$
7. When I is oxidised by MnO_4 in alkaline medium, I converts into
   (*a*) IO_3 (*b*) I_2
   (*c*) IO_4 (*d*) IO
8. Which of the following chemical reactions depicts the oxidizing behaviour of H_2SO_4?
   (*a*) $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$
   (*b*) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$
   (*c*) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$
   (*d*) $2PCl_5 + H_2SO_4 \rightarrow 2POCl_3 + 2HCl + SO_2Cl_2$
9. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite in an acidic solution is
   (*a*) 4/5 (*b*) 2/5
   (*c*) 1 (*d*) 3/5
10. Oxidation number of P in PO_4^{3-}, of S in SO_4^{2-} and that of Cr in $Cr_2O_7^{2-}$ are respectively
    (*a*) +3, +6 and +5 (*b*) +5, +3 and +6
    (*c*) –3, +6 and +6 (*d*) +5, +6 and +6

(B) Fill in the Blanks

Fill in the blank spaces:

1. Oxidation number of an element in the uncombined state is ________.
2. Oxidation number of hydrogen is +1 except in ________.
3. The oxidation number of fluorine is always ________ because it is ________ electronegative.
4. Sum of oxidation numbers of various atoms in a neutral molecule is zero while that in a charged ion, is equal to ________.
5. The sum of the oxidation numbers of all the atoms in C_6H_5CHO is ________.

6. The compound $YbBa_2Cu_3O_7$ which shows superconductivity, has copper in the oxidation state ________. Assume that the rare earth element ytterbium is in the usual +3 oxidation state.

(C) True/False Statements

Write T for True and F for False statements in the following:

1. Oxidation and reduction go hand in hand.
2. Zinc has higher tendency of losing electrons than copper.
3. Salt bridge helps to maintain the electrical neutrality of the solution.
4. The oxidation number of an element is maximum in uncombined state.
5. Decrease in oxidation number of an element in a chemical change is called oxidation.
6. Oxidation number of an element may vary in different compounds.
7. Oxidation number of hydrogen in lithium hydride is +1.

(D) Multiple Choice Questions (More than one correct answer.)

Choose the correct answer(s):

1. Carbon has zero oxidation number in:
   (*a*) CH_2O (*b*) CH_3Cl
   (*c*) CCl_4 (*d*) CH_2Cl_2
2. Oxidation is a process which involves
   (*a*) addition of oxygen
   (*b*) loss of electrons
   (*c*) removal of hydrogen
   (*d*) double displacement

(E) Matching Questions

Match the statements of Column A with those of Column B:

	Column A		Column B
1.	Oxidation number of two chlorine atoms in bleaching powder	*a.*	–3 and +5
2.	Simultaneous oxidation and reduction	*b.*	–2 and +2
3.	Oxidation numbers of first nitrogen and second nitrogen in NH_4NO_3.	*c.*	+1 and –1
4.	Loss of electron or removal of hydrogen	*d.*	Reduction
5.	Oxidation numbers of oxygen in H_2O and OF_2	*e.*	Disproportionation
6.	Gain of electrons or removal of oxygen	*f.*	Induced oxidation
7.	Oxidation of a substance in the presence of another substance.	*g.*	Oxidation

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. Which of the following is **not** an example of redox reaction?
   (*a*) $CuO + H_2 \longrightarrow Cu + H_2O$
   (*b*) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
   (*c*) $2K + F_2 \longrightarrow 2KF$
   (*d*) $BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$
2. Thiosulphate reacts differently with iodine and bromine in the reactions given below
   $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$
   $S_2O_3^{2-} + 2Br_2 + 5H_2O \longrightarrow 2SO_4^{2-} + 2Br^- + 10H^+$
   Which of the following statements justifies the above dual behaviour of thiosulphate?
   (*a*) Bromine is a stronger oxidant than iodine.
   (*b*) Bromine is a weaker oxidant than iodine.
   (*c*) Thiosulphate undergoes oxidation by bromine and reduction by iodine in these reactions.
   (*d*) Bromine undergoes oxidation and iodine undergoes reduction in these reactions.
3. The oxidation number of an element in a compound is evaluated on the basis of certain rules. Which of the following rules is **not** correct in this respect?
   (*a*) The oxidation number of hydrogen is always +1.
   (*b*) The algebraic sum of all the oxidation numbers in a compound is zero.
   (*c*) An element in the free or the uncombined state bears oxidation number zero.
   (*d*) In all its compounds, the oxidation number of fluorine is –1.
4. In which of the following compounds, an element exhibits two different oxidation states?
   (*a*) NH_2OH (*b*) NH_4NO_3
   (*c*) N_2H_4 (*d*) N_3H

5. Which of the following arrangements represents increasing oxidation number of the central atom?
   - (*a*) CrO_2^-, ClO_3^-, CrO_4^{2-}, MnO_4^-
   - (*b*) ClO_3^-, ClO_4^{2-}, MnO_4^-, CrO_2^-,
   - (*c*) CrO_2^-, ClO_3^-, MnO_4^-, CrO_4^{2-}
   - (*d*) CrO_4^{2-}, MnO_4^-, CrO_2^-, ClO_3^-

6. The largest oxidation number exhibited by an element depends on its outer electronic configuration. With which of the following outer electronic configurations, the element will exhibit largest oxidation number?
   - (*a*) $3d^1 4s^2$
   - (*b*) $3d^3 4s^2$
   - (*c*) $3d^5 4s^1$
   - (*d*) $3d^5 4s^2$

7. Identify disproportionation reaction
   - (*a*) $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
   - (*b*) $CH_4 + 4C1_2 \longrightarrow CCl_4 + 4HC1$
   - (*c*) $2F_2 + 2OH^- \longrightarrow 2F^- + OF_2 + H_2O$
   - (*d*) $2NO_2 + 2OH^- \longrightarrow NO_2^- + NO_3^- + H_2O$

8. Which of the following elements does **not** show disproportionation tendency?
   - (*a*) Cl
   - (*b*) Br
   - (*c*) F
   - (*d*) I

9. Which of the following statement(s) is/are **not** true about the following decomposition reaction.

   $$2KClO_3 \rightarrow 2KCl + 3O_2$$

   - (*a*) Potassium is undergoing oxidation
   - (*b*) Chlorine is undergoing oxidation
   - (*c*) Oxygen is reduced
   - (*d*) None of the species are undergoing oxidation or reduction

10. The exhibition of various oxidation states by an element is also related to the outer orbital electronic configuration of its atom. Atom(s) having which of the following outermost electronic configurations will exhibit more than one oxidation state in its compounds.
    - (*a*) $3s^1$
    - (*b*) $3d^1 4s^2$
    - (*c*) $3d^2 4s^2$
    - (*d*) $3s^2 3p^3$

11. Identify the correct statements with reference to the given reaction

    $$P_4 + 3OH^- + 3H_2O \rightarrow PH_3 + 3H_2PO_2^-$$

    - (*a*) Phosphorus is undergoing reduction only.
    - (*b*) Phosphorus is undergoing oxidation only.
    - (*c*) Phosphorus is undergoing oxidation as well as reduction.
    - (*d*) Hydrogen is undergoing neither oxidation nor reduction.

II. Matching Type Questions

1. Match Column I with Column II for the oxidation states of the central atoms.

Column I	Column II
(*i*) $Cr_2O_7^{2-}$	(*a*) +3
(*ii*) MnO_4^-	(*b*) +4
(*iii*) VO_3^-	(*c*) +5
(*iv*) FeF_6^{3-}	(*d*) +6
	(*e*) +7

2. Match the items in Column I with relevant items in Column II.

Column I	Column II
(*i*) Ions having positive charge	(*a*) +7
(*ii*) The sum of oxidation number of all atoms in	(*b*) –1
a neutral molecule	(*c*) + 1
(*iii*) Oxidation number of hydrogen ion (H^+)	(*d*) 0
(*iv*) Oxidation number of fluorine in NaF	(*e*) Cation
(*v*) Ions having negative charge	(*f*) Anion

III. Assertion-Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

1. ***Assertion* (A):** Among halogens fluorine is the best oxidant.

   ***Reason* (R):** Fluorine is the most electronegative atom.

   - (*i*) Both A and R are true and R is the correct explanation of A.
   - (*ii*) Both A and R are true but R is not the correct explanation of A.
   - (*iii*) A is true but R is false.
   - (*iv*) Both A and R are false.

2. ***Assertion* (A):** In the reaction between potassium permanganate and potassium iodide, permanganate ions act as oxidising agent.

   ***Reason* (R):** Oxidation state of manganese changes from +2 to +7 during the reaction.

   - (*i*) Both A and R are true and R is the correct explanation of A.

(*ii*) Both A and R are true but R is not the correct explanation of A.

(*iii*) A is true but R is false.

(*iv*) Both A and R are false.

3. ***Assertion*** **(*A*):** The decomposition of hydrogen peroxide to form water and oxygen is an example of disproportionation reaction.

Reason **(*R*):** The oxygen of peroxide is in –1 oxidation state and it is converted to zero oxidation state in O_2 and –2 oxidation state in H_2O.

(*i*) Both A and R are true and R is the correct explanation of A.

(*ii*) Both A and R are true but R is not the correct explanation of A.

(*iii*) A is true but R is false.

(*iv*) Both A and R are false.

4. ***Assertion*** **(*A*):** Redox couple is the combination of oxidised and reduced form of a substance involved in an oxidation or reduction half-cell.

Reason (*R*): In the representation $E_{Fe^{3+}}/Fe^{2+}$ and $E_{Cu^{2+}/Cu}$, Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu are redox couples.

(*i*) Both A and R are true and R is the correct explanation of A.

(*ii*) Both A and R are true but R is not the correct explanation of A.

(*iii*) A is true but R is false.

(*iv*) Both A and R are false.

ANSWERS

(A) Multiple Choice Questions

1. (*b*) 2. (*d*) 3. (*c*) 4. (*d*) 5. (*a*) 6. (*b*) 7. (*a*) 8. (*a*)
9. (*b*) 10. (*d*)

(B) Fill in the Blanks

1. zero 2. metal hydrides 3. –1 4. charge on ion
5. zero 6. 7/3

(C) True/False Statements

1. T 2. T 3. T 4. F 5. F 6. F 7. T

(D) Multiple Choice Questions (More than one correct answers)

1. (*a*), (*d*) 2. (*a*), (*b*), (*c*)

(E) Matching Questions

1. (*c*) 2. (*e*) 3. (*a*) 4. (*g*) 5. (*b*) 6. (*d*) 7. (*f*)

Some Additional Questions

I. Multiple Choice Questions

1. (*d*) 2. (*a*) 3. (*a*) 4. (*b*) 5. (*a*) 6. (*d*) 7. (*d*) 8. (*c*)
9. (*a*), (*d*) 10. (*c*), (*d*) 11. (*c*), (*d*)

II. Matching Type Questions

1. (*i*) → (*d*), (*ii*) → (*e*), (*iii*) → (*c*), (*iv*) → (*s*)
2. (*i*) → (*e*), (*ii*) → (*d*), (*iii*) → (*c*), (*iv*) → (*b*), (*v*) → (*f*)

III. Assertion-Reason Type Questions

1. (*ii*) 2. (*iii*) 3. (*i*) 4. (*ii*)

5

CHAPTER

Group-2 Alkaline Earth Metals

LEARNING OBJECTIVES

- Understand the trends in atomic radius, first ionization energy and melting points of the elements in group 2.
- Show the reactions of the elements in group 2 with oxygen, chlorine and water.
- Explain the trends in reactivity of group 2 elements.
- Compare the reactions of the oxides of group 2 elements with water and dilute acids and their hydroxides with dilute acid.
- Understand the trends in the thermal decomposition of group 2 carbonates and nitrates.
- Explain the trends in solubility of the hydroxides and sulphates of group 2.
- Make the uses of a variety of compounds of group 2 e.g. the use of calcium hydroxide in agriculture, magnesium hydroxide as an antacid, barium sulphate in medicine and calcium carbonate in making cement.

5.1 INTRODUCTION

The long form of the periodic table has been divided into four blocks *viz.*, *s*-, *p*-, *d*- and *f*-blocks, depending upon whether the last electrons are filled in *s*-, *p*-, *d*- or *f*-orbitals. *s*- and *p*-blocks elements collectively are also called as representative elements. *d*- and *f*-blocks elements are known as **transition** and **inner-transition elements** respectively.

s-block elements consist of group 1 and 2 elements. A few characteristics of *s*-block elements are:

1. *s*-block elements mostly form ionic compounds as they involve the transference of one or two electrons only.
2. Oxidation states of the *s*-block elements are +1 and +2.
3. *s*-block elements act as a strong reducing agent.

It is observed that first members of the group 1 and 2 differ markedly from the other members of the group. It is due to the following reasons:

(*i*) The small size of the first member compared to rest of the members of the group.

(*ii*) High electronegativity of the first member.

5.2 GROUP-2 ELEMENTS—THE ALKALINE EARTH METALS

The elements belonging to the group 2 are *beryllium* (Be), *magnesium* (Mg), *calcium* (Ca), *strontium* (Sr), *barium* (Ba) and *radium* (Ra). All these elements are metallic in nature. But of all these elements, radium is radioactive. *They are called alkaline earth metals* because their oxides occur in the earth's crust and are alkaline in nature.

These elements have two electrons in the *s*-orbital of the valence shell. Electronic configuration of alkaline earth metal may be represented as

$$[\text{Nobel gas}]\ ns^2;\ \text{where } n = 2 \text{ to } 7$$

Electronic configuration of alkaline earth metals are given in Table 5.1.

Table 5.1: Electronic Configuration of Alkaline Earth Metals

Element	Atomic Number	Electronic Configuration	
		Complete	With Inert Gas Core
Beryllium (Be)	4	$1s^2\ 2s^2$	$[He]\ 2s^2$
Magnesium (Mg)	12	$1s^2\ 2s^2\ 2p^6\ 3s^2$	$[Ne]\ 3s^2$
Calcium (Ca)	20	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	$[Ar]\ 4s^2$
Strontium (Sr)	38	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^2$	$[Kr]\ 5s^2$
Barium (Ba)	56	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 6s^2$	$[Xe]\ 6s^2$
Radium (Ra)	88	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4s^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^6\ 7s^2$	$[Rn]\ 7s^2$

5.2.1 General Trends in Physical Properties

The outer shell electronic configurations of all these elements are similar. Therefore, they exhibit similar properties. Compounds of these elements are predominantly ionic. The first member beryllium differs from the rest of the members, as was the case with lithium.

Different physical characteristics and their variation down the group are as discussed below:

1. **Density.** The alkaline earth metals show greater density and hardness than the corresponding alkali metals.

   Explanation. *The atoms of alkaline earth elements have smaller size and stronger intermetallic bonds, as compared to alkali metals. They are more closely packed in their crystal lattices which accounts for high density and hardness of these elements. (Smaller particles can pack more closely and tightly in the crystal lattice).*

   Density decreases up to calcium and then increases up to radium. The cause for decrease in density up to calcium shows imperfect packing of constituents in solid lattice.

2. **Melting Point and Boiling Point.** The alkaline earth metals show higher melting and boiling points than the alkali metals, because of small size and close packing. However, no regular trends are observed in the variation of melting and boiling points (Table 5.2).

3. **Atomic and Ionic Radii.** The atomic radii as well as ionic radii of the members of the family are smaller than the corresponding members of alkali metals.

   Explanation. *The alkaline earth metals have a greater nuclear charge due to which the electrons are attracted with greater force to the nucleus causing a decrease in atomic size.*

   Within the group, the atomic as well as ionic radii increase with atomic number. This is obviously due to the addition of new shells, the effect of which is more predominant than the increase in nuclear charge.

4. **Ionisation Enthalpy or Ionisation Energy and Electropositive Character.** The alkaline earth metals owing to their large size of atoms have fairly low values of ionisation enthalpies as compared to the *p*-block elements. But the values are higher as compared to those of corresponding alkali metals. Within the group,

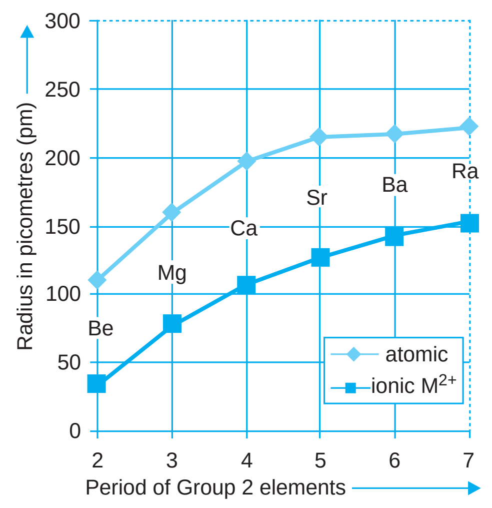


Fig. 5.1: *Variation of atomic radius and ionic radius down the group 2*

the ionisation enthalpy decreases as the atomic number increases. It is because of *increase in atomic size due to addition of new shells and increase in screening effect of the electrons in inner shells.*

Alkaline earth metals are fairly electropositive in nature, but due to greater ionisation enthalpies, these are less electropositive than alkali metals. Down the group electropositive character increases from Be to Ba.

A comparison of ionisation enthalpies (I.E.) of elements of groups 1 and 2 reveals that the members of group 2 have higher values. This is due to smaller size and higher nuclear charge of alkaline earth metals which keep the electrons in their outermost shell tightly held.

Element		:	Li	Na	K	Rb	Cs
Ionisation enthalpy (eV)	I_1	:	5.4	5.1	4.3	4.2	3.9
	I_2	:	75.6	47.4	32.0	28.0	25.0
Electropositive character		:	——— increasing ———→				

Element		:	Be	Mg	Ca	Sr	Ba	Ra
Ionisation enthalpy (eV)	I_1	:	9.3	7.6	6.1	5.7	5.2	5.3
	I_2	:	18.2	15.0	11.8	11.0	10.0	10.1
Electropositive character		:	——— increasing ———→					

It is clear from the above tables that the first I.E. of alkaline earth metals are higher than those of alkali metals, the second I.E. values are much lower than those of alkali metals.

Explanation. *The second electron in the case of alkali metals is to be removed from a cation which has stable noble gas configuration while in alkaline earth metals, the second electron is to be removed from a monovalent cation which is going to acquire the stable noble gas configuration. Therefore, the second electron can be removed more easily in the case of group 2 elements than in group 1 elements.*

5. **Oxidation States.** The alkaline earth metals have two electrons in their valence shell. If they lose these electrons, these atoms will acquire the stable noble gas configuration. Thus, the alkaline earth metals exhibit +2 oxidation state in their compounds.

$$\underset{\text{[Noble gas configuration] } ns^2}{M} \longrightarrow \underset{\text{[Noble gas]}}{M^{2+}} + 2e^-$$

In spite of higher second ionisation energies, these elements exist as divalent ions in most of their compounds because of the following reasons:

(*i*) *Divalent ions possess the stable noble gas configuration.*

(*ii*) *The divalent cations give rise to stronger lattices than monovalent cations and, hence, a lot of energy called lattice energy is released. This lattice energy easily compensates for the high second ionisation energy. This accounts for the existence of divalent ions in* **solid state**.

(*iii*) *The divalent cation has smaller size and, therefore, gets hydrated in water to a greater extent. Thus, the hydration energy released compensates for the high second ionisation energy. This accounts for the existence of divalent ions in* **aqueous state**.

6. **Reducing Properties.** Members of group 2, owing to their low ionisation energies have a tendency to lose their valence electrons and thus act as strong reducing agents. As the reduction potential values decrease while moving down the group (Table 5.2) it indicates that the reducing power increases. However, alkaline earth elements are weaker reducing agents than the alkali metals. *It is because of higher ionisation energy of alkaline earth metals as compared to alkali metals.*

Table 5.2: Physical Properties of Group 2 Elements (Alkaline Earth Metals)

Element	Atomic mass	Atomic radius (pm)	Ionic radius (pm)	Ionisation energy kJ/mol		Electro-negativity (Pauling scale)	Density (g cm^{-3}) at 293 K	Melting point (K)	Boiling point (K)	E° (volts) for M^{2+} (aq) +2e$^-$→M(s) at 298 K
				I	II					
Beryllium	9.01	112	27	899	1757	1.57	1.85	1560	2770	–1.70
Magnesium	24.31	160	72	737	1450	1.31	1.74	920	1378	–2.37
Calcium	40.08	197	100	590	1146	1.00	1.05	1112	1767	–2.87
Strontium	87.62	215	118	549	1064	0.95	2.03	1041	1654	–2.89
Barium	137.33	222	135	503	965	0.89	3.62	1000	1413	–2.90
Radium	226.03	–	148	509	979	0.90	5.5	973	–	–2.92

7. **Flame Colouration.** Members of this group except Be and Mg give characteristic colouration to the flame.
   Explanation. *Beryllium and magnesium do not impart any colour to the flame because of their small size and higher ionisation energies. Energy provided by the flame is insufficient to excite the valence electrons to higher shells. On the other hand, Ca (red colour), Sr (crimson colour), Ba (apple green) and Ra (crimson colour) give characteristic flame colouration. Colour shown by a substance is white light minus the colour absorbed by the substance.*

5.2.2 Chemical Properties of Alkaline Earth Metals

Because of *low ionization energies and high electropositive character,* the alkaline earth metals have a great tendency to lose valence electrons and, therefore, the reactivity of these elements increases in going down the group. These elements are less reactive compared to alkali metals, because they have relatively higher ionization energies. The important chemical reactions of alkaline earth metals are discussed as under:

1. **Hydrides.** All the members of the group, except beryllium form hydrides, MH_2 when they combine with hydrogen on heating.

$$M + H_2 \rightarrow MH_2$$

BeH_2 can be obtained indirectly by reduction of $BeCl_2$ with $LiAlH_4$.

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$

Characteristics of hydrides

(*i*) While MgH_2 is covalent in nature, CaH_2, SrH_2 and BaH_2 are ionic in nature. CaH_2 is commonly known as **hydrolith**.

(*ii*) These hydrides are highly reactive. They dissolve in water producing hydrogen gas as represented by the following equations.

$$MH_2\ (s) + 2H_2O\ (l) \rightarrow M^{2+}\ (aq) + 2OH^-\ (aq) + 2H_2\ (g)$$
$$CaH_2\ (s) + 2H_2O\ (l) \rightarrow Ca^{2+}\ (aq) + 2OH^-\ (aq) + 2H_2\ (g)$$

2. **Oxides.** All the alkaline earth metals burn in oxygen forming oxides. Beryllium, magnesium and calcium form monoxides while strontium and barium form peroxides. This is analogous to lithium forming monoxide and sodium forming peroxide.

$$2M + O_2 \rightarrow \underset{\text{(Monoxide)}}{2MO} \qquad (M = Be, Mg \text{ or } Ca)$$

$$M + O_2 \rightarrow \underset{\text{(Peroxide)}}{MO_2} \qquad (M = Ba \text{ or } Sr)$$

The reactivity of these metals towards oxygen increases as we move down the group. This is due to decreasing ionisation energy of the elements down the group.

Characteristics of oxides

(*i*) They are very stable compounds and form stable lattices.

(*ii*) BeO is amphoteric while oxides of other elements are basic in nature. The amphoteric substances are those which react with acids and alkalis both.

$$BeO + 2HCl \rightarrow BeCl_2 + H_2O$$

$$BeO + 2NaOH \rightarrow \underset{\text{(Sodium beryllate)}}{Na_2BeO_2} + H_2O$$

(*iii*) BeO and MgO are almost insoluble in water due to their large lattice energies (due to small ionic size) but oxides of other elements dissolve in water forming corresponding hydroxides in exothermic reaction.

$$MO\ (s) + H_2O\ (l) \rightarrow M^{2+}\ (aq) + 2OH^-\ (aq) + heat$$

3. **Hydroxides.** The hydroxides of these elements can be obtained either by dissolving metal oxides in water or by treating these elements with water.

Characteristics of hydroxides

(*i*) The hydroxides of magnesium, calcium, strontium and barium are **bases** and the basic strength increases from magnesium to barium. *It is because of increase in the ionic radius down the group due to which the strength of M–O bond in MOH decreases and, hence, causes an increase in basic character. This can also be explained in terms of decreasing ionisation energy.*

(*ii*) Although these hydroxides are less soluble in water as compared to the alkali metal hydroxides, they give strongly alkaline solutions due to their ready ionizability to form OH^- (*aq*). These bases neutralize acids to give salts and water.

$$M(OH)_2 + 2HCl \rightarrow MCl_2 + 2H_2O$$

(*iii*) The solubility of the hydroxides in water increases with the increase in atomic number. $Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble, $Ca(OH)_2$ is sparingly soluble while $Sr(OH)_2$ and $Ba(OH)_2$ are increasingly more soluble.

Explanation. *It is observed that the magnitude of hydration energy remains almost unaltered, whereas the magnitude of lattice energy decreases significantly down the group due to increase in size. As the lattice energy decreases the solubility increases and vice-versa.*

Solubility increases →

$Be(OH)_2$ $Mg(OH)_2$ $Ca(OH)_2$ $Sr(OH)_2$ $Ba(OH)_2$

Basic strength increases →

Aqueous solutions of calcium hydroxide (*lime water*) and barium hydroxide (known as *baryta*) are used to detect and estimate carbon dioxide because they give precipitates with the latter.

$$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{White ppt.}}{CaCO_3} + H_2O$$

$$Ba(OH)_2 + CO_2 \rightarrow \underset{\text{White ppt.}}{BaCO_3} + H_2O$$

With excess of CO_2, the precipitates dissolve due to the formation of soluble bicarbonates. It is found that the bicarbonates of alkaline earth metals are stable only in solution and decompose on heating even in the dissolved state.

$$CaCO_3 + H_2O \underset{-CO_2}{\overset{+CO_2}{\rightleftharpoons}} Ca(HCO_3)_2$$

4. **Reaction with Water.** Alkaline earth metals react with water to give the hydroxides and hydrogen. The reactivity increases with increasing atomic number. Beryllium does not react readily even with boiling water. Magnesium on the other hand reacts only with boiling water, whereas calcium, strontium and barium react vigorously with water even at room temperature.

$$M(s) + 2H_2O\ (l) \rightarrow M^{2+}\ (aq) + 2OH^-\ (aq) + H_2\ (g)$$

5. **Carbonates.** Carbonates of alkaline earth metals are insoluble in water. Carbonates can be obtained by addition of sodium or ammonium carbonate solution to the metal salts. For example,

$$CaCl_2 + Na_2CO_3 \rightarrow \underset{\text{ppt.}}{CaCO_3} + 2NaCl$$

All the carbonates decompose on heating to give carbon dioxide and metal oxide.

$$MCO_3 \xrightarrow{\Delta} MO + CO_2$$

As the atomic number increases, the stability of the carbonates towards heat **increases**. Beryllium carbonate is unstable and can be kept only in an atmosphere of CO_2. Solubility of carbonates decreases, because of decrease in hydration energy down the group.

Stability increases →

$BeCO_3$ $MgCO_3$ $CaCO_3$ $SrCO_3$ $BaCO_3$

Explanation. *The stability of carbonates towards heat depends upon the stability of the resulting metal oxide. Greater the stability of the resulting metal oxide smaller is the stability of the carbonate towards heat and vice-versa. Now the stability of resulting metal oxides decreases down the group due to decrease in lattice energy, (increasing size), therefore, the stability of carbonates towards heat increases.*

6. **Sulphates.** Sulphates of alkaline earth metals can be obtained by the reaction of H_2SO_4 with the metals, their oxides, hydroxides or carbonates as shown by the following equations:

$$Ca + H_2SO_4 \rightarrow CaSO_4 + H_2$$
$$CaO + H_2SO_4 \rightarrow CaSO_4 + H_2O$$
$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

The sulphates of alkaline earth metals are less soluble than the corresponding salts of alkali metals. Their solubilities decrease on going down the group.

Solubility in water decreases →

$BeSO_4$ $MgSO_4$ $CaSO_4$ $SrSO_4$ $BaSO_4$

Stability in water decreases →

Explanation. *It can be explained on the basis of hydration energy which decreases significantly, due to increase in the atomic size of alkaline earth metals, bringing about a decrease in solubility of their sulphates.*

Sulphates of alkaline earth metals are stable to heat. However, the stability decreases down the group.

7. **Halides.** Alkaline earth metals react with halogens directly to form halides, MX_2.

$$M + X_2 \rightarrow MX_2$$

Alkaline earth metal halides can also be obtained by the action of halogen acids on metals, their oxides, carbonates and hydroxides as given by the following equations:

$$M + 2HX \rightarrow MX_2 + H_2$$
$$MO + 2HX \rightarrow MX_2 + H_2O$$

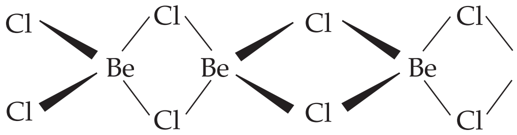
$$MCO_3 + 2HX \rightarrow MX_2 + H_2O + CO_2$$

$$M(OH)_2 + 2HX \rightarrow MX_2 + 2H_2O$$

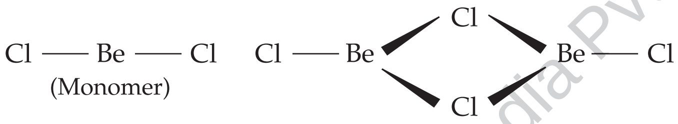
Indirect preparation of beryllium chloride is achieved as follows:

$$BeO + C + Cl_2 \xrightarrow{870-1070K} BeCl_2 + CO$$

Structure of $BeCl_2$. Beryllium chloride shows different structures in solid and vapour states. In **solid state**, it exists in the form of polymeric chain structure in which each Be atom is surrounded by four chlorine atoms. Two of the chlorine atoms are bonded by covalent bonds while the other two by coordinate bonds. The bridged structure consisting of infinite chains is shown below:



In the **vapour state**, it exists as a monomer having a linear structure and zero dipole moment above 1200 K. But below 1200 K, it exists as dimeric structure even in the vapour state.



(Monomer) (Dimer)

Characteristics of halides

(*i*) Beryllium halides are covalent, while halides of other alkaline earth metals are ionic. The ionic character of halides **increases** down the group due to gradual increase in ionic size and decrease in ionization energy.

(*ii*) Beryllium halides being covalent are soluble in organic solvents.

(*iii*) Fluorides of these elements have high lattice energy and are generally insoluble in water but bromides, chlorides and iodides are soluble in water.

(*iv*) The anhydrous halides are **hygroscopic**, *i.e.* become moist in air and form hydrates such as $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$. Because of this property anhydrous calcium chloride is used as a dehydrating agent. Beryllium chloride fumes in moist air due to its hydrolysis.

$$\underset{\text{(Moisture)}}{BeCl_2 + 2H_2O} \rightarrow \underset{\text{(Fumes)}}{Be(OH)_2 + 2HCl}$$

8. **Nitrides.** The alkaline earth elements combine with nitrogen on heating to form ionic nitrides with formula M_3N_2. Some examples are:

$$3Ca + N_2 \rightarrow Ca_3N_2$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$

The nitrides are, decomposed by water to produce ammonia and metal hydroxide,

$$Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3 \uparrow$$

9. **Complex Compounds.** Group 2 elements have a tendency to form stable complexes. This is because of the smaller size and higher charge of the alkaline earth metal ion. Among the elements of group 2, beryllium and magnesium, show greater capacity of complex formation.

PROBLEMS FOR PRACTICE

1. Out of Na and Mg which has higher ionisation energy?
2. Which element among group-2 elements has highest first ionisation energy?
3. How is beryllium chloride prepared?
4. What is the common oxidation state exhibited by group-2 elements?
5. Give equations to show the amphoteric character of beryllium oxide.
6. How do $Be(OH)_2$ and $Mg(OH)_2$ differ from each other?
7. What happens when water is added to quick lime (CaO)?

5.3 COMPOUNDS OF CALCIUM

1. Calcium oxide, Quick lime, CaO

Preparation. It is prepared by heating limestone in a rotatory kiln at 1070—1270 K, when the following reaction takes place.

$$CaCO_3 \rightleftharpoons CaO + CO_2;\ \Delta H = +\ 179.9\ kJ$$

Le Chatelier's Principle may be used to obtain a good yield of the product. *Carbon dioxide should be removed as soon as it is formed* in order to shift the equilibrium in the forward direction.

The temperature should not cross 1270 K as silica present as impurity in lime will combine with calcium oxide to form infusible calcium silicate, above this temperature.

$$CaO + SiO_2 \xrightarrow{\text{Above 1270K}} \underset{\text{Calcium silicate}}{CaSiO_3}$$

Properties

(i) It is a white amorphous solid melting at 2870 K.

(ii) It absorbs moisture and carbon dioxide forming slaked lime and calcium carbonate respectively.

$$CaO + \underset{(moisture)}{H_2O} \longrightarrow \underset{(slaked\ lime)}{Ca(OH)_2}$$

$$CaO + CO_2 \longrightarrow \underset{\text{Calcium carbonate}}{CaCO_3}$$

(iii) **Action of acids and acidic oxides.** It is a *basic oxide* and hence combines with acids and acidic oxides forming salts.

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O$$

$$CaO + SO_2 \longrightarrow CaSO_3$$

(iv) **Reaction with ammonium salts.** On heating with ammonium chloride, it liberates ammonia gas.

$$CaO + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + H_2O$$

(v) **On adding water.** It produces a hissing sound and a large amount of heat is evolved when water is added to it. This process is called *slaking of lime*.

$$CaO + H_2O \longrightarrow Ca(OH)_2;\quad \Delta H = -\ 63\ kJ$$

(vi) **Reaction with coke.** On heating with coke in an electric furnace at 2273-3273 K, it forms calcium carbide.

$$CaO + 3C \xrightarrow{2273-3273\ K} CaC_2 + CO$$

Uses

(*i*) It is used as a building material.
(*ii*) It is used for drying alcohols.
(*iii*) It is used in the preparation of ammonia and soda lime (CaO + NaOH).
(*iv*) It is used as a basic lining in furnaces.
(*v*) It is used in the preparation of cement, glass and calcium carbide.

2. Calcium hydroxide, Slaked lime, $Ca(OH)_2$

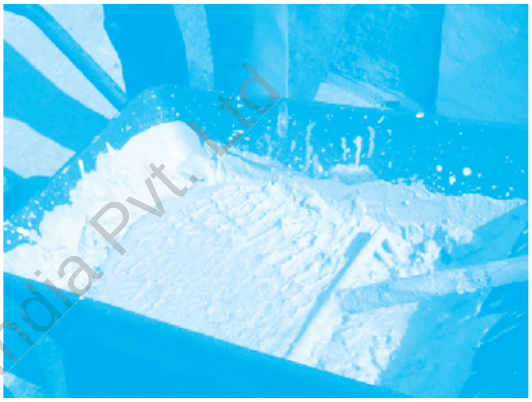
Preparation

(*i*) **From calcium chloride.** It is also obtained by treating calcium chloride with caustic soda.

$$CaCl_2 + 2NaOH \longrightarrow Ca(OH)_2 + 2NaCl$$

(*ii*) **From quick lime.** Calcium hydroxide is prepared on a commercial scale by adding water to quick lime. This process is called **slaking of lime**.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$



Preparation of slaked lime

Properties

(*i*) It is a white powder sparingly soluble in water. An aqueous suspension of calcium hydroxide in water is called **milk of lime.**

(*ii*) **Reaction with chlorine.** It reacts with chlorine to form bleaching powder according to the following reaction.

$$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow \underset{\text{Bleaching powder}}{CaOCl_2} + H_2O$$

(*iii*) **Reaction with acids.** Slaked lime being a strong base reacts with acids forming salts.

$$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$$

(*iv*) **Reaction with carbon dioxide.** When carbon dioxide is passed through lime water, it turns milky due to the formation of insoluble calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{(\textit{Milkiness})}{CaCO_3 \downarrow} + H_2O$$

With excess of carbon dioxide, the precipitates of calcium carbonate dissolve to form soluble calcium bicarbonate.

$$CaCO_3 + CO_2 + H_2O \longrightarrow \underset{(\textit{Soluble})}{Ca(HCO_3)_2}$$

If this clear solution of calcium bicarbonate is heated, the solution again turns milky due to the formation of calcium carbonate.

$$Ca(HCO_3)_2\ (aq) \xrightarrow{\text{Heat}} CaCO_3\ (s) + CO_2\ (g) + H_2O\ (l)$$

Uses

(*i*) It is used in white washing due to its disinfectant properties.
(*ii*) It is used in the manufacture of bleaching powder.
(*iii*) It is used in making glass, as a cheap alkali for neutralizing acids and to liberate ammonia from ammonium salts.
(*iv*) Calcium hydroxide is used as a building material.
(*v*) It is used for softening of hard water.
(*vi*) It is used as a reagent for detection of carbon dioxide.
(*vii*) It is used in agriculture to adjust the pH of soil.

3. Calcium carbonate, Limestone or Marble, $CaCO_3$

Preparation

(i) **From calcium chloride.** It is prepared by adding an aqueous solution of sodium carbonate to calcium chloride, when calcium carbonate precipitates out.

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 \downarrow + 2NaCl$$

(ii) **From slaked lime.** It is prepared by passing carbon dioxide through slaked lime.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

Properties

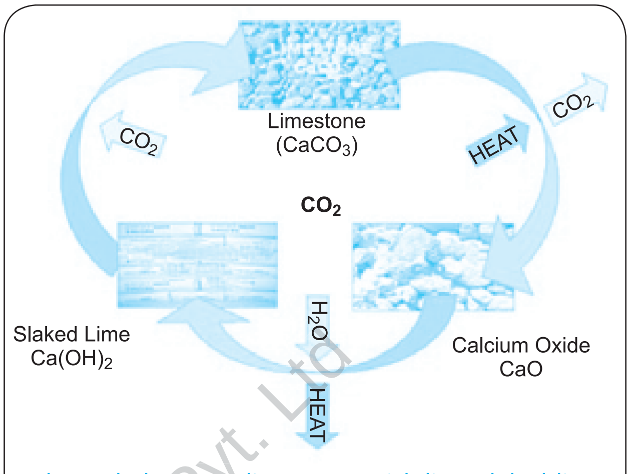
(*i*) It is a white fluffy powder insoluble in water.

(*ii*) On heating to 1270K, it decomposes to form quick lime

$$CaCO_3 \xrightarrow{1270\text{ K}} CaO + CO_2$$

(*iii*) It reacts with dilute acids producing CO_2 gas.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$
$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$



The cycle between limestone-quick lime-slaked lime

Uses

(*i*) It is used in the manufacture of quick lime.

(*ii*) It is used as a raw material for the manufacture of sodium carbonate by *Solvay-ammonia process.*

(*iii*) Calcium carbonate is used as a building material in the form of marble.

(*iv*) It is used in agriculture as a cheap material to neutralize the acidity of soil.

(*v*) Finely powdered $CaCO_3$ is used in tooth paste and cosmetics.

(*vi*) Along with $MgCO_3$ it is used for the extraction of metals such as iron.

(*vii*) It is an important constituent of cement.

4. Calcium sulphate, $CaSO_4$

Preparation. It is prepared by the action of the dilute sulphuric acid on lime or calcium carbonate.

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$$
$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

It can also be prepared by adding sodium sulphate to a soluble calcium salt solution.

$$CaCl_2 + Na_2SO_4 \longrightarrow CaSO_4 + 2NaCl$$

It is found in the earth's crust in large quantities as *gypsum,* $CaSO_4{\cdot}2H_2O$.

Properties

(*i*) Calcium sulphate dihydrate is sparingly soluble in water.

(*ii*) When gypsum is heated to about 390 K, it loses water partially and forms calcium sulphate hemihydrate, $CaSO_4{\cdot}\frac{1}{2}H_2O$ or $(CaSO_4)_2.H_2O$ which is commonly known as **Plaster of Paris**. Plaster of Paris in water has the feature of setting into a hard mass on standing.

$$\underset{\text{Gypsum}}{2CaSO_4{\cdot}2H_2O} \xrightarrow{390\text{ K}} \underset{\text{Plaster of Paris}}{2CaSO_4{\cdot}\frac{1}{2}H_2O} + 3H_2O$$

On further heating above 473 K, it loses water of crystallisation completely to form anhydrous $CaSO_4$. This is called **dead burnt plaster** because it has no tendency to absorb water.

$$2CaSO_4\cdot\frac{1}{2}H_2O \xrightarrow{473\ K} \underset{(Dead\ burnt\ plaster)}{2CaSO_4} + H_2O$$

Uses

(*i*) Calcium sulphate dihydrate (*gypsum*) is used in the manufacture of *Plaster of Paris* and cement.

(*ii*) Anhydrous calcium sulphate (*anhydrite*) is used as a drying agent.

(*iii*) It is used in the preparation of black board chalks.

5. Plaster of Paris, $CaSO_4\cdot\frac{1}{2}H_2O$ or $(CaSO_4)_2\cdot H_2O$

Preparation. It is prepared by heating gypsum to 390 K.

$$\underset{Gypsum}{2CaSO_4\cdot 2H_2O} \xrightarrow{390\ K} \underset{Plaster\ of\ Paris}{2CaSO_4\cdot\frac{1}{2}H_2O} + 3H_2O$$

To obtain the product with the right features, the temperature should not be allowed to rise above 390 K because above this temperature the whole of water of crystallisation is lost. The resulting anhydrous $CaSO_4$ is called **dead burnt plaster**. Dead burnt plaster loses the properties of setting with water.

Properties

(*i*) It is a white powder.

(*ii*) On mixing with three times its weight of water, it forms a mass which sets into a hard solid within 5 to 15 minutes. Due to this reason it is called **plaster**. It is believed that setting of Plaster of Paris is due to rehydration and reconversion into gypsum back.

$$\underset{Plaster\ of\ Paris}{2CaSO_4\cdot\frac{1}{2}H_2O} + 3H_2O \longrightarrow \underset{Gypsum}{2CaSO_4\cdot 2H_2O}$$

During the process of setting, slight expansion (1%) in volume occurs. Therefore, it can take the shape of the mould in which it is put.

Uses

(*i*) Plaster of Paris is used for producing moulds for pottery and ceramics.

(*ii*) It is used for making statues and models for decoration.

(*iii*) It is used in surgical bandages used for plastering broken or fractured bones of the body.

Some other compounds of group 2 elements that play an important role in medicines and healthcare are given below:

Plaster of Paris is used in surgical bandages

6. **Magnesium hydroxide, $Mg(OH)_2$:** It is used as a laxative to relieve occasional constipation and as an antacid to relieve indigestion, sour stomach and heartburn.
Barium sulphate, $BaSO_4$. This substance is non-toxic to humans. Its suspension is given orally to the patient before taking X-ray or CT scan of the gastrointestinal region.

7. **Nitrates:** Nitrates of group 2 elements can be obtained by the action of dilute nitric acid on metals or by the decomposition of carbonates using dilute nitric acid. On heating, the nitrates decompose into oxides with the evolution of nitrogen dioxide and oxygen. For example,

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

Stability of the nitrates towards heat increases as we go down the group

$$Be(NO_3)_2 < Mg(NO_3)_2 < Ca(NO_3)_2 < Sr(NO_3)_2 < Ba(NO_3)_2$$

$$\xrightarrow{\text{Thermal Stability increases}}$$

Explanation. *On decomposition, a nitrate changes into oxide. If the oxide formed is more stable, thermal stability of the nitrate would be less and vice versa.*

On moving down the group, the stability of the oxide decreases. This is because the force of attraction between the metal ion and oxide ion will decrease on account of increasing size of the metal ion. Smaller cations can fit more closely and strongly into the crystal lattice of substance. Therefore as we move down the group, thermal stability of the nitrate increases.

5.4 CEMENT

Joseph Aspdin, a mason of Leeds (U.K.) found that when a strongly heated mixture of limestone and clay was mixed with water and allowed to stand for some time, it hardened to a stone like mass resembling Portland rock. He, therefore, named it as **Portland cement.**

Cement is a finely powdered mixture of calcium silicates, aluminates and a little gypsum which sets into a hard mass when treated with water.

The chief components of cement are tricalcium silicate, $3CaO.SiO_2$ dicalcium silicate, $2CaO{\cdot}SiO_2$ and tricalcium aluminate $3CaO.Al_2O_3$. Out of these, tricalcium silicate is the most important since it has the property of setting quickly and acquiring considerable strength within a few days.

Composition of Portland cement. The average composition of portland cement is

Lime (CaO)..........50-60%

Magnesium oxide (MgO)..........2-3%

Silica (SiO_2)...........20-25%

Ferric oxide (Fe_2O_3)..........1-2%

Alumina (Al_2O_3)...........5-10%

Sulphur trioxide (SO_3).........1-2%

For a good quality cement, the ratio of alumina (Al_2O_3) to silica (SiO_2) should lie between 2.5 and 4 while that of lime (CaO) to silica + alumina + ferric oxide should be as close to 2 as possible. If lime is taken in excess, setting of cement is accompanied by cracking. If lime is in short quantity, cement remains weak in strength.

Raw materials. The essential raw materials required for the manufacture of cement are: (*i*) *limestone* $CaCO_3$, (*ii*) *clay* containing both silica and alumina and (*iii*) *gypsum*, $CaSO_4.2H_2O$. Also, small amounts of magnesia (MgO) and iron oxide (Fe_2O_3) are added for imparting suitable colour to cement.

Manufacture of Cement. Portland cement is manufactured by the following two processes:

(*i*) *Dry Process*

(*ii*) *Wet Process*

The dry process is preferred when the raw materials are hard.

The wet process is employed when the raw materials, *i.e.*, limestone and clay are soft, and climate is humid.

The main raw materials used in the manufacture of cement are *limestone* and *clay*. Limestone supplies lime while clay is a source of silica, alumina and iron oxide. The raw materials are crushed separately and are mixed in the required proportions (3 parts limestone + one part clay) and ground finely either by the *dry process* or by the *wet process*.

In the *dry process*, the raw materials are first dried and then mixed in desired proportions. The mixture is then finely powdered and made homogeneous. The homogeneous mass is called **'raw meal'**.

In the *wet process*, the clay is washed with water to remove flint and other foreign substances. It is then mixed with required quantity of limestone and ground in a special mill. The resulting paste is then thoroughly homogenised to get **'raw slurry'**.

The slurry or the raw meal is introduced into a rotary kiln as shown in the (Fig. 5.2) by means of screw conveyer. The kiln is an inclined steel rotating cylinder, 150–200 ft long and about 10 ft in diameter lined inside with bricks. The charge travels downwards slowly and is heated by burning coal dust which is blown in from the lower end. It takes about 2–3 hours for the charge to move down the kiln. Following changes occur in the kiln:

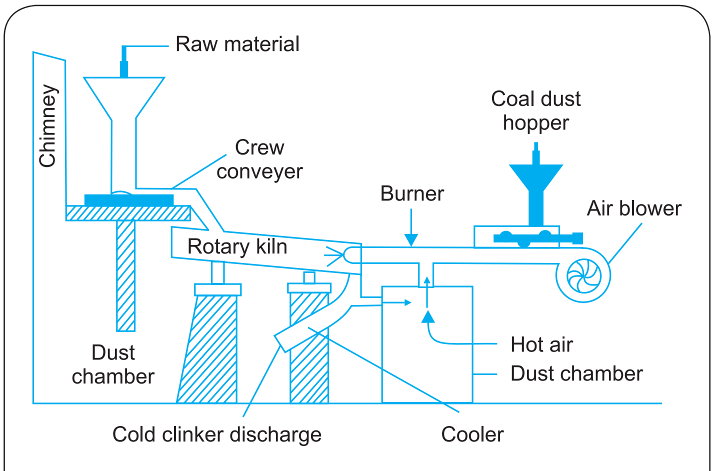


Fig. 5.2: *Manufacture of Portland cement*

(*i*) *In the upper part of the kiln* where the temperature is around 1000–1100 K, the charge loses all its water due to evaporation by hot gases.

(*ii*) *In the middle of the kiln* where the temperature is around 1100–1200 K, limestone decomposes into calcium oxide and carbon dioxide.

(*iii*) *The lower part of the kiln* is the hottest with the temperature ranging between 1770–1870 K. Chemical combination takes place between lime, alumina and silica to form calcium silicates and aluminates according to the following equations:

$$2CaO + SiO_2 \longrightarrow \underset{\text{Dicalcium silicate}}{2CaO\cdot SiO_2}$$

$$3CaO + SiO_2 \longrightarrow \underset{\text{Tricalcium silicate}}{3CaO\cdot SiO_2}$$

$$3CaO + Al_2O_3 \longrightarrow \underset{\text{Tricalcium aluminate}}{3CaO\cdot Al_2O_3}$$

$$2CaO + Al_2O_3 \longrightarrow \underset{\text{Dicalcium aluminate}}{2CaO\cdot Al_2O_3}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow \underset{\text{Tetracalcium aluminoferrite}}{4CaO\cdot Al_2O_3\cdot Fe_2O_3}$$

About 20–30% mass melts and combines with solid mass to form grey coloured balls called **cement clinkers.**

The hot clinkers are treated with cold air and mixed with 2—3% gypsum (to slow down the process of setting of cement). The mixture is finely powdered to give '*Portland cement*'.

Setting of Cement. When water is added to cement, an *exothermic reaction* occurs. During this process, the cement reacts with water to form a gelatinous mass which slowly sets into a hard mass having three-dimensional network structure involving — Si — O — Si — and — Si — O — Al — chains.

Out of the various constituents of cement, the most important is tricalcium silicate. It sets quickly and develops considerable strength within a few days. Dicalcium silicate sets slowly and develops appreciable strength after a month or so. Tricalcium aluminate sets instantaneously in presence of water. The internal strength acquired by cement is primarily due to the setting of tricalcium aluminate. Gypsum slows down the setting time and thus helps in imparting greater strength.

The various reactions involved in the *setting* process are as under:

(*i*) *Hydration of tricalcium aluminate to give hydrated gel*

$$\underset{\text{Tricalcium aluminate}}{3CaO{\cdot}Al_2O_3} + 6H_2O \longrightarrow \underset{\text{Hydrated gel}}{3CaO{\cdot}Al_2O_3{\cdot}6H_2O}$$

(*ii*) *Hydrolysis of tricalcium silicate to produce lime*

$$\underset{\text{Tricalcium silicate}}{3CaO{\cdot}SiO_2} + H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Dicalcium silicate}}{2CaO{\cdot}SiO_2}$$

(*iii*) *Hydration of dicalcium silicate to give hydrated colloidal gel in a slow process*

$$\underset{\text{Dicalcium silicate}}{2CaO{\cdot}SiO_2} + xH_2O \longrightarrow \underset{\text{Hydrated colloidal gel}}{3CaO{\cdot}SiO_2{\cdot}xH_2O}$$

(*iv*) *Partial hydrolysis of tricalcium aluminate to produce aluminium hydroxide*

$$\underset{\text{Tricalcium aluminate}}{3CaO{\cdot}Al_2O_3} + 6H_2O \longrightarrow 3Ca(OH)_2 + 2Al(OH)_3$$

(*v*) *Gypsum combines with tricalcium aluminate to form calcium sulphoaluminate*

$$\underset{\text{Tricalcium aluminate}}{3CaO{\cdot}Al_2O_3} + 3CaSO_4 + 2H_2O \longrightarrow \underset{\text{Calcium sulphoaluminate}}{3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}2H_2O}$$

The removal of fast-setting tricalcium aluminate brings about *slowing of setting* process.

5.5 ENVIRONMENTAL ISSUES IN BHUTAN

Bhutan has mineral deposits of beryl, copper, graphite, lead, mica, pyrite, tin, tungsten and tin. Bhutan's mineral industry is dominated by the production of cement, coal, dolomite, gypsum and limestone. A graphite processing plant was established in Paro. Bhutan Ferro Alloys Ltd produces mainly ferrosilicon which is exported to India and Japan. Indigenous quartzite produced by the company's own captive mines is supplied to the plant.

Dungsam Cement Corporation Ltd has set up a cement plant at Dungsam. It is a new, integrated and greenfield cement project with a capacity of 1.0 million tonnes of clinker and 1.36 million tonnes of cement a year. It was developed with the assistance of Government of India. Penden Cement Authority of Bhutan (PCA) was the first cement plant in Bhutan with production capacity of 1300 tonnes of cement every day.

5.5.1 Environmental Issues Arising from Cement Industry

Cement industry is one of the largest producers of CO_2. Cement manufacture contributes *greenhouse gases* both by the combustion of fossil fuels and decomposition of calcium carbonate. Cement production is also responsible for the production of nitrogen oxides and sulphur oxides.

Cement is used to create hard surfaces which contribute to surface runoff that may cause soil erosion, water pollution and floods.

Cement and its products cause health hazards through skin contact, eye contact and inhalation. Cement is highly alkaline (pH = 13), it can penetrate the skin and can cause burns and ulcers. Inhalation of cement dust causes irritation of nose and throat, its prolonged inhalation can cause the fatal disease silicosis.

Solutions to these issues

(*i*) A recent research has shown that dicalcium silicate (Y-phase) has the capacity to absorb CO_2 as the concrete cures. With the use of coal ash or another suitable substitute, this concrete will have CO_2 emission to an amazingly low level.

(*ii*) Concrete recycling is being used as a method of disposing of concrete structures. Concrete debris used to be shipped to landfills for disposal. Due to improved environmental awareness, governmental laws and economic benefits, it is being recycled now.

(*iii*) Control of dust can be made effective by using ventilation systems in conjunction with hoods and enclosures covering transfer points and conveyors. Dusty areas such as roads should be sprinkled with water to reduce dust generation. Use of electrostatic precipitators should be made to the maximum extent.

5.5.2 Environmental Issues Arising from Metallurgical Operations

The first step in metallurgy is combustion of carbonate ores to convert it into oxide ore or roasting of sulphide ore into oxide. These processes are carried out in furnaces at very high temperatures, which send fumes of CO, CO_2 and SO_2 into the atmosphere in high volumes. These gases are highly harmful to humans, plants and animals. It is highly desired that some alternative techniques should be developed for the extraction of metals from their ores.

Solution to these issues

The process of extraction of metals using furnaces that operate at high temperatures is called pyrometallurgy. This kind of metallurgy has been replaced by hydrometallurgy to extract certain metals. We use the principle of replacement of the metal from its salt in solution by using a more reactive metal. As the reactions take place in solution, the problem of toxic gases going into the atmosphere is avoided.

5.6 BIOLOGICAL ROLE OF SODIUM, POTASSIUM, MAGNESIUM AND CALCIUM

1. Role of Mg^{2+} and Ca^{2+} ions

(*i*) Magnesium ions are present in chlorophyll—a green colouring pigment in plants which absorbs light and is essential for photosynthesis.
(*ii*) Both magnesium and calcium ions catalyse a number of enzymatic reactions.
(*iii*) Calcium ions play an important role in muscle contraction.
(*iv*) Calcium is present in bones as phosphate.
(*v*) Deficiency of Ca^{2+} ions in children causes malnutrition.

Table 5.3: Group-2 Elements; Alkaline Earth Metals (Be, Mg, Ca, Sr, Ba and Ra)
Electronic configuration in their outer shell: ns^2

Increasing trends down the group	Decreasing trends down the group	Exceptions observed
Atomic radii (M)	IE_1 and IE_2 values	Density of Ca < Mg
Ionic radii (M^{2+})	Electronegativity	Halides of Be are covalent
Density	Solubility of CO_3^{2-} and SO_4^{2-}	
Reactivity	Tendency to form complexes diminishes after Mg	BeO and $Be(OH)_2$ are amphoteric
Reducing nature (E° values)		
Tendency to form peroxides	Solubility of hydroxides in water	
Basic strength of hydroxides.		
Ionic nature of halides hydrides (MH_3)		

QUICK SCAN (FOR REVISION)

1. Important minerals of magnesium are: carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$), magnesite ($MgCO_3$), dolomite ($CaCO_3{\cdot}MgCO_3$), Epsom salt ($MgSO_4{\cdot}7H_2O$).
2. Important minerals of calcium are: limestone ($CaCO_3$), dolomite ($CaCO_3{\cdot}MgCO_3$), gypsum ($CaSO_4{\cdot}2H_2O$) and fluorspar (CaF_2).
3. Magnesium is extracted by electrolysis of fused magnesium chloride or carnallite to which some $CaCl_2$ and NaCl have been added to reduce the melting point of $MgCl_2$ or carnallite.
4. Calcium is extracted by electrolysis of fused $CaCl_2$ to which some CaF_2 has been added to lower the fusion temperature of $CaCl_2$.
5. Magnesium burns in air to form a mixture of MgO and Mg_3N_2.
6. Calcium is preferred over Na to remove the last traces of moisture from alcohol since Na reacts rapidly but Ca reacts slowly with alcohol.
7. Due to high ionization energies, Be and Mg do not impart any colour to the Bunsen flame. Ca imparts *brick red*, Sr imparts *crimson red* while Ba imparts *apple green colour* to the flame.
8. Magnesium continues to burn in SO_2 since it reacts to form MgO and S.
9. Anhydrous $MgCl_2$ cannot be prepared by simply heating $MgCl_2{\cdot}6H_2O$ since it gets hydrolysed by its own water of crystallization. However, if $MgCl_2{\cdot}6H_2O$ is heated in an atmosphere of HCl gas, hydrolysis of $MgCl_2$ does not occur.
10. Magnesium powder is used in flash bulbs for photography.
11. Sorel cement or Magnesia cement is $MgCl_2{\cdot}5MgO{\cdot}xH_2O$.
12. **Quick lime** (CaO) is obtained by heating lime stone. It is used to dry NH_3 gas.
13. **Slaked lime** is calcium hydroxide and is obtained by dissolving CaO in H_2O.
14. Slaked lime reacts with Cl_2 to form **bleaching powder** ($CaOCl_2$).
15. A suspension of $Mg(OH)_2$ in water or *milk of magnesia* is used as an *antacid.*
16. Lime water is a clear solution of $Ca(OH)_2$ in water. It turns milky due to the formation of insoluble $CaCO_3$ when CO_2 is passed through it. On prolonged passing of CO_2 milkiness disappears and the solution becomes clear again due to the formation of soluble $Ca(HCO_3)_2$.
17. Gypsum is $CaSO_4{\cdot}2H_2O$. When heated to 390. K, it loses water partially to form *Plaster of Paris*, $CaSO_4{\cdot}\frac{1}{2}H_2O$. However, if gypsum is heated to 473 K, it loses water completely to form anhydrous calcium sulphate or *dead burnt plaster.*
18. The setting of Plaster of Paris is due to rehydration into gypsum.

$$2CaSO_4{\cdot}\frac{1}{2}\,H_2O + 3H_2O \longrightarrow 2CaSO_4{\cdot}2H_2O$$

19. **Cement** is essentially a finely powered mixture of calcium silicates and calcium aluminates with small amounts of gypsum. When mixed with water, it sets into a hard mass. It is also called *Portland cement.*

EXERCISES

Very Short Answer Type Questions

1. Why is it necessary to add gypsum in the final stage of preparation of cement?
2. What is dead burnt plaster?
3. Bones contain calcium ions. What do you think would be the anion associated with them?
4. Alkaline earth metals cannot be obtained by chemical reduction method. Explain.
5. What is quick lime? What happens when we add water to it?
6. Arrange the following ions in the order of increasing radii?

   Li^+, Mg^{2+}, K^+, Al^{3+}
7. What is Epsom salt? What is the action of heat on it?
8. What is the formula of gypsum? What happens when it is heated?
9. What is the formula of Plaster of Paris?

Explain the following with reasons:

10. $MgSO_4$ is highly soluble in water whereas $BaSO_4$ is insoluble.
11. The basic strength of the oxides of elements of group 2 increases regularly from BeO to BaO.
12. The solubility of sulphates of alkaline earth metals decreases on descending down the group from Be to Ba.

Short Answer Type Questions

1. State the reactions involved in the manufacture of sodium hydroxide from sodium chloride.
2. (*i*) What is the difference between milk of lime and lime water?
   (*ii*) Is it necessary to add gypsum in the final stages of preparation of cement? Why?
3. What is Portland cement? Give its average composition.
4. What happens when gypsum is heated?
5. What is the effect of heat on the following compounds (write equations for the reactions)?
   (*i*) Calcium carbonate.
   (*ii*) Gypsum.
6. Describe a method for the preparation of quick lime. What happens when water is poured over quick lime?
7. Explain the following:
   (*i*) Ionisation energies of alkaline earth metals decrease as the atomic number increases.
   (*ii*) Group 2 metals are harder and denser than group 1 metals.
8. How are the following compounds prepared?
   (*a*) Quick lime
   (*b*) Plaster of Paris
9. Name a few important uses of the following compounds:
   (*i*) Epsom salt
   (*ii*) Quick lime
   (*iii*) Slaked lime.
10. Why do alkaline earth metals not occur in free state?
11. Explain giving reason for the following:
    Gypsum is added to powered clinkers to get cement.
12. Describe a method for the preparation of quick lime. What happens when rain happens to fall on quick lime?
13. Name an element from Group 2 which forms an amphoteric oxide and a water soluble sulphate.
14. Discuss the trend of the following:
    (*a*) Thermal stability of carbonates of Group 2 elements.
    (*b*) The solubility and the nature of oxides of Group 2 elements.
15. Why are $BeSO_4$ and $MgSO_4$ readily soluble in water while $CaSO_4$, $SrSO_4$ and $BaSO_4$ are insoluble?
16. Why do beryllium and magnesium not impart colour to the flame in the flame test?
17. What is the structure of $BeCl_2$ molecule in gaseous and solid state?

Long Answer Type Questions

1. Describe the manufacture of cement and indicate the chemical reactions which occur in the rotary kiln.
2. Explain the following:
   (*i*) Beryllium chloride fumes in air.
   [**Hint:** $BeCl_2 + 2H_2O \rightarrow Be(OH)_2 + 2HCl$]
   (*ii*) Alkaline earth metals are weaker reducing agents than alkali metals.
   (*iii*) Alkaline earth metal salts are diamagnetic in nature.
   (*iv*) Magnesium oxide is used as a refractory material.
   [**Hint:** MgO has a very high m.p.]
   (*v*) Alkaline earth metal salts are less soluble than the corresponding alkali metal salts.
   [**Hint:** Lattice energy of GpII > GpI]
   (*vi*) First IE of alkaline earth metals is more than the first IE of alkali metals but reverse is true for the second IE.
   (*vii*) Ba^{2+} ion is poisonous, yet $BaSO_4$ is given to patients prior to taking stomach *X*-ray.
   [**Hint:** $BaSO_4$ is insoluble and does not pass from digestive system to circulatory system].
   (*viii*) Beryllium shows covalency whereas other members of the family show electrovalency.
   (*ix*) Lime water turns milky on passing CO_2, but milkiness disappears on passing excess of CO_2.
3. Give formulae and one important use of each of the following:
   (*i*) Gypsum
   (*ii*) Plaster of Paris
   (*iii*) Microscomic salt
4. The *s*-block elements are characterised by their larger atomic sizes, lower ionisation enthalpies, invariable +1 oxidation state and solubilities of their oxosalts. In the light of these features describe the nature of their oxides, halides and oxosalts.
5. Comment on the alkaline earth metals with respect to the following characteristics:
   (*i*) Tendency to form ionic/covalent compounds
   (*ii*) Nature of oxides and their solubility in water
   (*iii*) Formation of oxosalts
   (*iv*) Solubility of oxosalts
   (*v*) Thermal stability of oxosalts
6. When water is added to compound (A) of calcium, solution of compound (B) is formed. When carbon dioxide is passed into the solution, it turns milky due to the formation of compound (C). If excess of carbon dioxide is passed into the solution milkiness disappears due to the formation of compound (D). Identify the compounds A, B, C and D. Explain why the milkiness disappears in the last step.
7. An element of group 2 forms covalent oxide which is amphoteric in nature and dissolves in water to give an amphoteric hydroxide. Identify the element and write chemical reactions of the hydroxide of the element with an alkali and an acid.

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. Gypsum slows down the process of setting which helps to impart strength.
2. $CaSO_4$ which has no tendency to absorb water is called burnt plaster.
3. PO_4^{3-}
4. Refer to text.
5. CaO and $Ca(OH)_2$ are formed.
6. $Al^{3+} < Li^{+} < Mg^{2+} < K^{+}$
7. $MgSO_4{\cdot}7H_2O, MgSO_4{\cdot}7H_2O, \xrightarrow[423\ H]{-6H_2O} MgSO_4{\cdot}H_2O$
   $\xrightarrow[-H_2O]{506\ K} MgSO_4 \longrightarrow MgO + SO_3$
8. $CaSO_4{\cdot}2H_2O$. On heating to 393 K, it produces Plaster of Paris, $CaSO_4{\cdot}\frac{1}{2}H_2O$. But gives dead burnt plaster at 473 K.
9. $CaSO_4{\cdot}\frac{1}{2}H_2O$.

Short Answer Type Questions

4. $2CaSO_4{\cdot}2H_2O \xrightarrow[-3H_2O]{390\ K} (CaSO_4)_2{\cdot}H_2O \xrightarrow[437\ K]{Above}$
   $2CaSO_4 + H_2O$
6. $CaO\ (s) + H_2O\ (l) \longrightarrow Ca(OH)_2 + \text{heat}$
10. As they are very reactive with oxygen of the air as well as water.
11. To retard the setting of cement by removing tricalcium aluminate, (a fast setting material) by forming calcium sulphoaluminate, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}2H_2O$.

COMPETITION FILE

SUBJECTIVE PROBLEMS

Problem 1. *Calcium burns in nitrogen to produce white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds (A) and (B).*

Solution.

$$2Ca + O_2 \rightarrow 2CaO$$
$$3Ca + N_2 \rightarrow Ca_3N_2$$
$$Ca_3N_2 + 6H_2O \rightarrow Ca(OH)_2 + \underset{(A)}{2NH_3}$$
$$Ca(OH)_2 + CO_2 \rightarrow \underset{(B)}{CaCO_3} + H_2O$$

Problem 2. *The crystalline salts of alkaline earth metals contain more water of crystallization than the corresponding alkali metal salts. Why?*

Solution. Due to higher nuclear charge, alkaline earth metals have a higher tendency than alkali metals to attract water molecules and, therefore, contain more water of crystallization than alkali metals. For example lithium chloride exists as $LiCl.2H_2O$, whereas magnesium chloride exists as $MgCl_2.6H_2O$.

Problem 3. *Chlorination of calcium hydroxide produces bleaching powder. Write its chemical equation.*

Solution.

$$3Ca(OH)_2 + 2Cl_2 \rightarrow \underset{\text{Bleaching powder}}{Ca(OCl)_2 + Ca(OH)_2 + CaCl_2{\cdot}2H_2O}$$

Problem 4. *Why is $BaSO_4$ insoluble whereas $BeSO_4$ is soluble in water?*

Solution. The lattice energy of $BaSO_4$ is much greater than its hydration energy. Hence, it is insoluble in water. In contrast, because of the smaller Be^{2+} ions, $BeSO_4$ has a greater hydration energy than lattice energy. If hydration energy of a substance is greater than the lattice energy, then the substance is soluble.

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. Plaster of Paris is
   (*a*) $CaSO_4$ (*b*) $2CaSO_4{\cdot}H_2O$
   (*c*) $CaSO_4{\cdot}½H_2O$ (*d*) $CaSO_4{\cdot}2H_2O$
2. The difference in water molecule of gypsum and Plaster of Paris is
   (*a*) $\frac{5}{2}$ (*b*) 2
   (*c*) $\frac{1}{2}$ (*d*) $1\frac{1}{2}$
3. $MgCl_2{\cdot}6H_2O$ when heated gives
   (*a*) Magnesium oxychloride
   (*b*) Magnesium dichloride
   (*c*) Magnesium oxide
   (*d*) Magnesium chloride

4. Which one of the following statements regarding magnesia is not correct?
   - (*a*) It has very high m.p.
   - (*b*) It is an acidic oxide and reacts with bases to form salts.
   - (*c*) It is sparingly soluble in water.
   - (*d*) It is reduced by carbon at a very high temperature to form magnesium carbide.
5. Mg is an important component of which biomolecule occurring extensively in the living world?
   - (*a*) Haemoglobin
   - (*b*) Chlorophyll
   - (*c*) Florigen
   - (*d*) ATP
6. Halides of alkaline earth metals form hydrates such as $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}6H_2O$, $BaCl_2{\cdot}2H_2O$ and $SrCl_2{\cdot}2H_2O$. This shows that halides of group 2 elements
   - (*a*) are hygroscopic in nature.
   - (*b*) act as dehydrating agents.
   - (*c*) can absorb moisture from air.
   - (*d*) all of the above.
7. The set representing the correct order of first ionization potential is
   - (*a*) K > Na > Li
   - (*b*) Be > Mg > Ca
   - (*c*) B > C > N
   - (*d*) Ge > Si > C
8. Beryllium and aluminium exhibit many properties which are similar. But, the two elements differ in
   - (*a*) exhibiting maximum covalency in compounds
   - (*b*) forming polymeric hydrides
   - (*c*) forming covalent halides
   - (*d*) exhibiting amphoteric nature in their oxides
9. In which of the following the hydration energy is higher than the lattice energy?
   - (*a*) $MgSO_4$
   - (*b*) $RaSO_4$
   - (*c*) $SrSO_4$
   - (*d*) $BaSO_4$.
10. Which of the following oxides is not expected to react with sodium hydroxide?
    - (*a*) CaO
    - (*b*) SiO_2
    - (*c*) BeO
    - (*d*) Be_2O_3
11. Which of the following alkaline earth metal sulphates has hydration enthalpy higher than the lattice enthalpy?
    - (*a*) $CaSO_4$
    - (*b*) $BeSO_4$
    - (*c*) $BaSO_4$
    - (*d*) $SrSO_4$
12. Which of the following compounds is a peroxide?
    - (*a*) KO_2
    - (*b*) BaO_2
    - (*c*) MnO_2
    - (*d*) NO_2

(B) Fill in the Blanks

Fill in the blank spaces:

1. Alkaline earth metals cannot be prepared by the .... of their ....
2. The mineral dolomite has the chemical composition ....
3. Alkaline earth metals from .... ions.
4. Ca^{2+} has a smaller ionic radius than K^+ because it has ....
5. On heating, $Rb(ICl_2)$ will decompose giving ....

(C) True/False Statements

Write T for true and F for false statements:

1. All alkaline earth metals have two electrons in their outermost orbit.
2. Alkaline earth metals usually form ionic compounds.
3. Alkaline earth metals do occur in the native state in the nature.
4. Alkaline earth metals are stronger reducing agents than alkali metals.
5. Magnesium can be extracted from sea water by precipitating it as $Mg(OH)_2$.
6. Magnesium sulphate is more soluble in water than $BaSO_4$.
7. Magnesium is an essential constituent of chlorophyll.
8. Alkaline earth metals are strongly electronegative in character.
9. $MgCO_3$ is known as magnesite.
10. Alkaline earth metals are generally obtained by the electrolysis of their molten halides.
11. Magnesium is used to form alloys such as magnalium.
12. Magnesium hydroxide is a stronger base than calcium hydroxide.

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. Metal carbonates decompose on heating to give metal oxide and carbon dioxide. Which of the metal carbonates is most stable thermally?
   - (*a*) $MgCO_3$
   - (*b*) $CaCO_3$
   - (*c*) $SrCO_3$
   - (*d*) $BaCO_3$
2. Which of the carbonates given below is unstable in air and is kept in CO_2 atmosphere to avoid decomposition?
   - (*a*) $BeCO_3$
   - (*b*) $MgCO_3$
   - (*c*) $CaCO_3$
   - (*d*) $BaCO_3$
3. Metals form basic hydroxides. Which of the following metal hydroxide is the least basic?
   - (*a*) $Mg(OH)_2$
   - (*b*) $Ca(OH)_2$
   - (*c*) $Sr(OH)_2$
   - (*d*) $Ba(OH)_2$

4. Some of the Group 2 metal halides are covalent and soluble in organic solvents. Among the following metal halides, the one which is soluble in ethanol is
   (*a*) $BeCl_2$ (*b*) $MgCl_2$
   (*c*) $CaCl_2$ (*d*) $SrCl_2$
5. Amphoteric hydroxides react with both alkalies and acids. Which of the following Group 2 metal hydroxides is soluble in sodium hydroxide?
   (*a*) $Be(OH)_2$ (*b*) $Mg(OH)_2$
   (*c*) $Ca(OH)_2$ (*d*) $Ba(OH)_2$
6. By adding gypsum to cement
   (*a*) setting time of cement becomes less
   (*b*) setting time of cement increases
   (*c*) colour of cement becomes light
   (*d*) shining surface is obtained
7. Dead burnt plaster is
   (*a*) $CaSO_4$ (*b*) $CaSO_4 \cdot \frac{1}{2} H_2O$
   (*c*) $CaSO_4 \cdot H_2O$ (*d*) $CaSO_4 \cdot 2H_2O$
8. Suspension of slaked lime in water is known as
   (*a*) lime water (*b*) quick lime
   (*c*) milk of lime
   (*d*) aqueous solution of slaked lime
9. Which of the following elements does not form hydride by direct heating with dihydrogen?
   (*a*) Be (*b*) Mg
   (*c*) Sr (*d*) Ba
10. A substance which gives brick red flame and breaks down on heating to give oxygen and a brown gas is
   (*a*) Magnesium nitrate (*b*) Calcium nitrate
   (*c*) Barium nitrate (*d*) Strontium nitrate
11. Which of the following statements is true about $Ca(OH)_2$?
   (*a*) It is used in the preparation of bleaching powder
   (*b*) It is a light blue solid
   (*c*) It does not possess disinfectant property
   (*d*) It is used in the manufacture of cement
12. A chemical **A** is used for the preparation of washing soda to recover ammonia. When CO_2 is bubbled through an aqueous solution of **A,** the solution turns milky. It is used in white washing due to disinfectant nature. What is the chemical formula of **A**?
   (*a*) $Ca(HCO_3)_2$ (*b*) CaO
   (*c*) $Ca(OH)_2$ (*d*) $CaCO_3$
13. Dehydration of hydrates of halides of calcium, barium and strontium, *i.e.*, $CaCl_26H_2O$, $BaCl_2.2H_2O$, $SrCl_2.2H_2O$, can be achieved by heating. These become wet on keeping in air. Which of the following statements is correct about these halides?
   (*a*) Act as dehydrating agent
   (*b*) Can absorb moisture from air
   (*c*) Tendency to form hydrate decreases from calcium to barium
   (*d*) All of the above
14. Which of the following compounds are readily soluble in water?
   (*a*) $BeSO_4$ (*b*) $MgSO_4$
   (*c*) $BaSO_4$ (*d*) $SrSO_4$
15. Identify the correct formula of halides of alkaline earth metals from the following.
   (*a*) $BaCl_2 \cdot 2H_2O$ (*b*) $BaCl_2 \cdot 4H_2O$
   (*c*) $CaCl_2 \cdot 6H_2O$ (*d*) $SrCl_2 \cdot 4H_2O$
16. Choose the correct statements from the following.
   (*a*) Beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.
   (*b*) Beryllium sulphate is readily soluble in water as the greater hydration enthalpy of Be^{2+} overcomes the lattice enthalpy factor.
   (*c*) Beryllium exhibits coordination number more than four.
   (*d*) Beryllium oxide is purely acidic in nature.

III. Matching Type Questions

Match the compounds given in column I with their uses mentioned in column II.

Column I	Column II
(*i*) $CaCO_3$	(*a*) Dentistry, ornamental work
(*ii*) $Ca(OH)_2$	(*b*) Manufacture of sodium carbonate from caustic soda
(*iii*) CaO	(*c*) Manufacture of high quality paper
(*iv*) $CaSO_4$	(*d*) Used in white washing

IV. Assertion-Reason Type Question

In the following questions a statement of Assertion (A) followed by a statement of Reasons (R) is given. Choose the correct option out of the following choices.

1. ***Assertion* (*A*):** Beryllium carbonate is kept in the atmosphere of carbon dioxide.
   ***Reason* (*R*):** Beryllium carbonate is unstable and decomposes to give beryllium oxide and carbon dioxide.
   (*i*) Both A and R are correct and R is the correct explanation of A
   (*ii*) Both A and R are correct but R is not the correct explanation of A
   (*iii*) Both A and R are not correct
   (*iv*) A is not correct but R is correct

ANSWERS

(A) Multiple Choice Questions

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

(B) Fill in the Blanks

1. electrolysis, aqueous solutions 2. $MgCO_3 \cdot CaCO_3$ 3. M^{2+}
4. higher effective nuclear charge 5. RbCl, ICl

(C) True/False Statements

1. T 2. T 3. F 4. F 5. T 6. T 7. T 8. F
9. T 10. T 11. T 12. T

Some Additional Questions

I. Multiple Choice Questions

1. (*d*) 2. (*a*) 3. (*a*) 4. (*a*) 5. (*a*) 6. (*b*) 7. (*a*) 8. (*c*)
9. (*a*) 10. (*c*) 11. (*a*) 12. (*c*) 13. (*d*) 14. (*a*), (*b*) 15. (*a*), (*c*) 16. (*a*), (*b*)

III. Matching Type Questions

(*i*) → (*c*) (*ii*) → (*d*) (*iii*) → (*b*) (*iv*) → (*a*)

IV. Assertion-Reason Type Question

1. (*i*)

6

CHAPTER

Group-17 The Halogens

LEARNING OBJECTIVES

- Describe the trends in electronegativity and boiling points of the halogens.
- Describe the reactions of potassium halides with concentrated sulphuric acid.
- Describe the reactions of halide ions with silver ions and compare the trends in solubility of the silver halides in diluted and concentrated ammonia as a test halide ions in a solution.
- Describe the disproportionation reactions of chlorine, bromine and iodine with water, cold and hot alkali and outline the uses of the solutions formed.
- State the uses of chlorine e.g. its use in water treatments and its harmful effects (e.g. the toxic hazards of chlorine gas).
- Make predictions about fluorine and astatine and their compounds based on the physical and chemical properties of the halogens.

6.1 INTRODUCTION

Fluorine (F), *Chlorine* (Cl), *Bromine* (Br), *Iodine* (I) and *Astatine* (At) are members of group-17 of the periodic table. Their salts are present in seawater and, hence, they are collectively known as **halogens** (Greek, *halos* means sea salt producers). They have a very strong tendency to acquire a stable inert gas configuration by accepting one electron. For this reason, halogens exhibit non-metallic behaviour. Astatine, the last member of halogen family, is a radioactive element with a very short life. All other halogens exist in the combined state.

In the combined state, fluorine occurs as cryolite Na_3AIF_6, fluorspar CaF_2 and fluorapatite $Ca_5(PO_4)_3F$. Chlorine is found as sodium chloride present as *rock salt* or in the seawater. Bromine occurs in seawater as bromides of alkali earth metals. Iodine is found as sodium iodate in *chile-salt petre* and as alkali metal iodides and alkaline earth metal iodides in seawater.

Halogens exhibit a general electronic configuration: ns^2np^5 in their valence shells.

The electronic configurations of halogens are given in Table 6.1.

Table 6.1: Electronic Configuration and Oxidation States of Halogens

Element	Atomic Number	Electronic Configuration		Oxidation States
		Complete	With Inert Gas Core	
Fluorine (F)	9	$Is^2\ 2s^2\ 2p^5$	[He] $2s^2\ 2p^5$	–1
Chlorine (Cl)	17	$Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$	[Ne] $3s^2\ 3p^5$	–1, +1,+3,+5
Bromine (Br)	35	$Is^2\ 2s^2\ 2p^6\ 3s^2 3p^6\ 3d^{10}\ 4s^2\ 4p^5$	[Ar] $3d^{10}\ 4s^2\ 4p^5$	–1, +1, +3, +5, +7
Iodine (I)	53	$Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$	[Kr] $4d^{10}\ 5s^2\ 5p^5$	–1, +1, +3, +5, +7
Astatine (At)	85	$Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10} 4f^{14}\ 5s^2\ 5p^6\ 5d^{10}\ 6s^2\ 6p^5$	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$	

Halogens exist as diatomic molecules having a characteristic colour. Fluorine exhibits only negative oxidation state of –1. Other halogens exhibit positive oxidation states also in addition to –1 oxidation state.

Some of the properties of group-17 elements are given in Table 6.2.

Table 6.2: Some Properties of Group-17 Elements

Element	Atomic mass	Covalent radius (pm)	Ionic-radius (pm)	Ionisation enthalpy (kJ cm^{-3}) I	Electro-negativity (Pauling scale) II	Density (g cm^{-3}) at 193 K (liquid state)	Melting point (K)	Boiling point (K)	Distance X—X in X^2 (pm)	Heat of dissoc-iation $X_2(s) \rightarrow 2X$ (kJ mol^{-1})
Fluorine	19.00	72	133	1680	4	1.51 (85 K)	54.4	84.9	143	158.8
Chlorine	35.45	99	184	1256	3.2	1.66 (203 K)	172	239	199	242.6
Bromine	79.90	114	196	1142	3.0	3.19 (273 K)	265.8	332.5	228	192.8
Iodine	126.90	139	220	1008	2.7	3.96 (393 K)	386.6	457.4	266	151.1
Astatine	210.00	150	2	899	2.2	—	575	610	—	—

6.2 TRENDS IN PHYSICAL PROPERTIES

The regular graduation in the physical as well as chemical properties of halogens is discussed as under:

1. **Atomic and ionic radii.** Atomic and ionic radii of halogens are comparatively small and increase regularly down the group from fluorine to iodine because some new electronic shells are added. Small atomic and ionic radii of halogens are explained in terms of addition of electrons in the same shell successively.
2. **Melting and boiling points.** Melting and boiling points increase with increase in atomic number. The heat of fusion as well as heat of vaporisation also increase with the increase in atomic number. This is due to the increase in Van der Waals's forces of attraction between the molecules with the increase in atomic size.
3. **Ionization enthalpy.** Ionization enthalpies (energies) of halogens are very high and the value decreases down the group because the distance of valence shell from the nucleus increases. Iodine forms stable compounds in which it exists as I^+ ion.
4. **Colour.** Halogens are coloured substances. The colour of different halogens are as follows:

Halogen	*Colour*
Fluorine	Pale yellow
Chlorine	Greenish yellow
Bromine	Reddish brown
Iodine	Dark violet

Explanation. *The colour of the halogen is due to absorption of visible light by their molecules when the outer electron is excited to higher energy levels. Fluorine being smaller in size absorbs high energy violet light for excitation and appears pale yellow while iodine absorbs low energy yellow light for excitation and, therefore, appears violet black. In between, the colour of chlorine is yellowish-green and of bromine is reddish-brown or orange. Thus, the colour deepens down the group. It may be remembered that light required for excitation of electrons is proportionate to I.E. and the colour of the substance is the colour of transmitted light.*


Halogen lamp

5. **Physical state.** The halogens are all diatomic and exist as F_2, Cl_2, Br_2 and I_2. The intermolecular forces are very weak in halogens. The nature of forces correspond to van der Waals' forces and their magnitudes increase down the group.

   Thus, F_2 and Cl_2 are gases, bromine is a volatile liquid and iodine is a volatile solid.

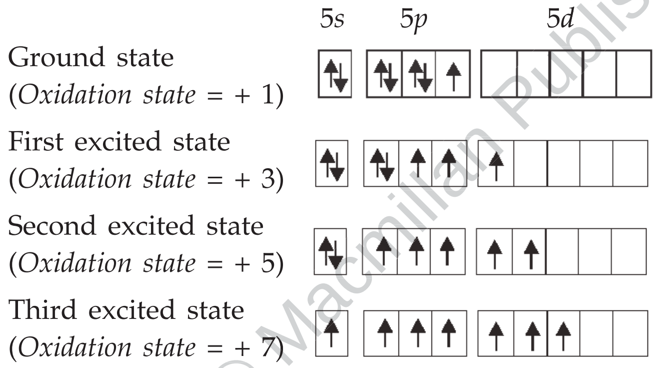
6. **Non-metallic character.** All the halogens have very high values of ionization energies and exhibit a non-metallic character. The non-metallic character, however, decreases down the group due to decrease in I.E. Iodine shows some distinct metallic properties.

7. **Electronegativity.** The tendency of an element to attract a bonding pair of electrons towards itself is called electronegativity. As the halogens are short of one electron to complete their octet, they are all electronegative elements. We observe that as we move down the group from F to At, electronegativity decreases. This is because with the increase of atomic radius, the power of the nucleus to attract the extra electron decreases. Electronegativity follows the order: F > Cl > Br > I.

8. **Electron affinities.** Halogens have strong tendency to accept electrons, therefore, they have high values of electron affinities. On moving down the group, electron affinity values decrease because size of the atom increases. However, fluorine has a smaller electron affinity than chlorine. *A low value of electron affinity for fluorine is due to the small size of fluorine atom. In a compact 2p-subshell of fluorine, the added electron faces repulsion. This gives rise to low values of electron affinity for fluorine.*

9. **Oxidation states.** The elements of the halogen family have a tendency to acquire noble gas electronic configuration by accepting an electron or by sharing one electron with those of other elements. Thus, they show an oxidation state of –1 or +1, depending on whether the element combining with halogens is less electronegative or more electronegative than halogen. Since fluorine is the most electronegative element, it always has –1 oxidation state. Fluorine cannot expand its valency beyond –1 as it does not have vacant *d*-orbitals.

   Other elements of this group exhibit oxidation states of +1, +3, +5 and +7 in addition to –1 state. Higher oxidation states of these elements are due to the presence of vacant *d*-orbitals. The excitation state of outer or *p*-electrons to these vacant *d*-orbitals is shown below in case of iodine.



10. **Nature of bonds with other elements.** The halogens combine with metals to form predominantly ionic halides. The ionic character of these halides decreases while covalent character increases on going down the halogen group. This is due to the reason that with increase in size of the halide ion, its polarizability increases (Fajan's rules) and this brings in a covalent character to the compound. For example, AlF_3 is an ionic compound whereas $AlCl_3$ and $AlBr_3$ are covalent compounds.

6.3 TRENDS IN CHEMICAL PROPERTIES

All the halogens are very reactive but amongst them fluorine is the most reactive. As we move down the group, reactivity of the halogens decreases. This is due to the decrease in their electronegativity. In general, a halogen of low atomic number oxidises halide ions of higher atomic number, *i.e.*, F_2 displaces Cl_2, Br_2 and I_2 from their salts, Cl_2 displaces Br_2 and I_2, whereas Br_2 displaces only iodine from its salts, *e.g.*,

$$F_2 + 2X^- \rightarrow 2F^- + X_2 \qquad (X = Cl, Br \text{ or } I)$$

$$F_2 + 2KX \rightarrow 2KF + X_2 \quad (X = Cl, Br \text{ or } I)$$

$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2 \quad (X = Br \text{ or } I)$$

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

1. **Oxidising power.** The halogens act as strong oxidising agents because of their high electron affinities. They have great tendency to take up electrons. The oxidising power of the halogens decreases on going down the group from fluorine to astatine. Reduction potentials of the halogens are given below:

X_2	F_2	Cl_2	Br_2	I_2	At_2
E°(volts)	2.87	1.40	1.09	0.62	–0.3

Greater the reduction potential of a substance, greater is its tendency to get reduced or in other words, greater is its oxidising power.

It is amazing to observe that fluorine is a better oxidising agent while chlorine has high electron affinity. In fact, reduction potential value, E°, of halogens refers to the processes:

$$\frac{1}{2}X_2(g) + e^- + aq \rightarrow X^-(eq)$$

(*a*) Dissociation:

$$\frac{1}{2}X_2(g) \rightarrow X(g);\ \frac{1}{2}\Delta H_{\text{Dissociation}} = +\text{ve}$$

(*b*) Accepting the electron:

$$X(g) + e^- \longrightarrow X^-(g);\ \Delta H\ = -\text{ve}$$

(*c*) Hydration of anion:

$$X^-(g) + aq \longrightarrow X^-(aq);\ \Delta H_{\text{Hydration}} = -\text{ve}$$

E° values in kJ for F_2 and Cl_2 are computed as under:

$$E^\circ(F_2) = \left(\frac{1}{2}\times 158.8\right) -333 - 460 = -713.6 \text{ kJ}$$

$$E^\circ(Cl_2) = \left(\frac{1}{2}\times 242.6\right) -384 - 383 = -645.7 \text{ kJ}$$

Thus, net energy change for $\frac{1}{2}F_2(g) \longrightarrow F^-(aq)$ is –713.6 kJ, whereas that for $\frac{1}{2}Cl_2(g) \longrightarrow Cl^-(aq)$ is –706.35 kJ, which accounts for higher oxidising power of F_2.

2. **Hydrides.** Halogens combine with hydrogen to form volatile halides of the formula HX. Some characteristics of these hydrides are given below:

   (*i*) Physical nature. Except HF, all other hydrides, *viz.*, HCl, HBr and HI are gases. HF is a liquid because of the *intermolecular hydrogen bounding:* —H—F—H—F—H—F ....

   Other halogens are unable to form effective hydrogen bonds because of insufficient electronegativity difference.

   The bond between hydrogen and halogen is covalent in all the cases.

   (*ii*) Acidic strength. All the hydrogen halides act as acids in their aqueous solutions. The acidic strength increases from HF to HI in the order:

   HF < HCl < HBr < HI.

   Explanation. *All the halogen acids ionise to give* H^+ *ion and halide ion,* X^-.

   $HX \longrightarrow H^+ + X^-$; (*where* $X^- = F^-, Cl^-, Br^-$ or I^-)

   The above order of acidic character can be explained in terms of strength of H—X bonds, which is in the order H—I < H—Br <H—Cl <H—F. Since H—I bond is the weakest, ***HI is the strongest acid.*** *On the other hand, H—F bond is strongest. Hence, it will ionise to the minimum extent and will be the weakest acid.*

Reducing character increases ⟶

HF HCl HBr HI

⟶ Thermal stability decreases

(*iii*) **Reducing character.** The reducing character of hydrides increases down the group. It again depends upon the strength of H—X bond which decreases from HF to HI. Smaller the bond strength greater is the ease with which it can be broken and, hence, greater the reducing power.

3. **Halides.** The halogens react with the metals and non-metals except He, Ne and Ar to form a wide variety of binary halides which may be simple or complex molecules.
   (*i*) With alkali and alkaline earth metals like Na, K, Mg, etc., having low ionisation energies, the halogens form ionic halides which have got high boiling and melting points. As the electronegativity of the halogens decreases down the group, the ionic character decreases in the order:

$$M—F > M—Cl > M—Br > M—I.$$

   This can be explained in terms of Fajan's rules.

   (*ii*) With metals having high ionisation energies, *e.g.*, Sn, Pb, Sb, etc., the halogens share the electrons and form covalent halides. The halides of these metals in higher oxidation states, *i.e.*, $SnCl_4$, $PbCl_4$, $SbC1_5$. etc., are more covalent than the halides in lower oxidation states. *viz*, $SnCl_2$, $PbCl_2$, $SbCl_3$, etc. This is because compounds with lower oxidation state, involve transference of electrons and those with higher oxidation state involve sharing of electrons.

   (*iii*) With non-metals like P, As and S, the halogens readily form covalent compounds such as PF_5, PCl_3, PBr_3, $AsCl_3$, S_2Cl_2, etc.

Reactions of halides with concentrated sulphuric acid. We shall explain the reactions of halides by taking the example of potassium halides. Concentrated sulphuric acid reacts with potassium halides to form the corresponding hydrogen halide.

$$KCl(s) + H_2SO_4(l) \longrightarrow KHSO_4(s) + HCl(g)$$

Concentrated H_2SO_4 is not strong enough to oxidise HCl into Cl_2, HBr is however oxidised to Br_2.

$$KBr(s) + H_2SO_4(l) \longrightarrow KHSO_4(s) + HBr(g)$$

$$2HBr(g) + H_2SO_4(l) \longrightarrow 2H_2O(l) + SO_2(g) + Br_2(g)$$

HI is even more easily oxidised to I_2.

$$KI(s) + H_2SO_4(l) \longrightarrow KHSO_4(s) + HI(g)$$

$$8HI(g) + H_2SO_4(l) \longrightarrow H_2S(g) + 4H_2O(l) + 4I_2(g)$$

Reactions of halide ions with silver ions. Silver ions form insoluble products with halide ions. The colour and behaviour of these silver halides can be used to identify the halide ions used:

Silver chloride is a *white* insoluble solid.

Silver bromide is a *creamy white* insoluble solid.

Silver iodide is a *yellow* solid.

The general equation for the formation of silver halide is as follows:

$$Ag^+(aq) + X^-(aq) \longrightarrow AgX(s)$$

Distinction between halides using ammonia solution. We can identify the particular halide in the solution by treating it with silver nitrate solution and then treating the halide formed with ammonium hydroxide solution. Ammonium molecules present in ammonium hydroxide solution form a simple complex ion with silver (I) ions which then allows the precipitate to dissolve.

The ease with which this happens depends upon the nature of the halide. Silver chloride forms a complex ion readily with a *dilute* solution of ammonia.

$$2NH_3 + AgCl \longrightarrow [Ag(NH_3)_2]^+ + Cl^-$$

Silver bromide also dissolves in ammonia, but only if a *concentrated* solution of ammonia is used.

$$2NH_3 + AgBr \longrightarrow [Ag(NH_3)_2]^+ + Br^-$$

Silver iodide (AgI) does not dissolve even in concentrated ammonia solution. Thus, this test can be used to distinguish between chlorides, bromides and iodides.

4. **Oxides.** Halogens combine with oxygen indirectly. For example, oxygen difluoride (OF_2) is prepared by the action of fluorine on 2% sodium hydroxide solution.

$$2F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O$$

Similarly, dichlorine oxide (Cl_2O) is obtained by passing chlorine over precipitated mercuric oxide at 575 K.

$$2Cl_2 + 2HgO \xrightarrow{575\text{ K}} HgO.HgCl_2 + Cl_2O$$

The compounds of oxygen with fluorine are called as fluorides because fluorine is more electronegative than oxygen. Most of these compounds are unstable and explode to form more stable products. Among oxides of a particular halogen the higher oxides are relatively more stable. Some of these oxides are given below in Table 6.3.

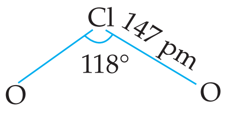
Table 6.3: Oxides of Halogens

Oxidation state	Fluorine	Chlorine	Bromine	Iodine
+1	OF_2	Cl_2O	Br_2O	—
+2	F_2O_2			
+3	—	Cl_2O_3		
+4	—	ClO_2	BrO_2	I_2O_4
+5	—	—	—	I_2O_5
+6	—	Cl_2O_6	—	—
+7	—	Cl_2O_7	—	—

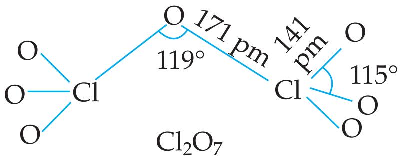
All the oxides are powerful oxidising agents and highly explosive.

The structures and molecular dimensions of some of the oxides are given below:

Cl_2O



ClO_2



Cl_2O_7

5. **Oxoacids.** Fluorine forms only one oxoacid, hypofluorous acid (HOF). Chlorine, bromine and iodine form four series of acids with compositions of HOX, HXO_2 and so on. Oxoacids of halogens are listed in Table 6.4.

Table 6.4: Oxoacids of Halogens

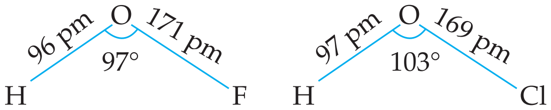
Oxoacids	Oxidation state	Fluorine	Chlorine	Bromine	Iodine
Hypohalous acids	+1	HOF	HOCl	HOBr	HOI
Halous acids	+3	—	$HClO_2$	—	—
Halic acids	+5	—	$HClO_3$	$HBrO_3$	HIO_3
Perhalic acids	+7	—	$HClO_4$	$HBrO_4$	HIO_4

Each one of them described as under:

(*i*) The **hypohalous acids** HOCl, HOBr and HOI are weak acids and are obtained in aqueous solutions by disproportionation of the halogen and water mixture.

$$X_2 + H_2O \rightleftharpoons HOX + HX \qquad (X=Cl, Br\ or\ I)$$

Their salts are known as hypohalites. Bleaching powder $CaOCl_2$ is a common example of this category. The structures of HOCl and HOF are shown below:



(*ii*) The **halic acids** $HClO_3$ and $HBrO_3$ are known in a solution form but iodic acid HIO_3 exists as a white solid. Stability of acids increases down the group. These acids acts as **strong oxidising agents.** They oxidise halides to give halogens in acidic medium.

$$XO_3^- + 5X^- + 6H^+ \longrightarrow 3X_2 + 3H_2O$$

Their salts are called **halates.** Amongst the halates, sodium chlorate ($NaClO_3$) and potassium chlorate ($KClO_3$) are prepared on a large scale. $NaClO_3$ acts as a powerful weed killer while $KClO_3$ is used in making fireworks and match boxes.

(*iii*) **Perhalic acid.** Perchloric and periodic acids and their salts perchlorates and periodates are known to exist. The perhalates (MXO_4) are prepared by the electrolytic oxidation of the corresponding halates, MXO_3.

$$4ClO_3^- \longrightarrow Cl^- + 3ClO_4^-$$

The disproportionation of BrO_3^- to BrO_4^- is unfavourable, therefore, perbromates are obtained only by oxidation of BrO_3^- by F_2 in a basic solution.

$$BrO_3^- + F_2 + 2OH^- \longrightarrow BrO_4^- + 2F^- + H_2O$$

Acidic Character of Oxoacids

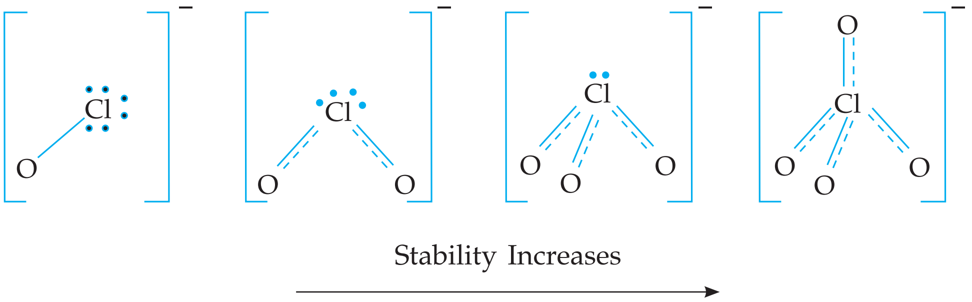
(*i*) The acid strength of oxoacid of the same halogen increases with the increase in oxidation number of the halogen. For example, among the different oxoacids of chlorine, the acidic character follows the order:

$$HOCl < HClO_2 < HClO_3 < HClO_4$$

Explanation. *The acid strength may be explained on the basis of Lowry-Bronsted concept that the* ***conjugate*** *base of a weak acid is strong and the conjugate base of a strong acid is weak.*

$$\underset{Acid_1}{HA} + H_2O \rightleftharpoons H_3O^+ + \underset{Conjugate\ Base_1}{A^-}$$

Now greater is the stability of A^- *ion, greater will be the tendency of HA to release* H^+ *ion. In other words, stronger will be the acid HA. Among the conjugate bases of the oxyacids, i.e.,* ClO^-, ClO_2^-, ClO_3^- *and* ClO_4^-, *the stability increases with the increase in the number of oxygen atoms in the anion. It is because, the dispersal of negative charge will be more if the number of oxygen atoms is more as illustrated below:*



Consequently, the strength of the corresponding acids increases in the following order:

$$HOCl < HClO_2 < HCO_3 < HClO_4$$

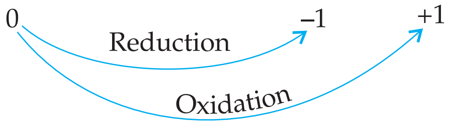
(*ii*) Among the oxyacids of different halogens having the same oxidation number, the acidic character decreases with the increase in atomic number. For example, the decreasing order of acidic character among hypohalous series is: HClO > HBrO > HIO.

Explanation. *Greater the size of the halogen atom, smaller will be its electronegativity and, hence, smaller will be the acidic character.*

6. **Disproportionation reactions of halogens.** Disproportionation reactions are those in which the same element is simultaneously oxidised and reduced.

Reaction with water

$$Cl_2\,(g) + H_2O\,(l) \rightleftharpoons HCl\,(aq) + HClO\,(aq)$$



In the above reaction, chlorine is getting oxidised as well as reduced simultaneously. The equilibrium mixture of (HCl + HClO) is called chlorine water. It is used as a reagent in analytical work. It is also used in water treatment to kill bacteria. It has been used to treat drinking water and the water in swimming pools.

Reaction with cold alkali

Cl_2, Br_2 and I_2 react with cold sodium hydroxide solution as under:

$$Cl_2\,(aq) + 2NaOH\,(aq) \longrightarrow NaCl\,(aq) + NaClO\,(aq) + H_2O\,(l)$$

The mixture of NaCl and NaClO is used as a bleach.

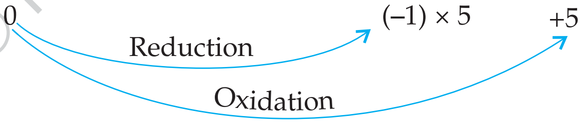
Br_2 and I_2 react with sodium hydroxide as under:

$$Br_2\,(aq) + 2NaOH \longrightarrow NaBr\,(aq) + NaBrO\,(aq) + H_2O\,(l)$$
$$I_2\,(aq) + 2NaOH \longrightarrow NaI\,(aq) + NaIO\,(aq) + H_2O\,(l)$$

Reaction with hot alkali

In hot alkali the disproportionation also occurs, but the halogen that is oxidised goes to a higher oxidation state.

$$3Cl_2\,(aq) + 6NaOH\,(aq) \longrightarrow 5NaCl\,(aq) + NaClO_3\,(aq) + 3H_2O\,(l)$$



Br_2 and I_2 give similar reactions.

$$3Br_2\,(aq) + 6NaOH\,(aq) \longrightarrow 5NaBr\,(aq) + NaBrO_3\,(aq) + 3H_2O\,(l)$$
$$3I_2\,(aq) + 6NaOH\,(aq) \longrightarrow 5NaI\,(aq) + NaIO_3\,(aq) + 3H_2O\,(l)$$

Anomalous Behaviour of Fluorine

Fluorine having extremely small size, high electronegativity, high ionisation potential and no availability of vacant d-orbitals in the valency shell exhibits some anomalous behaviour and differs from the other elements of the group. Some distinguishing features are given below:

(*i*) It shows oxidation state of –1 only. The other elements show variable oxidation states.
(*ii*) It does not form polyhalide ions. It is due to its inability to expand its valency and coordination.

(*iii*) The compounds of fluorine have maximum ionic character.

(*iv*) Bond dissociation energy of F_2 is the smallest. It is due to the repulsive interactions of lone pairs of electrons around F-atoms, thus, destabilising the bond.

(*v*) It is most reactive due to its low value of bond dissociation energy.

(*vi*) The hydride of fluorine (HF) is liquid (*due to intermolecular H-bonds*) at room temperature whereas hydrides of other elements of the group are gases.

PROBLEMS FOR PRACTICE

1. Name the strongest oxidising agent among all the elements.
2. What is the state of hybridisation of Br in (*i*) BrF_3 and (*ii*) BrF_5?
3. How do melting points change with the increase in atomic number among group-17 elements?
4. Among hydrides of halogens:
   (*i*) Which is most stable?
   (*ii*) Which is most acidic?
5. Among halogens:
   (*i*) Which element is most electronegative?
   (*ii*) Which element has the lowest boiling point?

6.4 PREPARATION OF CHLORINE

Laboratory Preparation. Chlorine is prepared in the laboratory by any one of the following methods:

1. By heating manganese dioxide with hydrochloric acid. In the laboratory, chlorine is generally prepared by heating manganese dioxide with concentrated hydrochloric acid.

$$\begin{array}{rcl} MnO_2 + 2HCl & \longrightarrow & MnCl_2 + H_2O + O \\ 2HCl + O & \longrightarrow & H_2O + Cl_2 \\ \hline MnO_2 + 4HCl & \longrightarrow & MnCl_2 + Cl_2 + 2H_2O \end{array}$$

Instead of hydrochloric acid, we may use a mixture of common salt and concentrated sulphuric acid. This method is cheaper than the previous one and is commonly used.

$$\begin{array}{rcl} NaCl + H_2SO_4 & \longrightarrow & NaHSO_4 + HCl] \times 2 \\ MnO_2 + H_2SO_4 & \longrightarrow & MnSO_4 + H_2O + O \\ 2HCl + O & \longrightarrow & H_2O + Cl_2 \\ \hline 2NaCl + MnO_2 + 3H_2SO_4 & \longrightarrow & 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2 \end{array}$$

If needed, the gas can be freed from HCl by bubbling through water and then dried by passing through concentrated sulphuric acid.

2. By the action of HCl on $KMnO_4$. This is the most convenient, though a little expensive method for the laboratory preparation of chlorine.

$$\begin{array}{rcl} 2KMnO_4 + 6HCl & \longrightarrow & 2KCl + 2MnCl_2 + 3H_2O + 5O \\ 2HCl + O & \longrightarrow & H_2O + Cl_2] \times 5 \\ \hline 2KMnO_4 + 16HCl & \longrightarrow & 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2 \end{array}$$

Purification of chlorine. Chlorine prepared by the above method contains impurities of hydrogen chloride and moisture. In order to remove these impurities, the gas is bubbled first through water which dissolves any hydrochloric acid gas present in it. It is then passed through conc. sulphuric acid which absorbs any moisture present in it.

Manufacture. This is achieved in a special type of cell known as **Nelson cell** fitted with a cathode and an anode. On passing electric current, chlorine is evolved at the anode. It comes out through an outlet at the top. It is then dried, compressed and stored in iron cylinders. Sodium ions pass through asbestos and are liberated as sodium atoms at the cathode. Here, these atoms come in contact with steam and react to form sodium hydroxide and hydrogen.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

Sodium hydroxide collects in the catch basin while hydrogen escapes through the outlet at the top and is collected as valuable by-product.

Electronic Configurations of Halogens

The electronic configurations of the halogens are given in Table 6.5.

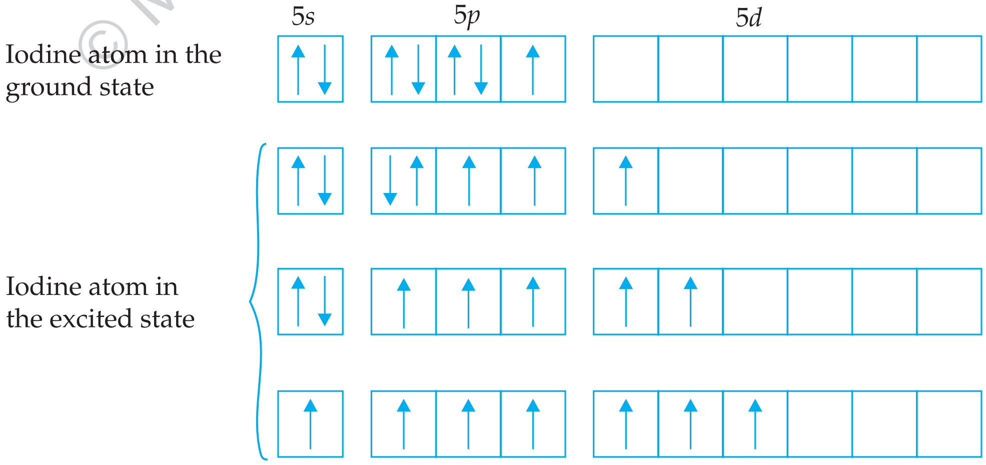
As is evident, the halogens have ns^2np^5 electrons in their respective valence shells. The five *p*-electrons are arranged in the three *p*-orbitals as $p^2_x\ p^2_y\ p_z^1$. Hence, there is only one half-filled *p*-orbital which is available for chemical bonding with other elements. Since the halogens possess only 1 electron less than the number present in the nearest inert gas, they show a great tendency to take up 1 electron to attain the stable noble gas structure. So halogens are amongst the most reactive elements in inorganic chemistry. In this process they form ions such as F^-, Cl^-, Br^- and I^-.

Table 6.5: Electronic Configuration of the Halogens

Element	Atomic number	Electronic configurations
Fluorine, F	9	$[He]\ 2s^2\ 2p^5$
Chlorine, Cl	17	$[Ne]\ 3s^2\ 3p^5$
Bromine, Br	35	$[Ar]\ 3d^{10}\ 4s^2\ 4p^5$
Iodine, I	53	$[Kr]\ 4d^{10}\ 5s^2\ 5p^5$
Astatine, At	85	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$

Fluorine is the most electronegative element. Therefore, it has a great tendency to accept an electron and form F^-. Thus, fluorine always exhibits –1 oxidation state in its compounds.

Since fluorine has very high ionisation energy and has no *d*-orbital in its valence shell hence it cannot have any excited states, it thus also does not exhibit any positive oxidation state. However, other halogens exhibit positive oxidation states such as +3, +5 and +7. These higher positive oxidation states for other halogens arise due to the availability of vacant *d*-orbitals in them. For example, iodine exhibits +3 (in ICl_3), and +7(in IF_7). Electronic configurations of iodine in various oxidation states (due to the available *d*-orbitals) are given below:



Configurations of iodine atom

6.5 HYDROCHLORIC ACID

In the 17th century, J. R. Glauber used sodium chloride salt and concentrated sulphuric acid to prepare sodium sulphate releasing hydrogen chloride gas in the Mannheim process. Davy in 1810, showed that hydrogen chloride is a compound of hydrogen and chlorine.

Laboratory Preparation: In the laboratory, this acid is obtained by heating sodium chloride with concentrated sulphuric acid. The reaction may be imagined to take place in two steps as under:

$$NaCl + H_2SO_4 \xrightarrow{420\text{ K}} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823\text{ K}} Na_2SO_4 + HCl$$

So, that the overall reaction may be represented as under:

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$

HCl gas obtained above is passed through water to obtain hydrochloric acid.

Physical Properties

1. HCl is a colourless and pungent gas.
2. It is easily liquefied to a colourless liquid with b.p. 189 K.
3. It freezes to a white crystalline solid with f.p. 159 K.
4. It is extremely soluble in water and ionises as under:

$$HCl\ (g) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-(aq)\ ,\ K_a = 10^7$$

High value of K indicates that it is a strong acid in water.

Chemical Properties

1. When we bring a rod dipped in hydrochloric acid near ammonia gas (or vice versa), we obtain thick white fumes due to the formation of ammonium chloride.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

2. Hydrochloric acid decomposes salts of weaker acids, e.g., carbonates, hydrogen carbonates, sulphites, sulphides, to form chlorides with liberation of a gas.

$$\begin{aligned} Na_2CO_3 + 2HCl &\longrightarrow 2NaCl + CO_2 + H_2O \\ NaHCO_3 + HCl &\longrightarrow NaCl + CO_2 + H_2O \\ Na_2SO_3 + 2HCl &\longrightarrow 2NaCl + SO_2 + H_2O \\ Na_2S + 2HCl &\longrightarrow 2NaCl + H_2S \end{aligned}$$

3. Three parts of concentrated hydrochloric acid and one part of concentrated nitric acid, when mixed together, give **aqua regia** which is used for dissolving noble metals like gold and platinum.

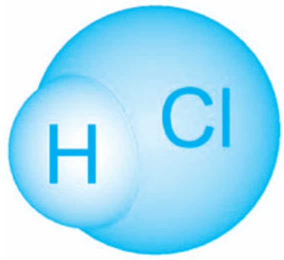
$$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$

$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

Uses

Hydrochloric acid is used

(*i*) in the manufacture of chlorine and ammonium chloride
(*ii*) for extracting glue from bones and purifying bone black
(*iii*) in medicines
(*iv*) as a laboratory reagent.



Hydrochloric acid

6.6 SOME TYPICAL REACTIONS OF HALOGENS

All the halogens are chemically very reactive. *Fluorine, however, is the most reactive of all the halogens.*

Reactivity of halogens decreases in the order: $F_2 > Cl_2 > Br_2 > I_2$.

Some important chemical reactions of halogens are discussed below:

1. **Reaction with hydrogen.** All the halogens react with hydrogen to form halogen acids (HX). *The reactivity towards hydrogen, however, decreases from fluorine to iodine.*

$$H_2 + X_2 \longrightarrow 2HX \text{ (where X = F, Cl, Br or I)}$$

2. **Reaction with alkalies.** Fluorine behaves differently from other halogens in the reaction with alkalies. Generally, different products are obtained in cold and hot solutions. *Fluorine* reacts with cold and dilute sodium hydroxide solution to give *oxygen difluoride* (OF_2).

$$2F_2 + 2NaOH\ (\textit{dil.}) \xrightarrow{\text{Cold}} 2NaF + H_2O + OF_2$$

However, with hot and concentrated sodium hydroxide, oxygen is obtained.

$$2F_2 + 4NaOH\ (\textit{conc.}) \xrightarrow{\text{Heat}} 4NaF + 2H_2O + O_2$$

Chlorine reacts with cold and dilute alkalies to form hypochlorite and with hot and concentrated alklies to form chlorate.

$$2NaOH\ (\textit{dil.}) + Cl_2 \xrightarrow{\text{Cold}} NaCl + \underset{\text{Sodium hypochlorite}}{NaOCl} + H_2O$$

$$6NaOH\ (\textit{conc.}) + 3Cl_2 \xrightarrow{\text{Heat}} 5NaCl + \underset{\text{Sodium chlorate}}{NaClO_3} + 3H_2O$$

3. **Reaction with metals and non-metals.** Halogens combine with most of the metals and non-metals to form their corresponding halides. The reactivity of halogens decreases in the order: $F_2 > Cl_2 > Br_2 > I_2$. With sulphur, fluorine gives sulphur hexafluoride (SF_6) while chlorine forms sulphur tetrachloride (SCl_4).

(*a*) **With metals:**

$$2Al + 3F_2 \xrightarrow{\text{Heat}} 2AlF_3$$

$$Mg + Cl_2 \xrightarrow{\text{Heat}} MgCl_2$$

(*b*) **With non-metals:**

$$P_4 + 10Cl_2 \longrightarrow \underset{\text{Phosphorus pentachloride}}{4PCl_5}$$

(*c*) **With metalloids:**

$$2As + 3Cl_2 \longrightarrow \underset{\text{Arsenic trichloride}}{2AsCl_3}$$

$$2Sb + 3F_2 \longrightarrow \underset{\text{Antimony trifluoride}}{2SbF_3}$$

4. **Oxidising agent.** Halogens have a strong tendency to accept electrons. Therefore, they are strong oxidising agents. Their oxidising power decreases from F to I. *Thus, Fluorine is the strongest oxidising agent of all the halogens.* As such, it oxidises all other halide ions to the corresponding halogens.

$$F_2 + 2X^- \longrightarrow 2F^- + X_2 \qquad \text{(X = Cl, Br or I)}$$

Similarly, Cl_2 oxidises Br ions to Br_2 and I^- ions to I_2 while Br_2 will oxidise only I^- ions to I_2.

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 \qquad \text{(X = Br or I)}$$

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

I_2 does not oxidise any halide ion to its corresponding halogen. But, when I_2 is heated with a concentrated solution of $KClO_3$ it displaces Cl_2 with the formation of potassium iodate (KIO_3).

$$2KClO_3 + I_2 \xrightarrow[\text{little conc. } HNO_3]{\text{Heat}} 2KIO_3 + Cl_2$$

5. **Reaction with water.** Because of the affinity of halogens for hydrogen, they readily decompose water. The order of reactivity follows the sequence: $F_2 > Cl_2 > Br_2 > I_2$.

   Fluorine reacts vigorously with water to give HF, O_2 and O_3.

$$2H_2O + 2F_2 \longrightarrow 4HF + O_2$$
$$3H_2O + 3F_2 \longrightarrow 6HF + O_3$$

   Chlorine and bromine react less vigorously forming a mixture of hydrohalic acid (HX) and hypohalous acid (HOX):

$$X_2 + H_2O \longrightarrow HX + HOX \qquad (X = Cl \text{ or } Br)$$

   Reactions with chlorine and bromine can be represented as under:

$$Cl_2 + H_2O \longrightarrow HCl + \underset{\text{Hypochlorous acid}}{HOCl}$$
$$Br_2 + H_2O \longrightarrow HBr + \underset{\text{Hypobromous acid}}{HOBr}$$

   Hypohalous acids when exposed to sunlight, liberate oxygen.

$$2HOCl \xrightarrow{h\nu} O_2 + 2HCl$$
$$2HOBr \xrightarrow{h\nu} O_2 + 2HBr$$

6. **Reaction with H_2S.** Fluorine and chlorine react with H_2S to form sulphur and corresponding halogen acids.

$$F_2 + H_2S \longrightarrow 2HF + S$$
$$Cl_2 + H_2S \longrightarrow 2HCl + S$$

   Reaction with NH_3. Reaction with ammonia takes place as under:

$$3F_2 + 2NH_3 \longrightarrow N_2 + 6HF$$
$$3Cl_2 + 2NH_3 \longrightarrow N_2 + 6HCl$$

Uses of Fluorine

(*i*) Fluorine is mainly used for the manufacture of uranium hexafluoride (UF_6) which is used for nuclear power generation.

(*ii*) Fluorine is used in the manufacture of sulphur hexafluoride (SF_6) which is used as an electrical insulator in gas-filled high voltage tensions.

(*iii*) CCl_2F_2 and CCl_3F known as **freons** are used as refrigerants.

(*iv*) Fluorine is used in the manufacture of a plastic known as teflon, $(–CF_2–CF_2—)_n$.

(*v*) Molten cryolite (Na_3AlF_6) is used in the electrolytic extraction of aluminium from alumina.

(*vi*) Sodium fluoride is added to toothpaste to prevent tooth decay, particularly in children.

(*vii*) HF is used as an *etching agent* in glass industry.

Uses of Chlorine

(*i*) Chlorine is used in sterilization of water.

(*ii*) Large quantities of chlorine are used for bleaching powder, pulp and textiles.

(*iii*) It is used in the manufacture of inorganic chemicals such a hydrochloric acid, sodium hypochlorite (NaOCl), bleaching powder ($CaOCl_2$), etc.

(*iv*) It is used in the manufacture of vinyl chloride which is a starting material for the plastic polyvinyl chloride (PVC).

(*v*) It is used in the manufacture of insecticides like D.D.T.

(*vi*) It is used in the manufacture of chlorinated organic solvents like $CHCl_3$, CCl_4, $CCl_2{=}CCl_2$ (*westron*), $CHCl{=}CCl_2$ (*westrosol*).

Harmful Effects of Chlorine

(*i*) Chlorine is often added to water systems as disinfectant. While disinfection of drinking water is a necessary measure to reduce diseases it also causes serious adverse health effects including dementia in elderly patients.

(*ii*) Studies show that long-term exposure to chlorinated pools can cause symptoms of asthma in swimmers. Eye and skin irritation in swimmers has been related to chlorine exposure.

(iii) Inhalation of chlorine gas, which emanates from laundry bleaches can cause difficulty in breathing, chest pain, cough, increased heartbeat, rapid breathing and ultimately death.

6.7 HYDROGEN HALIDES

Preparation of Hydrogen Halides

Preparation of HF and HCl. HF and HCl are prepared by heating fluorides and chlorides respectively with concentrated sulphuric acid.

$$CaF_2 + H_2SO_4 \xrightarrow{\text{Heat}} CaSO_4 + 2HF$$

$$2NaCl + H_2SO_4 \xrightarrow{\text{Heat}} Na_2SO_4 + 2HCl$$

Preparation of HBr and HI. *Unlike HF and HCl, HBr and HI cannot be prepared by the above method.* The reason being that both HBr and HI evolved are strong reducing agents and hence they reduce sulphuric acid to sulphur dioxide and are themselves oxidised to Br_2 and I_2 respectively.

$$\begin{array}{rcl} 2NaBr + H_2SO_4 & \longrightarrow & Na_2SO_4 + 2HBr \\ H_2SO_4 & \longrightarrow & H_2O + SO_2 + O \\ 2HBr + O & \longrightarrow & H_2O + Br_2 \\ \hline 2NaBr + 2H_2SO_4 & \longrightarrow & Na_2SO_4 + SO_2 + Br_2 + 2H_2O \end{array}$$

Similarly,

$$2NaI + 2H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + I_2 + 2H_2O$$

Therefore, phosphoric acid is used in the preparation of HBr and HI.

$$3NaBr + H_3PO_4 \xrightarrow{\text{Heat}} Na_3PO_4 + 3HBr$$

$$3NaI + H_3PO_4 \xrightarrow{\text{Heat}} Na_3PO_4 + 3HI$$

Properties of Hydrogen Halides

Some important properties of hydrogen halides are discussed below:

1. **Physical state.** Hydrogen fluoride is a low boiling liquid (*b.p.* 293 K) whereas HBr, HCl and HI are gases. The anomalous behaviour of HF is due to the presence of **intermolecular hydrogen bonding** in its molecules. Consequently, it exist as an associated molecule, $(HF)_n$.
2. **Melting points and boiling points.** Amongst the hydrogen halides, the boiling point of HF is the highest, i.e., 293 K due to extensive intermolecular hydrogen bonding. The other hydrogen halides do not show hydrogen bonding. Therefore, the boiling points of HCl, HBr and HI are much lower than that of HF. However, as we move from HCl to HI, their boiling points show a regular increase due to a corresponding increase in the magnitude of van der Waals' forces of attraction as the size of the halogen increases.

   Some important physical properties of hydrogen halides are given in Table 6.6.

Table 6.6: Some Physical Properties of Hydrogen Halides

Property	HF	HCl	HBr	HI
Melting point (K)	190	158	186	222
Boiling point (K)	293	189	206	238
Bond length (H–X)(pm)	91.7	127.4	141.4	160.9
Bond dissociation energy (kJ mol^{-1})	570	430	360	300

3. **Dipole moment. HI < HBr < HCl < HF.** Let us say we have a polar molecule represented by $A^{\delta+} B^{\delta-}$. Let q be the magnitude of change on each of them and r the distance between A and B. Then the dipole moment is given by $q \times r$.

   Amongst the halogens, fluorine is the most electronegative element while iodine is the least. As a result, HF has the maximum dipole moment (1.82 D), followed by HCl (1.08 D), followed by HBr (0.82 D) and HI has the least (0.44 D). Thus, *the increasing order of the dipole moments of halogen acids is HI < HBr < HCl < HF.*

4. **Percentage ionic character. HI < HBr < HCl < HF.** Percentage ionic character is a quantity that is dependent on dipole moment.

   Therefore, HF is most polar while HI is least polar. In other words, the percentage ionic character of halogen acids follows the sequence: HI < HBr < HCl < HF.

5. **Bond length. HF < HCl < HBr < HI.** The H-X bond in halogen acids is formed by the overlap of *s*-orbital of hydrogen and a *p*-orbital of halogen. As we move down the group from F to I, the size of the *p*-orbital increases, *i.e.*, 2*p* (F), 3*p* (Cl), 4*p* (Br) and 5*p* (I). As a result, the bond length also increases in the same order: HF < HCl < HBr < HI.

6. **Bond strength. HI < HBr < HCl < HF.** Bond strength or bond dissociation energy is inversely proportional to the bond length, *i.e.*, *shorter the bond length, greater is the bond strength.* Since the bond length increases in the order: HF < HCl < HBr < HI, therefore, bond dissociation energy increases in the reverse direction, *i.e.*, HI < HBr < HCl <HF.

7. **Thermal stability. HI < HBr < HCl < HF.** Thermal stability is directly proportional to the bond dissociation energy. Since bond dissociation energy of HF is the highest and that of HI is the lowest, therefore, HF is the most stable halogen acid while HI is the least stable halogen acid. In other words, the order of stability of the halogen acids increases in the order: HI < HBr < HCl < HF.

8. **Acid strength. HF < HCl < HBr < HI.** The strength of an acid depends upon its degree of ionization which, in turn, depends upon the bond strength.

$$HX(aq) \rightleftharpoons H^+ (aq) + X^- (aq)$$

   Thus, *higher the bond dissociation energy, lower is the degree of ionization and hence weaker is the acid*. Since the bond dissociation energies of the halogen acids increase in the order: HI < HBr < HCl < HF, therefore, strength of the acids increases in the reverse direction, *i.e.* HF < HCl < HBr < HI.

9. **Reducing power. HF< HCl < HBr < HI.** The reducing power of a halogen acid depends upon the ease with which it decomposes to give H_2 and X_2. This, in turn, depends upon the bond dissociation energy. Thus, greater the bond dissociation energy, more stable is the halogen acid and hence weaker is the reducing agent.

$$2HX \longrightarrow H_2 + X_2$$

   Since the bond dissociation energy of the halogen acids increases in the order: HI < HBr < HCl < HF, therefore, reducing power of these acids increases in the reverse direction: HF < HCI < HBr < HI.

Oxoacids of halogens (and their relative strength)

The oxoacids of halogens with their generalised names are listed below in Table 6.7. *Fluorine does not form any oxoacid because of its highly oxidising nature.* Chlorine, bromine and iodine mainly form four series of oxoacids with the formula of HXO, HXO_2, HXO_3, HXO_4.

Table 6.7: Oxoacids of Halogens

Oxidation State	Chlorine	Bromine	Iodine
+1	HClO Hypochlorous acid	HBrO Hypobromous acid	HIO Hypoiodous acid
+3	$HClO_2$ Chlorous acid		
+5	$HClO_3$ Chloric acid	$HBrO_3$ Bromic acid	HIO_3 Iodic acid
+7	$HClO_4$ Perchloric acid	$HBrO_4$ Perbromic acid	HIO_4 Periodic acid

If we study the relative strength of the aqueous solution of oxoacids of say chlorine, we find that HClO is a weak acid, $HClO_2$, is somewhat stronger, $HClO_3$ is quite strong and $HClO_4$ is the strongest in this series. *Acidic character of an oxoacid increases with increase in oxidation number of chlorine.* The order of increasing strength of oxoacids of chlorine is:

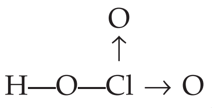
$$HClO_4 > HClO_3 > HClO_2 > HClO.$$

The structure of these oxoacids of chlorine are represented as under:

Hypochlorous acid: $\mathrm{H{-}O{-}Cl}$

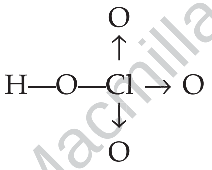
Chlorous acid: $\mathrm{H{-}O{-}Cl} \rightarrow \mathrm{O}$

Chloric acid:



$$\mathrm{H{-}O{-}}\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{Cl}} \rightarrow \mathrm{O}$$

Perchloric acid:



$$\mathrm{H{-}O{-}}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{Cl}}} \rightarrow \mathrm{O}$$

On looking at these structures, it becomes quite evident that in each case hydrogen-oxygen (H—O) bond must break in order to release a proton. Strength of acid would, therefore, depend upon the strength of H—O bond in it. Any factor which facilitates in the weakening of H—O bond, will lead to greater proton releasing tendency of the acid and therefore increasing strength of the acid. As the oxidation number of chlorine increases from +1 to +7 or the number of oxygen atoms bonded to the central chlorine atom increases, the halogen-oxygen bond (O—Cl) becomes more covalent resulting in increase in the acid strength. This is because each time, with additional oxygen atom bonded to chlorine atom some electric charge is withdrawn from the chlorine, i.e., from the O—Cl bond. This in turn leads to withdrawal of electron from the adjacent H—O bond, thereby weakening it and hence increasing the tendency to release proton and therefore more acid strength.

It may therefore be concluded that greater the number of oxygen atoms attached to the central atoms, greater is the oxidation number value of the central atom and hence, the stronger would be the acid. This explains why $HClO_4$ is the strongest oxoacid of chlorine.

GROUP-17 ELEMENTS (HALOGENS)

Electronic configuration in outer shell: ns^2np^5

Elements	*Increasing Trends Down the Group*	*Decreasing Trends Down the Group*	*Exceptions Observed*
	Atomic size	Ionisation energies	
F	Ionic radii X^-	Electronegativity	
	Melting/Boiling points	Electron affinity	E.A.$_1$. of Cl > E.A.$_1$ of F
Cl	Intensity of colour	Chemical reactivity	
	Electropositive character	E° values	
Br	Acidic nature of hydrides (HX)	Oxidising power	Dissociation energy [$X_2(g) \rightarrow 2X(g)$]
I	Reducing nature of hydrides (HX)	Thermal stability of HX	$I_2 < F_2 < Br_2 < Cl_2$
*At	Strength of oxoacids increases with increase in oxidation number of X.	$\Delta H_{diss.}$ of H—X Acid strength of HOX	F shows oxidation state of –1 while others show oxidation states +1, +3, +5 and +7

6.8 PREDICTION IN THE PROPERTIES OF FLUORINE AND ASTATINE

Physical State

Knowing the physical and chemical properties of halogens — chlorine, bromine and iodine, it is possible to predict the properties of fluorine and astatine.

Fluorine	Gas
Chlorine	Gas
Bromine	Liquid
Iodine	Solid
Astatine	Solid

Boiling point increases down the group.

We know that chlorine is a gas, bromine is a liquid and iodine is a solid at room temperature. Based on these information, we can predict that fluorine must be a gas and astatine must be a solid at room temperature.

Colour

Chlorine	Pale green
Bromine	Orange (or brown)
Iodine	Grey (as solid) and Purple (as gas)

We see from the above trend that the colour darkens as we move down the group of halogen. We can predict from this trend that fluorine should be *yellow* and astatine should be *black*.

Melting Point

The melting points of the halogens are: Chlorine (– 101°C), bromine (– 7°C) and iodine (114°C).

There is a difference of roughly 100°C between Cl and Br and between Br and I. Based upon this trend, astatine is expected to have a melting point of about 214°C and fluorine is expected to have a melting point of about –200°C.

Actual melting points of astatine and fluorine are 300°C and –219°C. Predictions don't have to be accurate but sensible!

QUICK SCAN (FOR REVISION)

1. Chlorine has the highest electron affinity. Order of electron affinity is: $F < Cl > Br > I$.
2. The halogen having some metallic character is I_2.
3. Oxidising power shows the order: $F_2 > Cl_2 > Br_2 > I_2$.
4. Acidic strength decreases in the order:

   $HF < HCl < HBr < HI$ (due to highest bond dissociation energy of H-F).
5. Reducing power decreases in the order: $I > Br^- > Cl^- > F^-$. Boiling points vary as: $HF > HCl < HBr < HI$.
6. Acidic strength of different acids shows the order: $HClO_4 > HClO_3 > HClO_2 > HClO > HBrO > HIO$.

   Acidic strength increases in the order:

   $Cl_2O < ClO_2 < Cl_2O_6 < Cl_2O_7$ (Acidic strength increases as the percentage of oxygen increases).
7. OF_2 is obtained by passing F_2 through 2% NaOH solution.
8. Oxidizing power shows the following order:

   $HClO_4 > HClO_3 > HClO_2 > HClO$

   $BrO_4^- > IO_4^- > ClO_4^-$.
9. I_2 is highly soluble in KI solution (due to the formation of KI_3).
10. HF is used for etching glass, in making thermometers, etc.
11.

Molecule	**XF_3**	**XF_5**	**IF_5**
Hybridisation	sp^3d	sp^3d^2	sp^3d^3
Shape	T-shaped	square pyramidal	pentagonal bipyramidal

12. Fluorine is found only in the combined state. The main ores of fluorine are: Fluorspar (CaF_2), cryolite (Na_3AlF_6)and fluorapatite, $[CaF_2.3Ca_3(PO_4)_2]$.
13. As F_2 is the strongest oxidising agent, therefore, it cannot be obtained by chemical oxidation of fluoride ions.
14. **Moissan** prepared fluorine by electrolysis of a molten mixture of KHF_2 + HF (1:5) in a vessel made up of *monel metal* (Ni-Cu-Fe alloy) using carbon electrodes.
15. Cl_2, Br_2 and I_2 can be prepared in the laboratory by heating a mixture of NaCl + MnO_2, NaBr + MnO_2, KI + MnO_2 with conc. H_2SO_4 respectively.
16. All halogens uniformly show an oxidation state of –1. Except fluorine, other halogens also show positive oxidation states of +1, +3, +5 and +7.
17. Under normal conditions, F_2 and Cl_2 are gases, Br_2 is a liquid and I_2 exist as a solid.
18. *F_2 does not show disproportionation reactions while other halogens do.* For example, F_2 reacts with cold and dil. NaOH solution forming OF_2 but with hot and conc. NaOH, it gives only O_2. In contrast, all other halogens react with cold and dil. NaOH to form hypohalites (XO^-) and with hot and conc. NaOH to form halates (XO_3^-).
19. Cl_2 bleaches vegetable colouring matter in the presence of moisture. *The bleaching action of Cl_2 is due to oxidation and hence is* ***permanent.***
20. I_2 displaces Cl_2 from $KClO_3$ to form KIO_3 and Cl_2.
21. Oxidising power of halogens is in the order: $F_2 > Cl_2 > Br_2 > I_2$. Thus, F_2 oxidises all other halide ions to halogens:

    $F_2 + 2X^- \rightarrow 2F^- + X_2$ (X = Cl, Br, I)

    Cl_2 will oxidise Br^- ions to Br_2 and I^- ions to I_2 while Br_2 will oxidise only I^- ions to I_2.
22. All the halogens react with hydrogen forming halogen acids. The order of reactivity is as follows:

    $F_2 > Cl_2 > Br_2 > I_2$.
23. Because of strong intermolecular H-bonds, HF is a liquid while all other halogen acids are gases.
24. HF can be prepared in the laboratory by the action of conc. H_2SO_4 on CaF_2 and HCl can be prepared by the action of conc. H_2SO_4 on NaCl. However, HBr and HI cannot be prepared by the action of conc. H_2SO_4 on NaCl, NaBr and NaI respectively. The reason being that HBr and HI are reducing agents and hence reduce H_2SO_4 to SO_2 while they are oxidised to Br_2 and I_2 respectively.
25. Different properties of halogen acids follows the order:

    Boiling points: HF > HI > HBr > HCl
    Melting points: HI > HF > HBr > HCl
    Dipole moment: HF >HCl > HBr > HI
    Bond lengths: HI > HCl > HBr > HF
    Thermal stability: HF > HCl > HBr >HI
    Acid strength: HI > HBr > HCl > HF
    Reducing power: HI > HBr > HCl >HF
26. The acid strength of oxoacids increases as the oxidation state of halogen increases:

    $HClO_4 > HClO_3 > HClO_2 > HClO$.
27. Due to the absence of *d*-orbitals, fluorine does not form polyhalides while all other halogens do. For example, I_2 dissolves in KI to form I_3^- ion.

28. F_2 does not form oxoacids while all other halogen form oxoacids; HOX, HXO_2, HXO_3, HXO_4, (X = Cl, Br, I).

29. Glauber first prepared hydrochloric acid by heating common salt with conc. sulphuric acid. In the laboratory it can be prepared by heating sodium chloride with conc. sulphuric acid. HCl gas evolved is dissolved in water to produce hydrochloric acid.

30. It is a colourless and pungent gas, extremely soluble in water and easily liquefiable.

31. With ammonia gas, it gives dense white fumes of ammonium chloride, salts of weaker acids are decomposed by hydrochloric acid.

32. A mixture of 3 parts of conc. hydrochloric acid and 1 part of conc. nitric acid is called aqua regia. It is used for dissolving noble metals like gold and platinum.

33. Hydrochloric acid is used in the manufacture of chlorine and ammonium chloride, in medicines and as a laboratory reagent.

EXERCISES

Very Short Answer Type Questions

1. What is the electronic configuration of bromine?

2. Give the colours of F_2, Cl_2, Br_2 and I_2.

3. Why does fluorine have a smaller electron affinity than chlorine?

4. Give the order of acidic strength of HBr, HCl, HF and HI.

5. How do you explain the following order of acidic strength of oxoacids?

$HOCl < HOCl_2 < HOCl_3 < HOCl_4$

6. Write equations for the preparation of chlorine using MnO_2 and HCl.

7. Why does fluorine always exhibit –1 oxidation state in its compounds?

8. Give two uses of hydrochloric acid.

9. Draw the shape of IF_5 molecule.

10. Give the oxidation state of chlorine in HClO, $HClO_2$, $HClO_3$ and $HClO_4$.

Short Answer Type Questions

1. What are interhalogen compounds? How are they formed? Discuss the structure of IF_7.

2. Explain why ClF_3 exists, whereas FCl_3 does not.

3. How do you explain the higher oxidation states shown by chlorine, bromine and iodine?

4. Give an account of the various oxidation states exhibited by the elements of group-17(Halogens). Why does fluorine not show positive oxidation state?

5. How do we prepare hydrochloric acid in the laboratory? Explain with the help of equations.

6. HCl has a high value of K for the reactions:

$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$

What is its significance?

7. How does hydrochloric acid react with carbonates and sulphites? Give relevant reactions.

8 Give four uses of hydrochloric acid.

Long Answer Type Questions

1. Write the electronic configurations of F, Cl, Br and I. Explain the trend in the physical properties under the following headings:

(*i*) Melting and boiling points.

(*ii*) Oxidation states.

2. Give a description of hydrides, halides and oxides of elements of group 17.

3. Describe two laboratory methods of preparation of chlorine giving chemical equations.

4. How does hydrochloric acid react with the salts of a weaker acid?

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

2. Fluorine: Pale yellow, Chlorine : Greenish yellow, Bromine: Reddish brown, Iodine: Dark violet.

3. Due to small size of fluorine.

4. HF < HCl < HBr < HI

5. The acidic strength is explained on the basis of Lowry-Bronsted concept that reveals that the conjugate base of a weak acid is a strong base and the conjugate acid of a strong base is a weak acid.

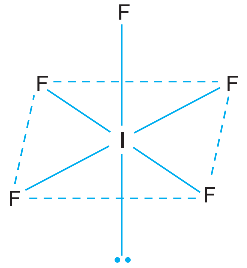
6.
$$\begin{aligned} MnO_2 + 2HCl &\longrightarrow MnCl_2 + H_2O + O \\ 2HCl + O &\longrightarrow H_2O + Cl_2 \\ \hline MnO_2 + 4HCl &\longrightarrow MnCl_2 + Cl_2 + 2H_2O \end{aligned}$$

7. Fluorine is the most electronegative element. It has a great tendency to accept an electron and form F^-.

8. (*i*) In the manufacture of chlorine and ammonium chloride.

(*ii*) For extracting glue from bones and purifying bone black.

9.



10. HClO : +1, $HClO_2$: +3, $HClO_3$: +5 and $HClO_4$: +7

COMPETITION FILE

SUBJECTIVE PROBLEMS

Problem 1. *A certain compound (X) is used in laboratory for analysis. Its aqueous solution gives the following reactions.*

(i) On addition to copper sulphate solution a brown precipitate is obtained which turns white on addition of excess of $Na_2S_2O_3$ *solution.*

(ii) On addition to Ag^+ *ion solution a yellow curdy precipitate is obtained which is insoluble in ammonium hydroxide.*

Identify (X) and give equations for the reactions at step (i) and (ii).

Solution:

(*i*) Since the compound 'X' on addition to a copper sulphate solution gives brown precipitate which turns white on addition of excess of $Na_2S_2O_3$, it contains iodide ions (I^-).

(*ii*) Addition of 'X' to Ag^+ ion solution gives yellow curdy precipitate which is insoluble in ammonium hydroxide, therefore 'X' contains iodide ions. Since X contains iodide (I^-) ions and is used as a laboratory reagent, the compound 'X' is potassium iodide (KI). The reactions are shown by the following equations:

(*i*) $4KI + 2CuSO_4 \longrightarrow I_2 + Cu_2I_2 + 2K_2SO_4$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

(*ii*) $KI + Ag^+ \longrightarrow AgI + K^+$

Problem 2. *When NaBr is heated with conc.* H_2SO_4*,* Br_2 *is produced but when NaCl is heated with conc.* H_2SO_4*, HCl is produced. Why?*

Solution: When NaBr is heated with conc. H_2SO_4, HBr is first produced which reduces H_2SO_4 to SO_2 while itself gets oxidised to Br_2.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$
$$2HBr + H_2SO_4 \longrightarrow 2H_2O + 5O_2 + Br_2$$

As a result, only Br_2 is produced.

NaCl reacts with conc. H_2SO_4 to form HCl but since HCl does not acts as a reducing agent, it does not get oxidised to Cl_2.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
$$HCl + H_2SO_4 \longrightarrow \text{No action}$$

As a result, only HCl is evolved.

Problem 3. *Out of fluorine, chlorine, bromine and iodine, select (a) best hydrogen bond former (b) best oxidising agent (c) whose hydride is a strong reducing agent.*

Solution:

(*i*) Fluorine is most capable of hydrogen bonding.

(*ii*) Fluorine is strongest oxidising agent.

(*iii*) The hydride of iodine, *i.e.*, hydrogen iodide (HI) is stronger reducing agent than other HX molecules.

Problem 4. *Why is fluorine a powerful oxidising agent?*

Solution: Fluorine has the highest tendency to accept the electron due to its small size, high electronegativity and low dissociation energy, which makes it a powerful oxidising agent.

Problem 5. *Xenon has closed shell configuration but is known to give compounds with fluorine why?*

Solution: The I.E. of Xenon is high. The elements forming bonds with it should be highly electronegative. This condition is satisfied by fluorine, so it forms compounds with xenon.

Problem 6. *How would you prepare (i) HF from* CaF_2 *(ii)* Br_2 *from seawater (iii)* I_2 *from* $NaIO_3$ *and (iv) HBr from NaBr?*

Solution: Various preparations are described as under:

(*i*) **HF from CaF:**

$$CaF_2 + H_2SO_4 \xrightarrow{\text{Heat}} CaSO_4 + 2HF$$

(*ii*) **Br_2 from seawater:** Seawater is acidified with H_2SO_4 and then treated with chlorine when bromine is liberated from bromides.

$$2KBr + Cl_2 \rightarrow 2KCl + Br_2$$
$$MgBr_2 + Cl_2 \rightarrow MgCl_2 + Br_2$$

(*iii*) **I_2 from $NaIO_3$:** By heating $NaIO_3$ with $NaHSO_3$ as:

$$2NaIO_3 + 5NaHSO_3 \rightarrow 2Na_2SO_4 + 3NaHSO_4 + H_2O + I_2$$

(*iv*) **HBr from NaBr:** Br heating NaBr with H_3PO_4:

$$3NaBr + H_3PO_4 \rightarrow Na_3PO_4 + 3HBr.$$

Problem 7. *Fluorine is more reactive than other halogens. Explain.*

Solution: Among halogens fluorine is highly reactive, because

(*a*) It has the smallest size.

(*b*) It has the highest electronegativity.

(*c*) It has the lowest dissociation energy.

Problem 8. *How is it that HCl is the most volatile and HF is the least volatile amongst hydrogen halides?*

Solution: The fluorine has small size and high electronegativity. So, HF is extensively hydrogen bonded and has high boiling point and is thus least volatile.

The boiling point increases from HCl to HI, because of increase of atomic size from chlorine to iodine. The increase in size increases the strength of van der Waals' forces of attraction and hence higher melting and boiling points.

Hence, HCI is the most volatile.

Problem 9. *A liquid A is reacted with hot aqueous sodium carbonate solution. A mixture of two salts B and C are produced in the solution. The mixture on acidification with H_2SO_4 and distillation produces the liquid A again. Identify A,B and C and write the equations involved.*

Solution:

(*i*) Halogens on treatment with a hot alkaline solution undergo disproportionation reaction to give a mixture of two salts, i.e, halides (X^-) and halates (XO_3^-). Since the given halogen A is a liquid, therefore, it must be Br_2.

(*ii*) Since A is Br_2, the mixture of two salts B and C which gives on treatment with hot aqueous Na_2CO_3 in solution must be sodium bromide (NaBr) and sodium bromate ($NaBrO_3$). The balanced equation for this reaction is

$$\underset{A}{3Br_2} + 3Na_2CO_3 \xrightarrow{\Delta} \underset{B}{5NaBr} + \underset{C}{NaBrO_3} + 3CO_2.$$

(*iii*) The mixture of A+B on acidification and subsequent distillation will first produce the corresponding acids, *i.e.*, HBr and $HBrO_3$. Since $HBrO_3$ is a moderately strong oxidising agent, it will oxidise HBr to Br_2. Thus, the liquid A is regenerated. The equations for these reactions are:

$$5NaBr + Na_2BrO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 5HBr + HBrO_3$$

$$5HBr + NBrO_3 \longrightarrow 3Br_2 + 3H_2O$$

$$5NaBr + NaBrO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 3Br_2 + 3H_2O$$

Problem 10. *Indicate whether the following statements are TRUE or FALSE. Justify your answer in not more than three lines:*

(*i*) *The decreasing order of electron affinity of F, Cl and Br: F > Cl > Br.*

(*ii*) *HBr is stronger acid than HI because of hydrogen bonding.*

Solution:

(*i*) False (F < Cl > Br).

(*ii*) I–atom is larger than Br-atom. As a result, bond dissociation energy of H—I is less.

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. The type of hybrid orbitals used by the chlorine atom in ClO_2^- is
   (*a*) sp^3 (*b*) sp^2
   (*c*) *sp* (*d*) none of these
2. Which of the following halides is most acidic?
   (*a*) PCl_3 (*b*) $SbCl_3$
   (*c*) $BiCl_3$ (*d*) CCl_4
3. Which of the following shows only negative oxidation states?
   (*a*) Chlorine (*b*) Bromine
   (*c*) Iodine (*d*) Fluorine
4. Which of the following hydrogen halides is most volatile?
   (*a*) HF (*b*) HCl
   (*c*) HBr (*d*) HI
5. Among the following which is the strongest oxidising agent?
   (*a*) Br_2 (*b*) I_2
   (*c*) Cl_2 (*d*) F_2
6. Hydrochloric acid decomposes
   (*a*) salts of stronger bases
   (*b*) salts of weaker bases
   (*c*) salts of stronger acids
   (*d*) salts of weaker acids
7. Which of the following is used in the preparation of chlorine?
   (*a*) Only MnO_2
   (*b*) Only $KMnO_4$
   (*c*) Both MnO_2 and $KMnO_4$
   (*d*) neither MnO_2 nor $KMnO_4$
8. Which one of the following orders is not in accordance with the property stated against it?
   (*a*) $F_2 > Cl_2 > Br_2 > I_2$: bond dissociation energy
   (*b*) $F_2 > Cl_2 > Br_2 > I_2$: oxidising power
   (*c*) HI > HBr > HCl > HF : acidic property in water
   (*d*) $F_2 > Cl_2 > Br_2 > I_2$: electronegativity

9. A metal, M forms chlorides in +2 and +4 oxidation states. Which of the following statements about these chlorides is correct?
   (*a*) MCl_2 is more volatile than MCl_4.
   (*b*) MCl_2 is more soluble in anhydrous ethanol than MCl_4.
   (*c*) MCl_2 is more ionic than MCl_4.
   (*d*) MCl_2 is more easily hydrolysed than MCl_4.

10. For (*i*) I^-, (*ii*) Cl^-, (*iii*) Br^-, the increasing order of nucleophilicity would be
   (*a*) $Cl^- < Br^- < I^-$ (*b*) $I^- < Cl^- < Br^-$
   (*c*) $Br^- < Cl^- < I^-$ (*d*) $I^- < Br^- < Cl^-$

(B) Fill in the Blanks

Fill in the blank spaces:

1. Halogens combine with each other to give rise to ______ .
2. ______ acid gives hypo ______ ion (hydrobromic, hypobromons, perbromic, bromide, bromite and perbromate.)
3. ______ is the most electronegative of all the halogens.
4. The strongest oxidising agent of all the halogens is ______ .

(C) True/False Statements

Write T for true and F for false statements:

1. The oxidation state of fluorine is one and that of chlorine can be as high as seven.
2. The electronic configuration of halogens is ns^2np^2.
3. Hydrochloric acid is obtained by passing hydrochloric acid gas in water.
4. Fluorine is most capable of forming hydrogen bonds.
5. Out of hydrides of halogens, HF is the strongest reducing agent.

ANSWERS

(A) Multiple Choice Questions

1. (*a*) 2. (*c*) 3. (*d*) 4. (*b*) 5. (*d*) 6. (*d*) 7. (*c*) 8. (*a*)
9. (*c*) 10. (*a*)

(B) Fill in the Blanks

1. interhalogen compounds 2. Hypobromous, bromite
3. Fluorine 4. fluorine

(C) True/False Statements

1. True 2. False 3. True 4. True 5. False

7
CHAPTER

Chemical Kinetics

LEARNING OBJECTIVES

- List the factors that affect the rate of reaction, e.g. concentration, temperature, pressure, surface area of a solid and catalysts.
- Compare the changes in rate from the effects of concentration, pressure, temperature, surface area using collision theory.
- Explain qualitatively the Maxwell Boltzmann distribution of molecular energies and its relationship to activation energy.
- Explain qualitatively the effect of temperature changes on the rate of reaction using the Maxwell Boltzmann model of the distribution of molecular energies.
- Using enthalpy level profile diagrams show that a catalyst speeds up a chemical reaction by allowing it to proceed via lower activation energy.
- Demonstrate catalytic behaviour in terms of the Maxwell Boltzmann model of the distribution of molecular energies.
- Discuss the benefits of using catalysts, e.g. catalysts in reducing energy demands, enzymes generating specific products; Ziegler-Natta catalyst in the production of polyethene and platinum or palladium or rhodium.

7.1 INTRODUCTION

Chemical kinetics is concerned with the study of rates of chemical reactions and the factors influencing them. The study of this subject is very useful in understanding the mechanism of a number of chemical reactions. The experimental data have led to the development of the theories of chemical activity of molecules.

In fact, a chemical reaction involves breaking of bonds in reactant molecules and formation of new bonds in product molecules.

Different bonds are present in different substances, therefore, chemical reactions differ from one another, and the rates at which chemical reactions take place are also different.

On one hand, we know the reactions involving ions which are over in a fraction of second. For example, precipitation of barium sulphate on mixing a solution of barium chloride and sodium sulphate takes place instantly.

$$\underset{\substack{\text{Barium ion in}\\ \text{barium chloride}}}{Ba^{2+}} + \underset{\substack{\text{Sulphate ion in}\\ \text{sodium sulphate}}}{SO_4^{2-}} \longrightarrow \underset{\substack{\text{Precipitate of}\\ \text{barium sulphate}}}{BaSO_4}$$

Another example is the reaction between Ag^+ and Cl^- ions to form AgCl when silver nitrate and sodium chloride are mixed. The rate of such reactions cannot be measured. In ionic reactions, no bonds are to be broken, that is why these reactions are very fast.

On the other hand, there are reactions which are very slow. For example, rusting of iron.

The reactions involving organic molecules take place in measurable period of time, *i.e.*, they proceed slowly. **For example,** inversion of cane sugar in aqueous solution or hydrolysis of ethyl acetate with sodium hydroxide.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

In such reactions, a number of bonds have to be broken in reactants and new bonds have to be formed in the products. That is why molecular reactions are slow.

It is clear from the above discussion that the rate of a reaction at a given temperature, depends upon the nature of the reactants and the products formed and upon experimental conditions.

However, there are reactions which take place extremely slowly and perhaps take hundreds or thousands of years to complete. Such reactions are unlikely not to be carried out in the laboratory. However, we observe them in nature. One such example is the formation of stalactite and stalagmite. These are two types of rock formation. Stalactites hang from the ceiling while stalagmites grow from the floors. Both are formed when minerals like calcium carbonate precipitate out of the dropping water or emerging water in caves.

Chemical kinetics *is that branch of chemistry which deals with the rates of chemical reactions, mechanisms and factors which influence the rate of the reactions.*

7.2 RATE OF REACTION

The rate of a reaction may be defined as the speed or velocity with which the reaction takes place. The rate of a reaction may also be defined as the change in the concentration of any one of the reactants or products per unit time. For example, consider the decomposition of hydrogen peroxide in an aqueous solution.

$$H_2O_2\,(aq) \longrightarrow H_2O\,(l) + \frac{1}{2}O_2\,(g)$$

$$\text{Rate of this reaction} = \frac{\text{Decrease in the conc. of } H_2O_2}{\text{Time taken}} = \frac{\Delta[H_2O_2]}{\Delta t}$$

$$= \frac{\text{Amount of } H_2O_2 \text{ consumed}}{\text{Time taken}}$$

where, $\Delta[H_2O_2]$ is the change in concentration of H_2O_2 in time Δt.

or $$\text{Rate of this reaction} = \frac{\text{Amount of } O_2 \text{ produced}}{\text{Time taken}} = \frac{\Delta[O_2]}{\Delta t}$$

where, $\Delta[O_2]$ is the change in concentration of O_2 in time Δt.

According to the Law of Mass Action, the rate of a reaction depends upon the molar concentration of the reactants. The concentration of the reactants keeps on decreasing with the passage of time (while that of the products keeps on increasing). Therefore, the rate of a reaction does not remain constant throughout the reaction but changes with time. Thus, it would not be correct to express the rate of the reaction by merely dividing the total change in concentration by total time taken. This would give us only the *average rate*. On the other hand, the rate of a reaction must be expressed with respect to a particular instant of time.

Hence, *the rate of reaction, at a particular moment of time may be defined as the rate of change of concentration of any one of the reactants or products over a very small interval of time* (Fig. 7.1). This is also called *Instantaneous Rate.*

7.2.1 Expressing the Rate of a Reaction

Since the rate of a reaction keeps on changing every moment, therefore if at any instant, dx is the small change in the concentration of any one reactant or product in a small interval of time dt. Then the rate of a reaction may be expressed as:

$$\text{Rate of reaction} = \frac{dx}{dt}$$

If the rate of a reaction is expressed in terms of the concentration of the reactant, then since the concentration decreases with time, the rate of reaction is written as $= -\dfrac{dx}{dt}$.

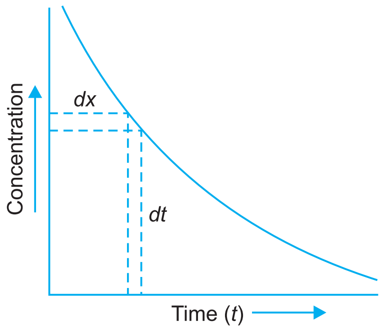


Fig. 7.1: *Variation of velocity of reaction with time*

On the other hand, if the rate of a reaction is expressed in terms of the concentration of the product, then since the concentration of the product increases with time, therefore, the rate of the reaction is expressed as:

$$\text{Rate of reaction} = +\frac{dx}{dt}$$

Let us consider the gaseous reaction:

$$H_2\,(g) \;+\; I_2\,(g) \longrightarrow 2HI\,(g)$$

The rate of this reaction is given by the rate of disappearance of one of reactants $H_2\,(g)$ or $I_2\,(g)$.

$$\text{Rate of reaction} = -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt}$$

where $\dfrac{d[H_2]}{dt}$ and $\dfrac{d[I_2]}{dt}$ both are negative since their concentrations decrease with time and the reaction rate itself will be positive as it should be. We can also express the reaction rate in terms of the rate of formation of HI, *e.g.*, $\dfrac{d[HI]}{dt}$ which is a positive quantity. From the stoichiometry of the reaction, for every mole of H_2 or I_2 reactants, two moles of HI are being formed.

7.2.2 Determination of the Rate of a Reaction

Consider a general reaction

$$A + B \longrightarrow C + D$$

The concentration of any one of the reactants or products (say, in this case, of the reactant A) is determined at regular intervals of time (say, after every 2 minutes), then these values of the concentration are plotted against time. A graph shown in Fig. 7.2 is obtained. The rate of the reaction at any time is then calculated by drawing a tangent to the curve at the point corresponding to that time and extending the tangent on either side so as to cut the axes, say at points P and Q. Then,

$$\text{Rate of reaction} = \text{Slope of the tangent}$$

$$= \frac{\Delta x}{\Delta t} = \frac{OQ}{OP}$$

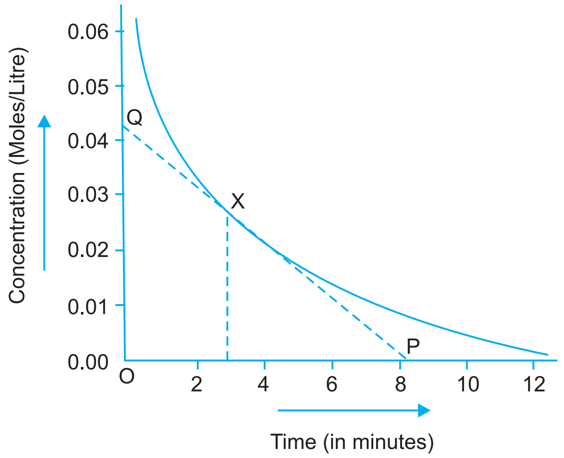


Fig. 7.2: *Determination of the rate of reaction at any particular instant of time*

Let us consider the reaction between acetic acid and methanol in an aqueous solution to form methyl acetate.

$$CH_3COOH\,(aq) + CH_3OH\,(aq) \longrightarrow CH_3COOCH_3\,(aq) + H_2O\,(l)$$

We can measure the rate of the reaction by determining the rate at which acetic acid disappears or the rate at which methanol disappears or the rate at which methyl acetate forms.

In a typical experiment carried out at 298 K, 500 cm^3 of 1M solution of acetic acid was mixed with 500 cm^3 of 1M solution of methanol and the concentrations of acetic acid and methyl acetate were determined as a function of time. The observations are given in Table 7.1.

Table 7.1

Time (seconds) (Time of mixing)	Concentration of acetic acid (mol L^{-1})	Concentration of methyl acetate (mol L^{-1})
0	0.500	0
2	0.442	0.054
4	0.405	0.101
6	0.372	0.135
8	0.338	0.165
10	0.321	0.182
12	0.290	0.211
14	0.275	0.225
16	0.258	0.242

The rate of reaction is the rate of disappearance of the reactant (acetic acid) or the rate of formation of the product (methyl acetate).

The instantaneous rate at any time is given by the slopes of either of the two curves at the point corresponding to the time and this is done by drawing the tangents to the two curves and calculating the slopes of the tangents. From the graph, it can be noted that:

(*i*) The amount of acetic acid reacted = the amount of methyl acetate formed at any given time.
(as according to the balanced equation, one mole of acetic acid produces one mole of methyl acetate)

(*ii*) The rate of disappearance of acetic acid
= the rate of formation of methyl acetate
= the rate of the reaction.

(*iii*) The rate of reaction is not constant but decreases with time.

It is also possible to work out on an **average rate** at a given time from the data given by taking the difference in concentration at two equidistant points in time and calculating an average rate of change.

For example, to calculate an average rate at 10 seconds, we take the reading at 8 and 12 seconds and divide by 4. The rate of disappearance of acetic acid (substitute the values from Table 7.1).

$$= \frac{0.338 - 0.290}{4} = 0.012 \text{ mol } L^{-1}s^{-1}$$

The rate of appearance of methyl acetate

$$= \frac{0.211 - 0.165}{4} = 0.012 \text{ mol } L^{-1}s^{-1}$$

Another method to estimate the **average rate of the reaction, is to find out the time taken for a certain per cent (say 10%) of the reactant to disappear and construct the following table** (Table 7.2) and then calculate the average rate of reaction of the concentration changes.

Table 7.2

% reacted	Amount of acetic acid reacted (mol L^{-1})	Time taken (s)	Average rate of reaction (mol L^{-1} s^{-1})
0 – 10	0.05	1.7	0.029
10 – 20	0.10	2.5	0.020
20 – 30	0.15	3.0	0.017
30 – 40	0.20	4.2	0.012
40 – 50	0.25	4.8	0.010
50 – 60	0.30	8.8	0.0057
60 – 70	0.35	15.0	0.0031
70 – 80	0.40	27.5	0.0018
80 – 90	0.45	68.0	0.00073

Most reactions slow down as they proceed. This is a direct consequence of the fact that reactions can occur only on the encounter of reactant molecules and the rate of encounter will decrease with decrease in the concentration of the reactants. Since the reaction rate is not constant, it is meaningless to talk about the rate of reaction between methanol and acetic acid unless we specify concentration and temperature. To compare rates of different reactions we can compare the rates at a specified concentration of reactants (say 1 mol L^{-1} for all the reactants) or compare the time it takes for the reaction to go to completion when we start with same concentration of reactants. **The second method is difficult since most reactions slow down as they proceed.**

We, therefore, compare the time it takes for the reactions to proceed to a definite stage, say 98% completion. **This time is denoted as the reaction Life Time. The shorter the reaction life time the faster the reaction.**

Therefore, the rate of formation of HI will be twice the rate of disappearance of either H_2 or I_2. Therefore, to normalize we divide the rate of disappearance of the reactants or formation of the products by the number of moles involved in the reaction.

Thus, for the given reaction:

$$\text{Rate of reaction} = -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$$

$$\text{Rate of reaction} = \text{Rate of disappearance of } H_2 \text{ or } I_2$$

$$= \frac{1}{2}\,(\text{Rate of formation of HI})$$

For a general reaction:

$$n_1A + n_2B \longrightarrow n_3C + n_4D$$

Rate of the reaction can be expressed as:

$$-\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = \frac{1}{n_3}\frac{d[C]}{dt} = \frac{1}{n_4}\frac{d[D]}{dt}$$

7.2.3 Units of the Rate of Reaction

Because the concentration is expressed in moles/litre and the time in seconds or minutes, therefore, the units of the rate of reaction are moles litre^{-1} sec^{-1} or moles litre^{-1} min^{-1}.

7.3 REACTION RATE (VELOCITY) AND RATE CONSTANT

If dx be the amount of reactant transformed in an infinitesimally small interval dt, the $\frac{dx}{dt}$ is called the velocity of the reaction.

Let a and b be the initial concentrations of the reactants A and B respectively. Let x moles of each of these transformed in time t.

$$\mathrm{A} \quad + \quad \mathrm{B} \longrightarrow \mathrm{C} + \mathrm{D}$$

Initial conc. $\quad a \quad b$

Conc. after time t $\quad (a - x) \quad (b - x)$

Then by Law of Mass Action

$$\frac{dx}{dt} \propto (a - x)\,(b - x)$$

or

$$\frac{dx}{dt} = k\,(a - x)\,(b - x) \qquad \text{...}(i)$$

If

$$(a - x)\,(b - x) = 1$$

Then

$$\frac{dx}{dt} = k \qquad \text{...}(ii)$$

where k is the *rate constant* and may be defined as the rate of a reaction when the product of concentrations of the reactants is unity.

7.3.1 Significance of Rate Constant (*k*)

The value of rate constant is independent of the concentration of the reactants but varies with temperature. The numerical value of k indicates whether the reaction is fast or slow. A high value of k indicates a fast reaction and low value a slow reaction.

Example. *For the reaction* $3H_2\,(g) + N_2\,(g) \longrightarrow 2NH_3(g)$, *express the rate of the reaction in terms of* $-d[H_2]/dt$, $-d[N_2]/dt$ *and* $d[NH_3]/dt$.

Solution.

$$\text{Rate of disappearance of hydrogen} = -\frac{d[\mathrm{H_2}]}{dt}$$

$$\text{Rate of disappearance of nitrogen} = -\frac{d[\mathrm{N_2}]}{dt}$$

$$\text{Rate of appearance of ammonia} = +\frac{d[\mathrm{NH_3}]}{dt}$$

To obtain the rate of the reaction, the above three rates of disappearance or formation will have to be divided by the coefficient, appearing before them in the balanced equation.

$$\text{Rate of the reaction} = -\frac{1}{3}\frac{d[\mathrm{H_2}]}{dt} = -\frac{d[\mathrm{N_2}]}{dt} = \frac{1}{2}\frac{d[\mathrm{NH_3}]}{dt}$$

PROBLEMS FOR PRACTICE

1. Nitrogen dioxide (NO_2) reacts with fluorine (F_2) to yield nitryl fluoride (NO_2F)

$$2NO_2\,(g) + F_2\,(g) \longrightarrow 2NO_2F\,(g)$$

Write the rate of reaction in terms of (*i*) rate of formation of NO_2F, (*ii*) rate of disappearance of NO_2 and (*iii*) rate of disappearance of F_2.

[**Ans.** (*i*) $-\frac{1}{2}\frac{d[\mathrm{NO_2}]}{dt}$, (*ii*) $-\frac{d[\mathrm{F_2}]}{dt}$, (*iii*) $\frac{1}{2}\frac{d[\mathrm{NO_2F}]}{dt}$]

2. Write the rate of reaction in terms of disappearance of A, B and formation of C for the following reaction:

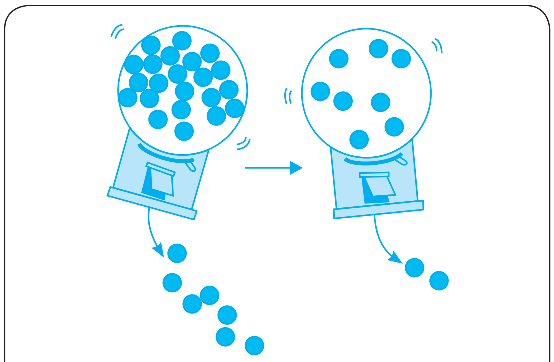
$$2A + 3B \longrightarrow 2C$$

[**Ans.** $-\frac{1}{2}\frac{d[\mathrm{A}]}{dt}$, $-\frac{1}{3}\frac{d[\mathrm{B}]}{dt}$, $\frac{1}{2}\frac{d[\mathrm{C}]}{dt}$]

7.4 FACTORS INFLUENCING THE RATE OF REACTION

The rate of a chemical reaction depends upon a number of factors. A few important factors are:

1. Concentration of the reactants
2. Nature of the reactants and products
3. Presence of catalyst
4. Temperature of the system
5. Surface area
6. Radiation.



Reaction rate dependent on concentration. More the marbles inside the container, more of them will come out.

1. Effect of concentration. Experimentally, it is observed that the rate of a reaction decreases with the passage of time since concentrations of the reactants decrease with time. This is because the number of collisions per second which governs the rate of reaction depends upon the concentrations of the reactants.

The greater the concentration, larger is the number of molecules per litre and larger the number of collisions.

2. Effect of the nature of the reactants and products. A chemical reaction involves the breaking of the bonds in reactants and formation of new bonds in the products. The number of bonds and nature of the bonds to be broken or formed are different in different reactions. Hence, the rates are different. For example,

Acidified $KMnO_4$ can be decolorised by $FeSO_4$ instantaneously while slowly by oxalate.

(*a*) $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O$

(*b*) $5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O$

The first reaction is faster than the second. This is because of the difference in the nature of the Fe^{2+} and $C_2O_4^{2-}$ ions. Ferrous ion is simple while oxalate ions contain a number of covalent bonds.

3. Effect of catalyst. A catalyst generally increases the rate of a reaction at a given temperature. It is specific in its action. According to the collision theory, a catalyst changes the path of the reaction. When a catalyst is added, a new reaction path is provided for which the magnitude of the energy barrier is decreased. As a result of this, a larger number of particles of the reactants can get over it. This increases the rate of the reaction.

In reversible reactions, a catalyst increases both the forward and the backward reactions by the same amount.

Therefore, a catalyst does not alter the position of equilibrium in a reversible reaction. The function of the catalyst is to help reaction molecules approach the equilibrium in less time.

4. Effect of temperature. The rate of a reaction increases with temperature. Generally, a rise of 10°C in temperature increases the rate of reaction by two to five times. As the temperature increases, the kinetic energy of the molecules also increases. As a result of this, the fraction of the energetic molecules increases. This results in the increase in the numbers of effective collisions per second. The effective collisions can bring a chemical change of molecules and increase the reaction rate.

5. Surface area. In heterogeneous reactions, the surface area of the reactants plays an important role. For a given mass, the total surface area increases if it is divided into particles. Therefore, a substance in smaller particles reacts more rapidly than that in larger particles.

For example, coal or wood burns readily in smaller pieces than in lumps.

6. Effect of radiations. Some chemical reactions proceed only under the influence of light radiations which provide the necessary energy to overcome the energy barrier and start the reaction. For example:

(*i*) Photosynthesis occurs in sunlight.

(*ii*) H_2 and Cl_2 gases react to form hydrogen chloride only when the mixture is exposed to sunlight.
(*iii*) A photographic plate is affected by visible light, ultraviolet light, X-rays, etc.
(*iv*) Methane reacts with Cl_2 in the presence of light.

Out of the above factors, the effect of concentration and temperature are being considered in some detail.

7.5 COLLISION THEORY OF REACTION RATES

It is observed that most of the reactions show increased rate of reaction with increase of temperature. For every 10° rise in temperature, the rate of reaction nearly becomes double. It is also observed that a number of reactions which do not occur at room temperature, proceed readily at a higher temperature. For example, a mixture of hydrogen and oxygen remains as such at room temperature, but reacts to form water when an electric spark is passed through it.

These observations can be explained with the help of collision theory of reaction rates. According to this theory:

(*i*) Substances react because their molecules collide with one another.
(*ii*) All the collisions are not effective. An effective collision is that which results into a chemical reaction.
(*iii*) For a collision to be effective it is necessary that the colliding molecules must possess a certain minimum amount of energy called **threshold energy**.
(*iv*) The colliding molecules must be properly oriented at the moment of collision.

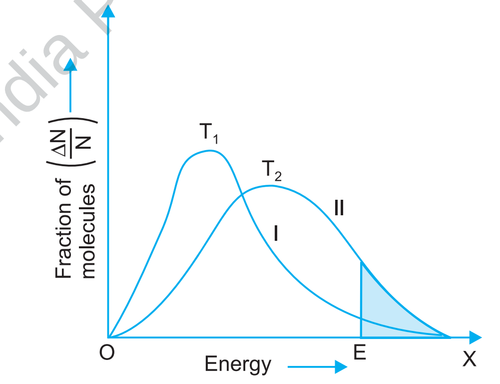
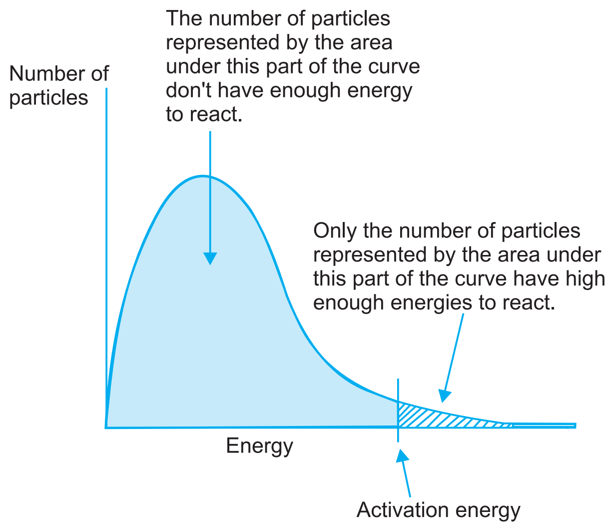


Fig. 7.3: *Energy of distribution at two different temperatures T_1 and T_2 ($T_2 > T_1$)*

7.5.1 Explanation of Increase in Reaction Rate with Rise of Temperature

Just as we have Maxwell distribution of velocities of molecules, we have Maxwell distribution of energies of molecule given in Fig. 7.3.

Curve I is the plot of fraction of molecule possessing a certain energy against that energy at the temperature T_1. In this diagram, E denotes the threshold energy. The shaded region under this curve gives a number of molecules with energies equal to or greater than the threshold energy. As the temperature is increased from T_1 to say T_2, the curve shifts towards the right-hand side. Curve II is the energy distribution curve of the molecules. The shaded region under the curve II beyond E now becomes larger. This shows that molecules having energy equal to or greater than the threshold energy becomes more. Thus, the rate of the reaction also increases. It is found that the shaded area becomes almost double for 10° rise of temperature. Hence, the rate of reaction also doubles for every 10° rise in temperature.



Rate of reaction increases with rise of temperature

Explanation of the Non-occurrence of Reaction at Room Temperature and Occurrence at Higher Temperature

At room temperature, there are no molecules having energy greater than the threshold energy and so the reaction do not occur. When temperature is increased, the molecules of the reactants absorb heat energy and hence, a number of molecules start attaining energy equal to or greater than the threshold energy and thus the reaction starts.

7.5.2 Concept of Activation Energy

The extra amount of energy which the molecules of the reactants have to absorb so that their energy becomes equal to the threshold energy is called the **activation energy**. In other words,

Activation energy = Threshold energy – Energy actually possessed by the reacting molecules.

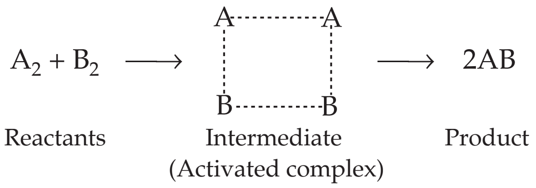
Thus, in order that the reactants may change over to products, they have to absorb some energy and, hence, cross a barrier called **Activation Energy Barrier**. The situation is shown graphically in Fig. 7.4.

The concept of energy barrier may be further explained as follows:

Let us suppose a hypothetical gaseous reaction

$$A_2 + B_2 \longrightarrow 2AB$$

In order that the collision between the molecules A_2 and B_2 may be effective, they must first form a transitory (short lived) intermediate called Activated complex. In the formation of this complex, the bonds in the A_2 and B_2 molecules are loosened and new loose bonds between A and B are formed. Hence the formation of AB molecules may be shown as follows:



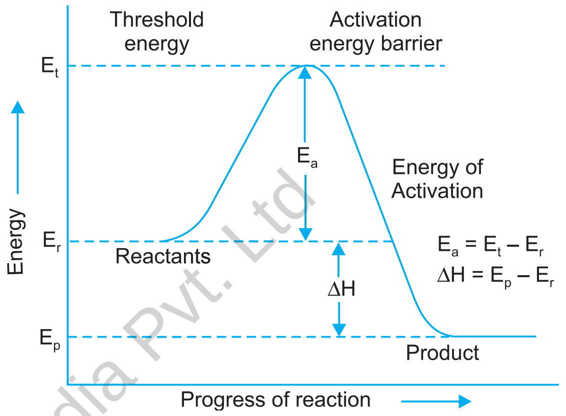


Fig. 7.4: *Concept of activation energy*

Therefore, the energy barrier corresponds to the formation of an activated complex. Hence, the energy of activation may be defined as the difference between the energy of the activated complex and the average energy of the reacting molecules. Thus,

Activation energy = Energy of the activated complex – Average energy of the reacting molecules.

It is a fact, that the reactants will not be able to react unless given this much energy. According to the concept of activation energy, the reactants are not directly converted into products. In fact, the molecules of reactants must first acquire energy to form the activated complex, which then decomposes to give the product. It is shown in the Fig. 7.4 that the energy equal to E_a (activation energy) must be absorbed to form an activated complex. The activated complex then further decomposes to give the product, and energy equal to $E_t - E_p$ or E'_a is released in the process which is the energy of activation of the reverse process.

The change in energy ΔH, for the reaction is given by the relation:

$$\Delta H = E_p - E_R$$

Exoergic (exothermic) Reactions and Endoergic (endothermic) Reactions.

Two conditions arise:

(*i*) If $E_p < E_R$; ΔH is –ve, the energy is released and the reaction is exothermic.

(*ii*) If $E_p > E_R$; ΔH is +ve, the energy is absorbed and the reaction is endothermic.

ΔE (or ΔH) does not depend on the absolute value of E_a.

An exoergic or exothermic reaction is illustrated in Fig. 7.4 in which energy of the product E_P is less than that of the reactant E_R *i.e.*, $E_P < E_R$.

The endoergic or endothermic reaction is illustrated in Fig. 7.5.

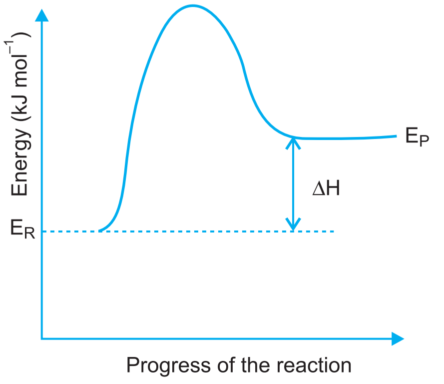


Fig. 7.5: *Representation of an endoergic reaction*

In an endoergic reaction $E_P > E_R$

From Fig. 7.4, it is explained that even though the energy of the product is lower than that of the reactants and the overall reaction is exothermic, still the system has to cross the energy barrier before it can change over to product with lower energy.

Another important result that follows from the above discussion is given below:

Some reactions look to be similar but have different rates (even when all other factors are kept the same). This is due to the fact that their energies of activation are different. Lower the value of activation energy, higher will be the rate of reaction.

Further, it is experimentally seen that the rates of certain reactions are much smaller than expected on the basis of activation energy. This is made more clear on the basis of orientation factor as given in the next section.

Arrhenius gave the following equation relating the rate constants at different temperatures and the activation energy:

$$k = Ae^{-E_a/RT} \quad ...(i)$$

where k = Rate constant
E_a = Energy of activation
A = Frequency factor
R = Gas constant
T = Temperature on absolute scale

Taking natural logarithm of equation (*i*), we have

$$l_n\, k = l_n\, A - \frac{E_a}{RT} \quad ...(ii)$$

Arrhenius

or

$$\log k = \log A - \frac{E_a}{2.303\,RT} \quad ...(iii)$$

If k_1 and k_2 are the rate constants at temperatures T_1 and T_2, we can write

$$\log k_1 = \log A - \frac{E_a}{2.303\,RT_1} \quad ...(iv)$$

and

$$\log k_2 = \log A - \frac{E_a}{2.303\,RT_2} \quad ...(v)$$

Subtracting equation (*iv*) from equation (*v*), we have

$$\log k_2 - \log k_1 = \frac{E_a}{2.303\,RT_1} - \frac{E_a}{2.303\,RT_2}$$

or

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where k_1 and k_2 are the rate constants at the temperatures T_1 and T_2. E_a is the activation energy for the reaction and R is gas constant. If we know the rate constants k_1 and k_2 at two different temperatures, the energy of activation E_a can be calculated.

Orientation Factor: All the collisions between molecules possessing the required energy of activation does not lead to a chemical reaction. An effective collision also requires in addition to threshold energy, a proper geometrical alignment (orientation) of the molecules for reaction to take place. A large number of collisions become ineffective if the colliding molecules are not properly oriented at the time of collision. That means it is important to know the manner in which the molecules collide which is clear in Fig. 7.6.

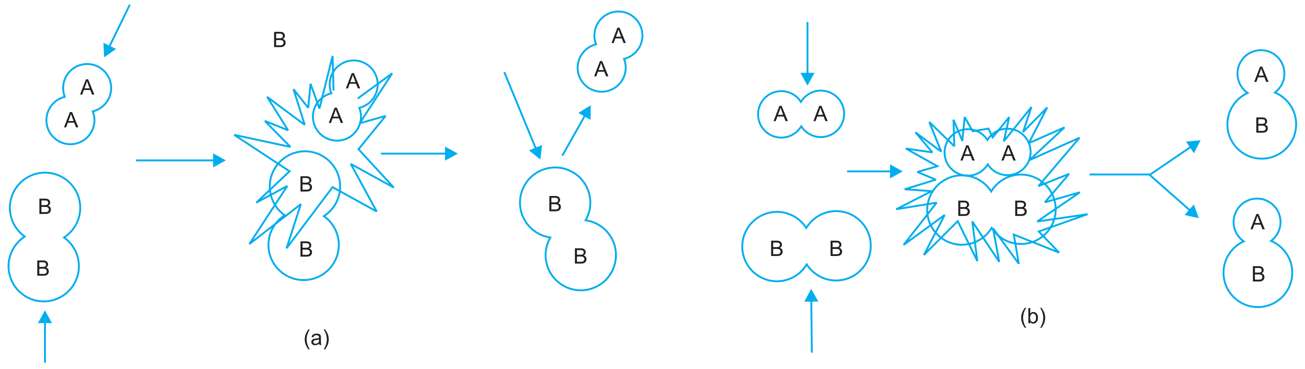


Fig. 7.6: *Importance of proper orientation in the reaction (a) unfavourable collision, (b) favourable collision*

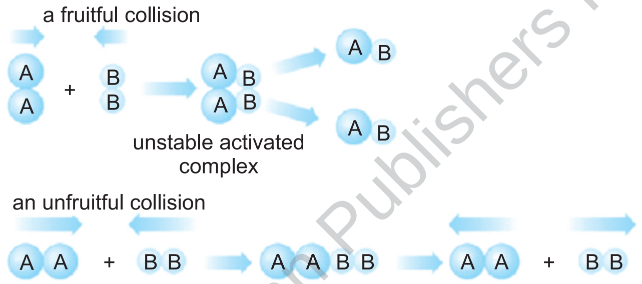
To know the orientation at the time of collision in the calculation of the rate constant, the following expression for the rate of reaction is employed:

$$\textbf{Rate of reaction} = \mathbf{F \times P}$$

where F = Fraction of molecules having energy equal to or more than the threshold energy

P = Number of properly oriented molecules per unit volume (steric factor)

The parameter P can be given values from 1 to 10^{-9}.



Favourable and unfavourable collisions

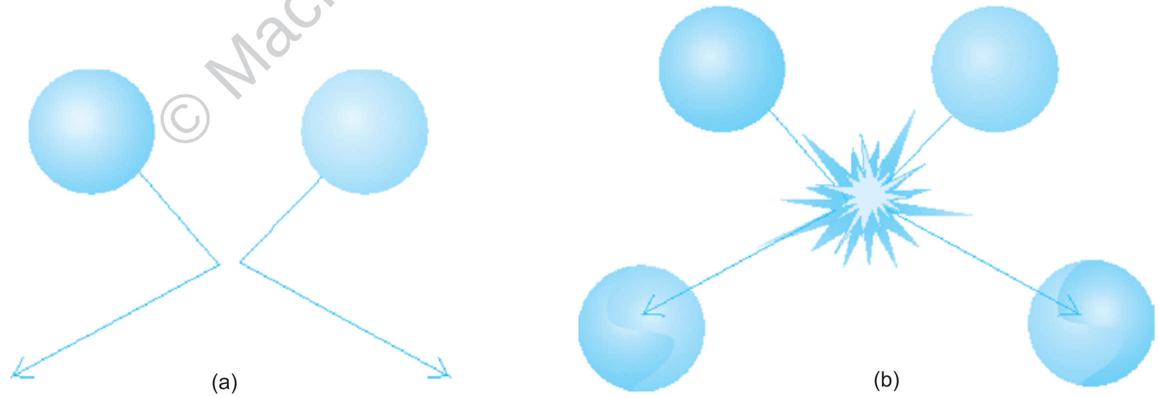


Illustration of Collision theory

Example. *The reaction* $NO_2Cl\ (g) + NO(g) \longrightarrow NO_2\ (g) + NOCl\ (g)$ *is a single step reversible reaction. The energy of activation for forward reaction.* $E_a(f)$ *is 28.9 kJ and that for the backward reaction* $E_a(b)$ *is 41.8 kJ. Draw an energy diagram for the reaction. Indicate* $E_a(f)$ *and* $E_a(b)$ *and* ΔH *for the reaction.*

Solution. The diagram (Fig. 7.7) for the reaction can be drawn as shown below:

$$\Delta H = E_a(f) - E_a(b)$$
$$= 28.9 - 41.8 = -12.0 \text{ kJ}$$

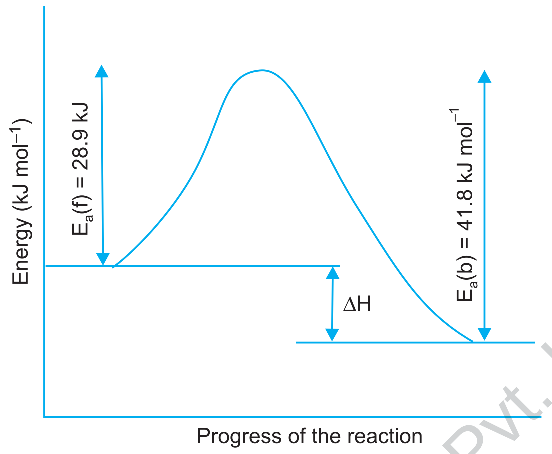


Fig. 7.7: *Progress of the reaction*

PROBLEMS FOR PRACTICE

1. An exothermic reaction X → Y has an activation energy of 51 kJ mol^{-1} of X. The heat of reaction is 107 kJ. Find the activation energy of the reverse reaction Y → X. [**Ans.** 158 kJ]
2. For a reaction X → Y, the heat of reaction is +83.68 kJ, energy of reactant X is 167.36 kJ and the energy of activation is 209.20 kJ. Calculate the (*i*) threshold energy, (*ii*) energy of the product Y, (*iii*) energy of activation for the reverse reaction Y → X. [**Ans.** (*i*) 376.56 kJ, (*ii*) 251.04 kJ, (*iii*) 125.52 kJ]

7.6 RATE LAW

Mathematical expression which gives the relation between the concentration of reactants and the reaction rate is called **Rate Law**. Consider a reaction:

$$aA + bB \longrightarrow \text{Products}$$

We find from our observation that the rate of the reaction may not depend upon all the a molecules of A and all the b molecules of B. Instead, it could depend upon p concentration in terms of A and q concentration in terms of B. Then, the rate of reaction could be given as:

$$\frac{dx}{dt} \propto [A]^p\,[B]^q \text{ and not } [A]^a\,[B]^b$$

$$= k\,[A]^p\,[B]^q \qquad \ldots(i)$$

Here [A] and [B] stand for the active masses of A and B and k is called the **rate constant**.

The equation (*i*) above is called the **rate equation**. It is the expression of the **rate law**. This rate law gives us the actual rate of a reaction in terms of the concentration of the reactants actually involved. As all the molecules of the reactants given by the chemical reaction do not participate in the reaction, the rate of the reaction is bound to be different from what we calculate from the law of mass action which takes into account the number of molecules of the reactants given by the balanced chemical equation.

Points of difference between the rate of reaction and rate constant are given in Table 7.3.

Table 7.3: Differences between Rate of Reaction and Rate Constant

Rate of reaction	Rate constant
1. This stands for the rate of decrease of the concentration of the reactants or rate of increase of concentration of the products with time.	1. It is the rate of reaction when each product of concentration of the reactants is unity.
2. The rate of reaction is dependent upon the concentration of the reactants at that particular moment.	2. Rate constant is independent of the concentration of the reactants. It, however, depends upon the temperature.
3. The units of the rate of reaction are moles litre^{-1} time^{-1}.	3. The units of the rate constant depend upon the order of the reaction.

Consider the reaction: $2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$

The rate of this reaction is found to be proportional to the conc. of N_2O_5.

Rate of the reaction $\propto [N_2O_5]$

or Rate $= k\,[N_2O_5]$,

where $k =$ Rate constant.

This expression is called the **Rate Law**. It gives the relation between the rate and the concentration of the reactants. The rate constant k is independent of the concentration. At a given temperature, it shows a constant value for a particular temperature. For the above reaction at 308 K, the value of k is 1.4×10^{-4} sec^{-1}. However the value of k changes with temperature. At 318 K, it changes to 5.0×10^{-4} sec^{-1}. As has been explained earlier, the rate constant is equal to the rate of the reaction when the concentration of the reactant is unity. Rate constant is, thus, a measure of the *intrinsic rate* of the reaction. In general, we can write:

$$\text{Rate} = k\,[\text{Concentration of the reactant}]$$

7.7 ORDER OF THE REACTION

Consider a general reaction

$$aA + bB + cC \longrightarrow \text{Products}$$

where a moles of the substance A react with b moles of B and c moles of C to give the products. If we study the rate of this reaction, we find that

$$\text{Rate} \propto [A]^p\,[B]^q\,[C]^r \quad \text{or} \quad \text{Rate} = k\,[A]^p\,[B]^q\,[C]^r$$

This shows that the rate of the reaction is proportional to pth power of A, qth power of B and rth power of C. These quantities are called the order of the reaction. Thus, p is the order of the reaction with respect to A, q is the order of reaction w.r.t. B and r is the order of the reaction w.r.t. C.

Total order of reaction $= p + q + r$

Order of a reaction *may be defined as the sum of the powers to which concentration terms must be raised to express the rate of the reaction.*

This is different from the *molecularity of the reaction which is the sum of the coefficients of the reactant molecules as given by the balanced equation*.

Molecularity of the reaction $= a + b + c$

In the reaction $2N_2O_5 \longrightarrow 4NO_2 + \frac{1}{2}O_2$

Rate $= k\,[N_2O_5]$

The power of the concentration term is 1. Therefore, the order of the reaction is one. The order of a reaction can be determined only by performing the experiment. It cannot be judged by the coefficient of reactant molecules given by the balanced equation. Whereas, the molecularity of a reaction can be a whole number, the order can be fractional, zero or positive integer. In order to find the order of a reaction, we must find the order with respect to each reactant. The sum of these values gives the order of the reaction.

Example 1. *Calculate the overall order of a reaction which has the rate expression.*

(*a*) $\text{Rate} = k\,[A]^{\frac{1}{2}}\,[B]^2$

(*b*) $\text{Rate} = k\,[A]^{\frac{3}{2}}\,[B]^{-\frac{1}{2}}$

Solution.

(*a*)
$$\text{Rate} = k\,[\text{A}]^p\,[\text{B}]^q$$
$$\text{Order} = p + q$$
$$\text{So order} = \frac{1}{2} + 2 = 2.5$$

(*b*)
$$\text{Order} = \frac{3}{2} - \frac{1}{2} = 1$$

Example 2. *For the reaction R $\longrightarrow$ P, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.*

Solution.
$$\text{Average rate} = -\frac{\Delta[\text{R}]}{\Delta t} = \frac{[\text{R}]_2 - [\text{R}]_1}{t_2 - t_1}$$
$$= \frac{0.02\text{ M} - 0.03\text{ M}}{25\text{ minutes}} = \frac{-0.01\text{ M}}{25\text{ minutes}}$$
$$= 4 \times 10^{-4}\text{ mol litre}^{-1}\text{ minute}^{-1} \qquad \text{(Ignoring –ve sign)}$$
$$= \frac{-0.01\text{ M}}{25 \times 60\text{ S}} = 6.66 \times 10^{-6}\text{ mol litre second}^{-1} \qquad \text{(Ignoring –ve sign)}$$

Example 3. *The conversion of the molecules X to Y follows second order kinetics. If the concentration of X is increased to three times, how will it affect the formation of Y?*

Solution. For the reaction X $\longrightarrow$ Y, as it follows second order kinetics, the rate law equation can be written as

$$\text{Rate} = k\,[\text{X}]^2 \qquad ...(i)$$

If the concentration of X is increased to three times, then

$$\text{Rate} = k\,[3\text{X}]^2 \quad \text{or} \quad \text{Rate} = 9k\,[\text{X}]^2 \qquad ...(ii)$$

Comparing eq. (*i*) and (*ii*), we can say that the rate of formation of *Y* will increase 9 times.

7.8 MOLECULARITY OF A REACTION

It may be defined as the number of atoms, ions or molecules actually taking part at a particular moment in a single-step chemical reaction.

Unimolecular reaction is a reaction in which the molecularity is one, *i.e.*, one species is taking part in the reaction. For example:

$$N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$$

Bimolecular reaction is a reaction in which two molecules of the reactants are taking part. For example:

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

Trimolecular reaction is a reaction in which three molecules of the reactants are participating. For example:

$$2NO + O_2 \longrightarrow 2NO_2$$

The molecularity of a reaction does not have any meaning for a complex reaction. It is applicable to elementary steps only.

Molecularity of a reaction is always a whole number, whereas the order could be fractional or zero. Main points of difference in order of a reaction and molecularity are given in Table 7.4.

Table 7.4: Differences between Order of a Reaction and Molecularity

Order of a reaction	Molecularity of a reaction
1. It is the sum of the powers to which concentration terms must be raised to express the rate equation.	1. It is the number of atoms or molecules or ions taking part in a single step reaction.
2. It could be in whole number or in fraction or zero.	2. It is always a whole number.
3. It can be obtained only from the experiment.	3. It is obtained by adding up the coefficients of reactants in the reaction.
4. Order of a complex reaction is equal to the order of the slowest step of the reaction.	4. The overall molecularity of a complex reaction has no meaning. It is considered for simple elementary steps.

7.9 PHOTOCHEMICAL REACTIONS

Photo means light and light is a form of energy. There are certain reactions which take place by the absorption of radiations. Such reactions are called **photochemical reactions**. There is a particular wavelength or a range of wavelength which is absorbed by a molecule to give the products. There are some reactions which take place by the absorption of red light (light of lower energy), while there are others which absorb violet light (light of higher energy). There are reactions which take place with the absorption of ultraviolet light of very high energies. One well-known example of photochemical reaction is the combination of hydrogen and chlorine to give hydrochloric acid.

$$H_2(g) + Cl_2(g) \xrightarrow{\text{Sunlight}} 2HCl(g)$$

It is believed that a photochemical reaction involves a number of steps. The above reaction which is believed to take place by free radical mechanism involves three steps.

(*i*) **Chain initiation:** $Cl_2 \xrightarrow{\text{Sunlight}} 2Cl\bullet$

Chlorine molecule is broken into two chlorine radicals with the absorption of light.

(*ii*) **Chain propagation:**

$$Cl\bullet + H_2 \longrightarrow HCl + H\bullet$$

(**Ist step:** Slow step: Rate determining step)

$$H\bullet + Cl_2 \longrightarrow HCl + Cl\bullet$$

More and more molecules of HCl are formed. Alternately hydrogen and chlorine radicals, which are reactive species are formed.

(*iii*) **Chain termination:** $Cl\bullet + Cl\bullet \longrightarrow Cl_2$

The chain is terminated by the combination of two radicals.

Two other famous examples of photochemical reactions are photosynthesis and vision. These are described in some detail below:

Photosynthesis. Carbon dioxide and water react together in the presence of chlorophyll which is present in green plants and sunlight to produce carbohydrates. This reaction is called photosynthesis. In some cases, the molecule absorbs light and transfers its extra energy to another molecule which may undergo reaction. This process is called **photosensitisation**.

$$Chl \xrightarrow{\text{Photon}} Chl^* \qquad \text{(excited chlorophyll molecule)}$$

$$Chl^* + A \longrightarrow Chl^+ + A^- \qquad \text{(1st step of the reaction)}$$

$$A^- + B \longrightarrow A + B^-$$

$$B^- + C \longrightarrow B + C^- + \text{ Energy}$$

Chlorophyll pigment present in the green plants absorbs light and is represented as excited chlorophyll (with a star *). This excited chlorophyll transfers its energy to a nearby molecule A by transferring its electron to it. Energy is released as a result. A in turn gives its electron to B and, thus, transfers its energy to B, and so on. The final photosynthesis reaction is

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

Vision. The phenomenon of vision also involves photochemical reaction. The retina of the eye possesses a light sensitive molecule called **retinal**. This molecule absorbs a photon of light and becomes excited. On absorption of light, it undergoes a geometrical isomerism and stores the extra energy in the form of chemical energy. Then after a very short interval, the retinal converts back into the original geometrical form and the energy released sends a sensory signal to the brain which acknowledges the absorption of light.

7.10 MECHANISM OF A REACTION

How to arrive at it?

A series of step reactions, proposed to account for the overall reaction is called the **mechanism of the reaction**.

The writing of reaction's steps is usually based upon experimental evidences. **Slowest step** (called the *rate determining step) must involve the molecules on which the rate of reaction actually depends as observed experimentally. The slowest step in a reaction is referred to as the* **bottleneck.** *The term 'bottleneck' comes from the area at the top of the bottle that limits the flow of the liquid coming out. It does not matter how big the rest of the bottle is –liquid will only flow out as fast as the size of the neck will allow. Bottleneck creates the limiting factor that prevents greater conversion into products.* The following examples will illustrate the point more clearly:

(*i*) Thermal decomposition of dinitrogen pentaoxide. The balanced equation may be written as

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

However, according to the rate law, it is found that

$$\text{Rate of reaction} = k\,[N_2O_5]$$

Hence, the above reaction must be split into steps in such a way that the slowest step should involve only one molecule of N_2O_5. Thus, the probable mechanism is as follows:

$$N_2O_5 \xrightarrow{\text{Slow}} NO_2 + NO_3$$

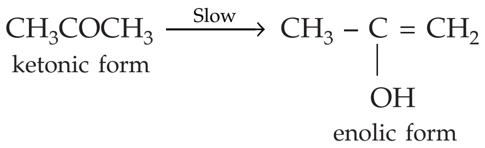
$$N_2O_5 + NO_3 \xrightarrow{\text{Fast}} 3NO_2 + O_2$$

Hence, the above reaction is *unimolecular reaction or a reaction of the first order.*

(*ii*) Bromination of propanone (acetone). The bromination of propanone in dilute aqueous solution is represented by the equation

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr$$

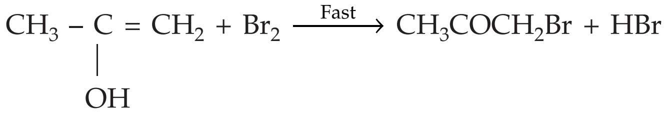
Experimentally, it is found that the Rate of reaction ∝ $[CH_3COCH_3]$ only (and is independent of the concentration of bromine). Hence, the rate determining step (slow step) would involve a molecule of acetone only. The suggested steps are as follows:

(*a*)


$$CH_3COCH_3 \xrightarrow{\text{Slow}} CH_3-\underset{\substack{|\\ OH}}{C}=CH_2$$

ketonic form

enolic form

(*b*)


$$CH_3-\underset{\substack{|\\ OH}}{C}=CH_2 + Br_2 \xrightarrow{\text{Fast}} CH_3COCH_2Br + HBr$$

(*iii*) Combination of NO_2 and F_2 to form NO_2F. The reaction may be represented as

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

Experimentally, it is found that the Rate of reaction = $k\,[NO_2]\,[F_2]$ *i.e.*, the rate law equation involves only one molecule of NO_2 and one molecule of F_2. Hence, the probable mechanism is as follows:

$$NO_2 + F_2 \xrightarrow{\text{Slow}} NO_2F + F$$

$$NO_2 + F \xrightarrow{\text{Fast}} NO_2F$$

Hence, the above reaction must be a *bimolecular reaction* or a *reaction of the second order*.

(*iv*) Oxidation of hydrogen bromide with oxygen. The oxidation of hydrogen bromide with oxygen in the temperature range 400°C – 600°C takes place rapidly as follows:

$$4HBr(g) + O_2(g) \longrightarrow 2H_2O(g) + 2Br_2(g)$$

Experimentally, it is found that the Rate of reaction $\propto$ [HBr] [O_2]

This implies that the slowest step of the mechanism of the above reaction should involve only one molecule of HBr and one molecule of O_2. Hence, the probable mechanism is as follows:

$$HBr + O_2 \xrightarrow{\text{Slow}} HOOBr$$

$$HOOBr + HBr \xrightarrow{\text{Fast}} 2HOBr$$

$$HOBr + HBr \xrightarrow{\text{Fast}} H_2O + Br_2\,] \times 2$$

$$\text{Overall reaction: } 4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

(*v*) Reduction of nitric oxide with hydrogen. The reaction is

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

The rate law equation is found to be

$$\text{Rate}\left(\frac{dx}{dt}\right) = k\,[NO]^2\,[H_2]$$

This suggests that the reaction is of the third-order and the rate determining step (slow step) should involve two molecules of NO and one molecule of H_2. Thus, the following mechanism has been proposed:

$$2NO + H_2 \xrightarrow{\text{Slow}} N_2 + H_2O_2$$

$$H_2O_2 + H_2 \xrightarrow{\text{Fast}} 2H_2O$$

Example 1. *Nitric oxide NO reacts with oxygen to produce NO_2:*

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

What is the predicted rate law, if the mechanism is

$$NO + O_2 \overset{k}{\rightleftharpoons} NO_3 \qquad (\textit{Fast})$$

$$NO_3 + NO \overset{k}{\rightleftharpoons} NO_2 + NO_2 \qquad (\textit{Slow})$$

Solution. From the slow step,

$$\text{Rate} = k_1\,[NO_3]\,[NO] \qquad ...(i)$$

From the fast step, equilibrium constant

$$k = \frac{[NO_3]}{[NO][O_2]} \qquad ...(ii)$$

Substituting the value of [NO_3] from (*ii*) in (*i*), we get

$$\text{Rate} = k'\,[NO]^2\,[O_2].$$

Example 2. *The rate law for the reaction* $2NO_2 + F \longrightarrow 2NO_2F$ *is given by* $-\dfrac{dx}{dt} = k\,[NO_2]\,[F_2]$. *Suggest a mechanism of the reaction.*

Solution. The rate of the reaction varies with the concentration of NO_2 and F_2 both raised to power one. This means all molecules each of NO_2 and F_2 are involved in the slow step. The proposed mechanism is

$$\begin{array}{lll} NO_2 + F_2 \longrightarrow NO_2F + F & & \text{(Slow step)} \\ F + NO_2 \longrightarrow NO_2F & & \text{(Fast step)} \\ \hline 2NO_2 + F_2 \longrightarrow 2NO_2F & & \text{(Overall reaction)} \\ \hline \end{array}$$

7.11 CATALYSIS

Catalysis. *A catalyst is a substance that changes (usually increases) the rate of a reaction but is recovered chemically unchanged at the end of the reaction and the phenomenon is called* **catalysis**.

Positive Catalyst. *If a catalyst increases the rate of a reaction, it is called a* **positive catalyst** *and the phenomenon is called positive catalysis.* A few examples of positive catalysis are given below:

(*i*) **Decomposition of potassium chlorate in presence of MnO_2 as catalyst.**

$$2KClO_3(s) \xrightarrow{MnO_2(s)} 2KCl(s) + 3O_2(g)$$

(*ii*) **Oxidation of SO_2 to SO_3 using NO as catalyst.**

$$SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{NO_2(g)} SO_3(g)$$

(*iii*) **Manufacture of ammonia by Haber process using finely divided iron as catalyst.**

$$N_2(g) + 3H_2(g) \xrightarrow{Fe} 2NH_3(g)$$

Negative Catalyst. *If a catalyst decreases the rate of a reaction, it is called a* **negative catalyst** *and the phenomenon is called negative catalysis.* A few examples of negative catalysis are given below:

(*i*) **Oxidation of chloroform is retarded in the presence of a small quantity of ethyl alcohol.**

$$\underset{\text{Chloroform}}{2CHCl_3} + O_2 \longrightarrow \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

(*ii*) **Decomposition of H_2O_2 is retarded in the presence of traces of acetanilide.**

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

Function of a Catalyst

A catalyst decreases the activation energy of the reactants. It lowers the energy barrier and thus makes the reaction fast as shown in Fig. 7.8. However in a reversible reaction the catalyst decreases the activation energy of the forward reaction as well as that of the backward reaction by the same amount. Thus, both the forward and the backward reactions are accelerated to the same extent. As a result, the equilibrium is attained quickly but does not change position.

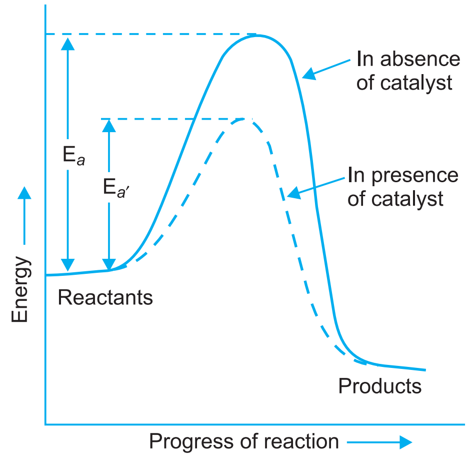


Fig. 7.8: *Activation energy diagram for uncatalysed and catalysed reactions*

7.11.1 Homogeneous Catalysis

When in a reaction the catalyst is present in the same phase as the reactants, it is called **homogeneous catalysis**.

Examples of homogeneous catalysis are given below:

A. Gaseous Phase

(*a*) Decomposition of acetaldehyde in the presence of iodine vapours.

$$CH_3CHO(g) \xrightarrow{I_2(g)} CH_4(g) + CO(g)$$

(*b*) Decomposition of ozone in presence of NO or N_2O_5.

$$2O_3(g) \xrightarrow{NO(g)} 3O_2(g)$$

(*c*) Reaction between SO_2 and O_2 to form SO_3 in the presence of nitric oxide (NO).

$$2SO_2(g) + O \xrightarrow{NO(g)} 2SO_3(g)$$

(*d*) Decomposition of vapours of N_2O at 1000 K in the presence of traces of chlorine gas.

$$2N_2O(g) \xrightarrow[1000\text{ K}]{Cl_2(g)} 2N_2(g) + O_2(g)$$

B. Liquid Phase

(*a*) Acid-Base Catalysis

(*i*) Hydrolysis of methyl acetate by an acid or a base.

$$CH_3COOCH_3(aq) + H_2O(l) \xrightarrow[OH^-(aq)]{H^+(aq)} CH_3COOH(aq) + CH_3OH(aq)$$

(*ii*) Decomposition of H_2O_2 in the presence of I^- ion or Br_2.

$$2H_2O_2(aq) \xrightarrow[\text{or } Br_2]{I^-(aq)} 2H_2O(l) + O_2(g)$$

(*iii*) Hydrolysis of cane-sugar (sucrose) in the presence of a mineral acid. (Inversion of cane-sugar).

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H^+(aq)} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

(*iv*) Hydrolysis of starch to glucose in presence of an acid.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2 \xrightarrow{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

Mechanism of Homogeneous Catalytic Reactions (Intermediate Compound Formation Theory)

A homogeneous catalytic reaction usually takes place in two steps as follows:

1st step: The catalyst reacts with the reactant to form an intermediate complex

$$A + C \longrightarrow AC$$

2nd step: The complex then decomposes to form the product regenerating the catalyst or reacts with a second reactant to give the product and regenerating the catalyst, *i.e.*,

$$AC \longrightarrow \text{Product} + C$$

or $$AC + B \longrightarrow \text{Product} + C$$

This is illustrated with examples given below:

(1) Mechanism of the reaction

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

1st step: $H_2O_2 + I^- \longrightarrow H_2O + IO^-$

2nd step: $H_2O_2 + IO^- \longrightarrow H_2O + O_2 + I^-$

In this reaction I^- acts as catalyst.

(2) Mechanism of the reaction

$$2SO_2 + O_2 \xrightarrow{NO} 2SO_3$$

1st step: $2NO + O_2 \longrightarrow 2NO_2$

2nd step: $2NO_2 + 2SO_2 \longrightarrow 2NO + 2SO_3$

Both the above steps are fast. Hence, the overall reaction is also fast whereas in the absence of catalyst the reaction is slow.

(3) Mechanism of the reaction

$$2N_2O \xrightarrow{Cl_2} 2N_2 + O_2$$

1st step: $Cl_2 \xrightarrow{1000\text{ K}} 2Cl$

2nd step: $N_2O + Cl \longrightarrow N_2 + ClO$

3rd step: $2ClO \longrightarrow Cl_2 + O_2$

(4) Mechanism of the reaction

$$CH_3CHO \xrightarrow{I_2} CH_4 + CO$$

Ist step: $CH_3CHO + I_2 \longrightarrow CH_3I + HI + CO$

2nd step: $CH_3I + HI \longrightarrow CH_4 + I_2$

(5) Mechanism of the reaction

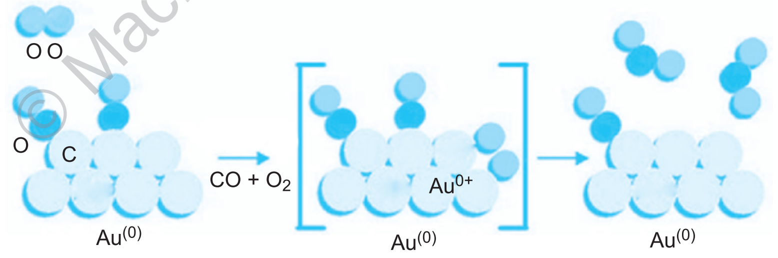
$$2O_3 \xrightarrow{N_2O_5} 3O_2$$

1st step: $2N_2O_5 \longrightarrow 2N_2O_4 + O_2$

2nd step: $O_3 + N_2O_4 \longrightarrow O_2 + N_2O_5$

7.11.2 Heterogeneous Catalysis

If the catalyst is present in a different phase from that of the reactants in a reaction, it is called **heterogeneous catalyst**. The catalysts are usually solids whereas the reactants are gaseous or liquid. The reactions occur at the surface of the catalyst. That is why this type of catalysis is also called as **surface catalysis** or **contact catalysis**. Evidently, greater the surface area of the catalyst, greater is the efficiency of the catalyst. For this reason, finely divided solids are usually used as heterogeneous catalysts.



The reaction $CO + O_2 \longrightarrow CO_2$ is catalysed by gold catalyst

Examples of Heterogeneous Catalytic Reactions

(*i*) **Manufacture of methyl alcohol from CO and H_2 using ZnO and Cr_2O_3 as catalysts.**

$$CO(g) + 2H_2(g) \xrightarrow{ZnO/Cr_2O_3} CH_3OH(g)$$

(*ii*) **Manufacture of ammonia from nitrogen and hydrogen using finely divided iron as a catalyst.**

$$N_2(g) + 3H_2(g) \xrightarrow[\text{divided Fe}]{\text{finely}} 2NH_3(g)$$

(*iii*) Formation of SO_3 from SO_2 and O_2 in contact process, using finely divided platinum or vanadium pentoxide as catalyst for manufacturing sulphuric acid.

$$2SO_2(g) + O_2(g) \xrightarrow[\text{or } V_2O_5]{\text{Pt}} 2SO_3(g)$$

Heterogeneous Catalysis is Surface Catalysis and a Heterogeneous Catalyst is Specific.

(*i*) Consider the bromination of ethylene

$$CH_2 = CH_2(g) + Br_2(g) \longrightarrow BrCH_2 - CH_2Br(g)$$

This reaction takes place readily in a glass vessel at 470 K. It was thought to be an ordinary homogeneous catalytic reaction. However, it was found that the rate is higher in a smaller reaction vessel or in a vessel packed with glass beads but the rate is reduced when the vessel is coated on the inside with paraffin wax. This shows that the reaction is not occurring in the gas phase but is occurring on the glass surface of the vessel. The glass acts as a catalyst.

(*ii*) Consider the decomposition of formic acid. If the acid vapour is passed through a heated glass tube, the reaction is about 50% dehydration and 50% dehydrogenation, *i.e.*,

(*a*) $HCOOH \longrightarrow H_2O + CO$

(*b*) $HCOOH \longrightarrow H_2 + CO_2$

If the tube is packed with Al_2O_3, only reaction (*i*) occurs but if it is packed with ZnO, only reaction (*ii*) occurs. This illustrates specificity of a heterogeneous catalyst.

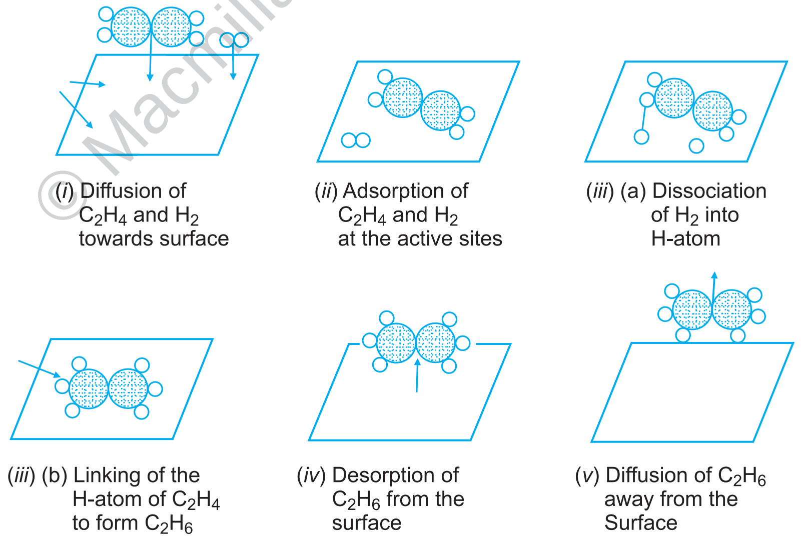
Mechanism of Heterogeneous Catalytic Reactions (Adsorption Theory)

It is believed that a heterogeneous catalytic reaction takes place through the following sequence of steps (See Fig. 7.9).

(*i*) Diffusion of the reactant molecules towards the surface of the catalyst.

(*ii*) Adsorption of the reactant molecules on the surface of the solid.

(*iii*) Chemical reaction of the adsorbed molecules with the surface of the catalyst resulting into stretching and weakening of bonds forming an activated complex with the catalyst which then decomposes or even break the bonds of reactant molecules.



(*i*) Diffusion of C_2H_4 and H_2 towards surface

(*ii*) Adsorption of C_2H_4 and H_2 at the active sites

(*iii*) (a) Dissociation of H_2 into H-atom

(*iii*) (b) Linking of the H-atom of C_2H_4 to form C_2H_6

(*iv*) Desorption of C_2H_6 from the surface

(*v*) Diffusion of C_2H_6 away from the Surface

Fig. 7.9: *Mechanism for the reaction between ethylene and hydrogen on a catalytic surface*

Steps (*ii*) and (*iii*) are jointly called **chemisorption**.

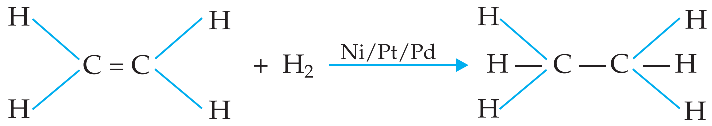
(*iv*) Desorption of the products from the surface.

(*v*) Diffusion of the products away from the surface.

The various steps are illustrated with the following examples:

(*a*) *Hydrogenation of ethylene in presence of finely divided Ni, Pt or Pd.*

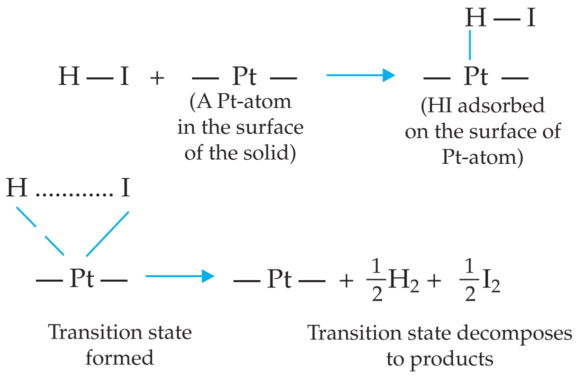
It is illustrated as under:

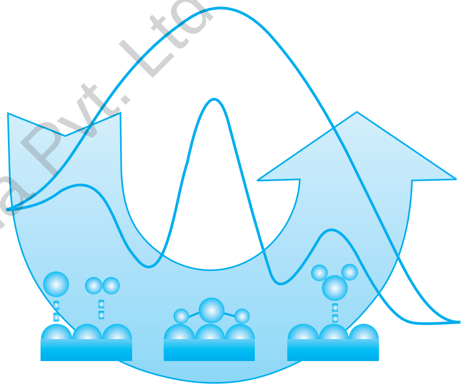


(*b*) *Decomposition of HI in the presence of platinum.*

$$2HI(g) \xrightarrow{Pt} H_2(g) + I_2(g)$$

The mechanism of this reaction may be represented as follows:





Different steps involved in catalysis

Kinetics of Heterogeneous (surface) Catalytic Reactions

A heterogeneous catalytic reaction takes place in a number of consecutive steps. Although any of these steps may be slowest and, hence, rate determining, yet from the point of view of the study of the kinetics of these reactions, the reaction of the adsorbed molecules is considered to be the rate determining. Further, the rate of reaction is supposed to be proportional to the fraction θ of the surface covered by the reactant molecules.

Thus, the two *assumptions* in the study of kinetics of the surface reactions are:

(*i*) The rate determining step of a surface reaction is the reaction of the adsorbed molecules with the surface of the catalyst.

(*ii*) The rate of reaction is proportional to the fraction (θ) of the surface covered by the reactant molecules.

To understand the kinetics of surface reactions, we consider here the simplest case involving only one *gaseous reactant* decomposing on the surface of a solid catalyst according to the reaction.

$$A \longrightarrow \text{Products}$$

Then if θ_A is the fraction of the surface covered by A at any time t when the pressure of the gas is P, then according to assumption (*i*), the rate of reaction would be

$$\text{Rate} = k'\,\theta_A \qquad ...(i)$$

where k' is a proportionality constant.

The fraction θ is related to the pressure of the gas according to the Langmuir equation, *viz.*,

$$\theta = \frac{bP}{1+bP} \qquad ...(ii)$$

where b is a constant.

Substituting this value in equation (*i*), we get

$$\text{Rate} = -\frac{bP}{bt} = k'\frac{bP}{1+bP} \qquad ...(iii)$$

7.12 CHARACTERISTICS OF CATALYSTS

7.12.1 Catalytic Behaviour in Terms of Maxwell Boltzmann Distribution of Energies

It has been mentioned earlier, a catalyst changes the reaction pathway corresponding to a lower activation energy to complete the reaction. The progress of the reaction depends upon the proportion of molecules having energy greater than a specific value typical of each reaction.

If you consider the K.E. distribution curve (Fig. 7.10) at a fixed temperature, area A_1 shows the molecules that have sufficient K.E. to react and overcome the activation energy E_{a_1} for the uncatalysed reaction.

However, in the presence of a catalyst, the lower activation energy E_{a_2} allows a much greater proportion of molecules to have enough energy to react at the same temperature. In this case, the areas A_1 + A_2 represent the number of molecules having sufficient energy to react. This explains the action of the catalyst to accelerate the reaction.

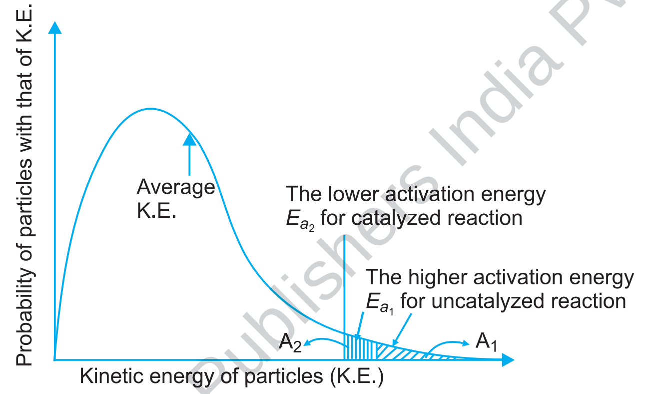


Fig. 7.10: *Maxwell-Boltzmann energy distribution diagram*

Catalysts remain unchanged qualitatively and quantitatively.

Catalysts are regenerated without any change after performing their function and after the completion of the reaction.

For example, Ni is used in the hydrogenation of oils into fats

$$\text{Oil} + \text{H} \xrightarrow{\text{Ni}} \text{Fats}$$

The nickel powder is recovered unchanged in quality and quantity after the process is completed.

Quantity Ratio

There is an optimal ratio of the catalyst/reactants at which maximum conversion of the reactants to the products takes place. We should not expect greater conversion of reactants into the products simply by enhancing the quantity of the catalyst. We should restrict ourselves to the quantity ratio, which is specific for a reaction, to obtain optimal results. However, if the quantity ratio of catalyst/reactants is lower than the optimal ratio, we obtain poor yields of the products.

Action of Promoters and Inhibitors (Poisons)

Promoters *are the substances that enhance the activity of the catalysts.* They are, in fact, catalysts for the catalysts. They may not act alone as catalyst for the same reaction or may act only as feeble catalysts. A well known example is the manufacture of NH_3 from N_2 and H_2 by Haber's process in which iron is used as a catalyst and potassium or vanadium as promoter.

$$N_2(g) + 3H_2(g) \xrightarrow[\text{K or V (Promoter)}]{\text{Fe (Catalyst)}} 2NH_3(g)$$

The action of promoters is explained on the basis that the lattice defects or the irregularities on the surface of the catalyst are the active sites for catalysis. The addition of a promoter encourages the formation of lattice defects and, hence, the active sites. Consequently, the activity of the catalyst is enhanced.

Inhibitors (poisons) *are the substances that inhibit the activity of the catalysts.* A few examples are given below:

(*i*) Oxidation of SO_2 to SO_3 by oxygen in the presence of platinum as catalyst is slowed down if arsenic is present.

(*ii*) Hydrogenation of ethylene in the presence of copper is slowed down if CO is present.

The action of inhibitors is explained in different ways as follows:

(*a*) The catalytic poison may have a strong preferential adsorption on the surface of the catalyst. Thus, the entire surface of the catalyst may be covered with the catalytic poison and no adsorption of the reactants may take place on the catalytic surface. Example (*ii*) above is a case of this type.

(*b*) The catalytic poison may react chemically with the catalytic surface and form a new surface which may be catalytically inert. For example, the catalytic poison arsenic reacts with platinum to form platinum arsenide at the surface.

The fact that a very small amount of the poison is sufficient to stop the activity of the catalyst completely suggests that the surface of a catalyst is irregular with high catalytic activity only at certain spots on the catalytic surface. As soon as these spots are covered with the poison, the activity of the surfaces reduces to zero.

Specificity of the Catalyst

A striking feature of a catalyst is that it can catalyse only a particular specific reaction. For example, to obtain ammonia from a mixture of hydrogen and nitrogen, we use finely divided Fe as a catalyst. Similarly to obtain methanol from a mixture of CO and H_2, we use ZnO/Cr_2O_3 as a catalyst. We cannot interchange the catalysts for the two processes. Thus there is a specific catalyst for a particular reaction.

Surface Area of the Catalyst

Surface area is an important parameter of a catalyst. Greater the surface area, greater is the performance of the catalyst. This is because as per the theory of catalysis (heterogeneous catalysis) the reactant molecules get adsorbed on the active sites of the catalyst, resulting in increase in their concentration on the surface compared to that in the bulk. Increase in concentration of the reactants on the surface results into the products. Obviously, greater the surface area, greater the concentration of the reactants per unit mass of the catalyst and hence faster the reaction.

Enzyme Catalysis

Enzymes are protein molecules present in the living systems. Their molecular weights range from $10^4 - 10^6$ g/mol. They are highly efficient biological catalysts which catalyse the reactions taking place in the living cells and also help in controlling their reaction rates.

The reaction in enzyme catalysis occurs at a specific site on the protein molecule. This is called the **active site**. The reactants in an enzyme reaction are referred to as **substrates**.

A few examples of enzyme-catalysed laboratory reactions are given below:

(*i*) Cane sugar $\xrightarrow[+H_2O]{\text{Invertase}}$ Invert sugar $\xrightarrow{\text{Zymase}}$ Alcohol + CO_2
(Glucose + Fructose)

(*ii*) Starch $\xrightarrow{\text{Diastase}}$ Maltose $\xrightarrow{\text{Maltase}}$ Glucose $\xrightarrow{\text{Zymase}}$ Alcohol + CO_2

The names of the enzymes are written on the arrows.

Enzymes possess certain characteristics which are different from other types of catalysts. A few of these are briefly described below:

(*a*) **Their efficiency is very high,** *i.e.*, many of them are so powerful catalysts that they increase the rate of reaction by many orders of magnitude even at quite low concentrations.

(*b*) **They are highly specific in their catalytic action.** For example, urease even in very low concentration catalyses the hydrolysis of urea but it has no detectable effect on the hydrolysis rate of substituted urea such as methyl urea. There are many such examples to quote. However, there are some exception to this generalization.

(*c*) **They are highly sensitive to temperature.** The activity of the enzyme is usually found to be maximum at the normal temperature of the organism in which the enzyme is found. Above this temperature, usually the activity is first found to increase temporarily and then drops to zero when the protein is denatured.

(*d*) **They are highly sensitive to the acidity or basicity of the solution.** It is found that the enzymes show a sharp change in activity if the pH of the solution is changed.

Ziegler-Natta Catalyst

A Ziegler-Natta catalyst named after the scientists Karl Ziegler and Giulis Natta is a catalyst used in the production of polyethene. Ziegler-Natta catalysts are used to polymerise terminal 1-alkenes (ethylene and alkenes with vinyl double bonds) as per the following reaction

$$nCH_2 = CHR \longrightarrow -[CH_2 - CHR]_n-$$

Ziegler-Natta catalysts are usually $TiCl_3$ or $TiCl_4$ along with an aluminium based co-catalyst (alkyl derivative of Al).

QUICK SCAN (FOR REVISION)

1. **Chemical kinetics** is that branch of chemistry which deals with the rate of chemical reactions, mechanisms and factors which influence the rate of reactions.
2. **Instantaneous rate** of a reaction may be defined as the rate of change of concentration of any one of the reactants or products over a very small interval of time.
3. The reaction between $AgNO_3$ and NaCl or $BaCl_2$ and H_2SO_4 is very fast because the ions are already present in the solution but dissociation of PCl_5, H_2O_2, etc., is slow because it involves **breaking** of **old** and **making** of new covalent bonds.
4. The rate of a reaction does not remain constant throughout. It **decreases** as the reaction proceeds because concentration of **reactant decreases**.
5. **Units** of the **rate of reaction do not depend** upon the **nature of reaction** or **order of reaction**. They are expressed as moles L^{-1} $time^{-1}$ or atm $time^{-1}$.
6. For the reaction $aA + bB \longrightarrow xX + yY$

$$\text{Rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$

$$= +\frac{1}{x}\frac{d[X]}{dt} = +\frac{1}{y}\frac{d[Y]}{dt}$$

$$\text{Rate of disappearance of A} = -\frac{d[A]}{dt}$$

$$\text{Rate of formation of X} = +\frac{d[X]}{dt}$$

They are not divided by their coefficients.

7. **Reaction life time** is the time taken by a reaction to proceed to a definite stage say 98% completion.
8. Different reactions have different rates because their activation energies are different. **Smaller the activation energy faster is the reaction**.
9. For the reaction $aA + bB \longrightarrow$ Products, Rate of reaction $= k\,[A]^\alpha\,[B]^\beta$, where α and β are found experimentally and k is called **rate constant** or **specific reaction rate**. This is called **Rate Law**. $\alpha + \beta$ is called '**order of reaction**'. According to Law of Mass Action, Rate $= k\,[A]^a\,[B]^b$.
10. **The rate constant** of a reaction depends only on the nature of the reactants and temperature. It does not depend upon concentration of the reactants.

11. Various steps involved in a reaction constitute the **mechanism** of the reaction.

12. Rate of reaction and, hence, order of the reaction depends upon the **slowest step,** e.g., for the reaction

    $2NO_2 + F_2 \longrightarrow 2NO_2F$, the reaction takes place in two steps, as under:

    (*i*) $NO_2 + F \xrightarrow{\text{Slow}} NO_2F + F$

    (*ii*) $NO_2 + F \xrightarrow{\text{Fast}} NO_2F$, from (*i*), order = 2.

13. **Proper orientation** of the reacting molecules at the time of collision also determines the rate of reaction.

14. The fraction of molecules having energy greater than E at temp. T is $x = e^{-Ea/RT}$ (from kinetic theory).

15. **For every 10° rise in temp.,** the rate of reaction becomes nearly **double**. This is because number of molecules with energy greater than threshold value becomes nearly double.

16. For a reaction for which $E_a = 0$, there will be no effect of temperature on the rate constant.

17. A photochemical reaction which takes place in the presence of violet light may not take place in the presence of other coloured radiations of visible light because violet light has maximum energy.

18. Quantum efficiency of the photochemical reaction: $H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$, is very high while that of $H_2 + Br_2 \xrightarrow{h\upsilon} 2HBr$, is very low. This is because after the chain initiating step ($X_2 \xrightarrow{h\upsilon} 2\dot{X}$), $\dot{Cl} + H_2 \longrightarrow HCl + \dot{H}$ is **exothermic** while $\dot{Br} + H_2 \longrightarrow HBr + \dot{H}$ is **endothermic**.

19. **Photosynthesis** of carbohydrates in plants is a fast photochemical reaction.

20. The reaction taking place in our eyes which helps us to see is a fast photochemical reaction involving geometrical isomerisation of the compound, **retinal**, present in the eye.

21. **Catalyst** is a substance which can change the speed of a chemical reaction without being consumed in the reaction.

22. When the catalyst and the reactants are in the same phase, it is a case of **homogeneous** catalysis.

23. When the catalyst and reactants are in different phases, it is a case of **heterogeneous** catalysis.

EXERCISES

Very Short Answer Type Questions

1. For the straight reaction:

   $$X_2(g) + 2Y_2(g) \longrightarrow 2XY_2(g),$$

   write the rate equation in terms of disappearance of Y_2.
2. Give one example of a reaction where order and molecularity are equal.
3. How does the catalyst work?
4. What is meant by activity of a catalyst?

Short Answer Type Questions

1. What are photochemical reactions? Discuss the mechanism of the reaction:

   $$H_2 + Cl \xrightarrow{\text{Sunlight}} 2HCl$$

2. Define photochemical reaction and photosensitisation. Give one example in each case to support your answer.
3. What reactions take place in the retina of the eye which help us in seeing?
4. Define the following:

   (*i*) Order of a reaction

   (*ii*) Molecularity of a reaction

   (*iii*) Rate law

   (*iv*) Law of mass action.
5. What do you understand by 'Rate of reaction'?
6. For a reaction $A \longrightarrow B$, the rate of reaction can be denoted by $-\frac{dA}{dt}$ or $+\frac{dB}{dt}$. State the significance of plus and minus signs in this case.
7. Define the term 'Chemical Kinetics'.
8. What is meant by reaction rate? Give its symbolic expression and units for the reaction

   $CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$
9. Write a note on factors influencing reaction rate.
10. How does average rate of reaction differ from instantaneous reaction rate?
11. For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, express the rate of reaction in terms of $-d[N_2]/dt$, $-d[H_2]/dt$ and $d[NH_3]/dt$.
12. List the factors affecting the rate of reaction.

13. Explain the effect of:
    (*a*) concentration of the reactants,
    (*b*) presence of a catalyst on the rate of a chemical reaction.
14. Express the relationship between the rate of production of HCl and the rate of disappearance of H_2 in the following reaction:

$$H_2 + Cl \longrightarrow 2HCl$$

15. Explain the rate of the following reaction

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

using (*a*) concentration change of N_2O_5,
(*b*) concentration change of O_2.
16. Explain with suitable example, how the molecularity of a reaction is different from the order of a reaction.
17. Define the term 'Rate constant' or 'Specific reaction rate'.
18. Comment on the statement that molecularity of the slowest step in a reaction gives the overall molecularity of the reaction.
19. What is meant by the rate controlling step in a reaction?
20. How do you differentiate between reaction rate and reaction rate constant?
21. Define the terms "order of reaction and rate constant".
22. Give any four points of difference between molecularity and order of a reaction.
23. Show graphically how the rate of a reaction depends upon the concentration of the reactant when there is only one reactant.
24. The reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$ is feasible. How is that hydrogen and oxygen mixture allowed to stand at room temperature shows no formation of water at all?
    [**Hint:** The reaction has a high activation energy at room temp.]
25. What are unimolecular reactions? Give two examples.
26. What are photochemical reactions? Give two examples.
27. Explain why photochemical reactions which can take place with red light can take place with blue light also but the reverse is not true.
28. Give four examples of heterogeneous catalysis.
29. Write short notes on:
    (*i*) Homogeneous catalysis.
    (*ii*) Heterogeneous catalysis.
30. Differentiate between homogeneous and heterogeneous catalysis with one example of each.
31. What do you mean by activity and selectivity of catalysts?
32. What is a catalyst? How does the phenomenon of adsorption explain the role played by a catalyst?
33. State the role of activated complex in a reaction and state its relation with activation energy.
34. Give a short note on Ziegler-Natta catalyst.

Long Answer Type Questions

1. What is meant by the rate of a reaction? How is the rate of a reaction determined?
2. What do you understand by the order of a reaction? Describe any one method for the determination of order of a reaction.
3. Write short notes on:
    (*i*) Fast reactions.
    (*ii*) Photochemical reactions.
4. Differentiate between:
    (*i*) Rate of a reaction and rate constant of a reaction.
    (*ii*) Order of a reaction and its molecularity.
5. What is the difference between homogeneous and heterogeneous catalysis? Illustrate with examples.
6. How does the catalyst speed up the rate of a reaction? Explain with the help of intermediate compound formation theory.

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. Rate = $\dfrac{dy_2}{dt} = k\,[y_2]$
2. Order and molecularity are same in a single step reaction. Example of such a reaction is

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)$$

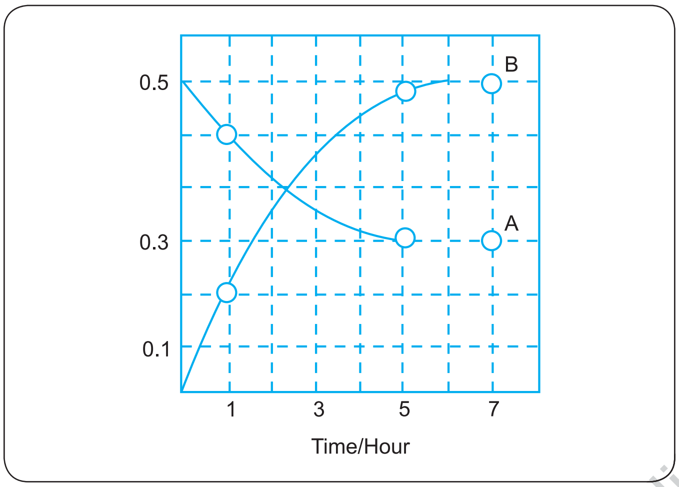
3. It provides an alternate path with lower activation energy for the reaction.
4. Ability of a catalyst to accelerate chemical reactions is called its activity.

NUMERICAL PROBLEMS

1. The progress of the reaction $A \rightleftharpoons nB$ with time is presented in the figure below:

   Determine:
   (*i*) the value of *n*.
   (*ii*) the equilibrium constant K, and
   (*iii*) the initial rate of conversion of A.

   [**Ans.** 0.1 mol L^{-1} hr^{-1}]



2. The following data is for the reaction between A and B:

[A], mol lit^{-1}	*[B], mol lit^{-1}*	*Initial rate, mol lit^{-1} s^{-1} at*	
		300 K	*320 K*
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	—
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	—

   Determine:
   (*i*) the rate constant at 300 K.
   (*ii*) the pre-exponential factor.

   [**Ans.** (*i*) 2.67×10^{8}; (*ii*) 1.107×10^{18}]

3. For the reaction,

$$A + B \longrightarrow \text{Products}$$

   the following initial rates were obtained at various given initial concentrations.

S. No.	*[A]*	*[B]*	*Rate (mol L^{-1} sec^{-1})*
1	0.1	0.1	0.05
2.	0.2	0.1	0.10
3.	0.1	0.2	0.05

   Write rate law and find the rate constant of the above reaction.

HINTS AND SOLUTIONS TO ABOVE PROBLEMS

1. (*i*) From time $t = 1$ hour to $t = 5$ hour, $\Delta t = 4$ hr

   Decrease in conc. of A $= 0.5 - 0.3 = 0.2$ mol L^{-1}.

   Increase in conc. of B $= 0.6 - 0.2 = 0.4$ mol L^{-1}.

   Thus, in the same time interval, increase in conc. of B is double the decrease in the conc. of A. Hence, $n = 2$.

   (*ii*) At equilibrium, there is no further change in conc. Hence, concentrations at equilibrium are:

$$[A] = 0.3 \text{ mol L}^{-1} \text{ and } [B] = 0.6 \text{ mol L}^{-1}$$

$$\therefore \text{ Equilibrium const. } K = \frac{[B]^2}{[A]} = \frac{[0.6]^2}{[0.3]} = 1.2$$

   (*iii*) From $t = 0$ to $t = 1$ hour, for A,

$$\Delta x = 0.6 - 0.5 = 0.1 \text{ mol L}^{-1}$$

   ∴ Initial rate of conversion of A

$$= \frac{\Delta x}{\Delta t} = \frac{0.1\text{mol L}^{\ 1}}{1 \text{ hr}} = 0.1 \text{ mol L}^{-1} \text{ hr}^{-1}.$$

2. (*i*) Rate law equation is

$$\text{Rate} = k\,[A]^2\,[B] \quad \text{or} \quad k = \frac{\text{Rate}}{[A]^2\,[B]}$$

   At 300 K,
   From expt. 1,

$$k = \frac{5 \times 10^{-4}}{(2.5 \times 10^{-4})^2 \times (3.0 \times 10^{-5})}$$
$$= 2.67 \times 10^{8}$$

   From expt. 2,

$$k = \frac{4 \times 10^{-3}}{(5 \times 10^{-4})^2 \times (6 \times 10^{-5})}$$
$$= 2.67 \times 10^{8}$$

   From expt. 3,

$$k = \frac{1.6 \times 10^{-2}}{(1 \times 10^{-3})^2 \times (6 \times 10^{-5})}$$
$$= 2.67 \times 10^{8}$$

(*ii*) Applying Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303\ RT}$$

or $$\log A = \log k + \frac{E_a}{2.303\ RT}$$

$$= \log(2.67 \times 10^8) + \frac{55.34}{2.303 \times 0.008314 \times 300}$$

$$= 8.4099 + 9.6342 = 18.0441$$

$$A = \text{Antilog } 18.0441 = 1.107 \times 10^{18}.$$

3. From the given data it is evident that the reaction is of first order with respect to reactant A and is of zero order with respect to reactant B. Therefore, the rate law of the reaction is

$$-\frac{dc}{dt} = k[A]^1 [B]^0 = k[A]$$

On putting the value of concentration of reactant A and rate of reaction from set of data first (S. No. –1), we get

$$\text{Rate constant, } k = \frac{0.05}{0.1} = 5 \times 10^{-1}\ s^{-1}$$

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. The rate constant for the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, is $3.0 \times 10^{-5}\ s^{-1}$. If the rate is 2.40×10^{-5} mol $L^{-1}\ s^{-1}$, then the concentration of N_2O_5 (in mol L^{-1}) is:

   (*a*) 1.4 (*b*) 1.2

   (*c*) 0.04 (*d*) 0.8

2. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process $AB + h\nu \rightarrow AB^*$, the rate of formation of AB* is directly proportional to:

   (*a*) C (*b*) I

   (*c*) I^2 (*d*) C.I.

3. Consider the chemical reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. The rate of this reaction can be expressed in terms of time derivative of concentration of $N_2(g)$, $H_2(g)$ or $NH_3(g)$. Identify the correct relationship amongst the rate expressions.

   (*a*) Rate $= -d[N_2]/dt = -1/3\ d[H_2]/dt = 1/2\ d[NH_3]/dt$

   (*b*) Rate $= -d[N_2]/dt = -3\ d[H_2]/dt = 2\ d[NH_3]/dt$

   (*c*) Rate $= d[N_2]/dt = 1/3\ d[H_2]/dt = 1/2\ d[NH_3]/dt$

   (*d*) Rate $= -d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

4. Identify the correct statement regarding enzymes:

   (*a*) Enzymes are specific biological catalysts that can normally function at very high temperatures (T ~ 1000 K).

   (*b*) Enzymes are normally heterogeneous catalysts that are very specific in their action.

   (*c*) Enzymes are specific biological catalysts that cannot be poisoned.

   (*d*) Enzymes are specific biological catalysts that possess well-defined active sites.

5. For the reaction, $2A + B \rightarrow 3C + D$, which of the following does not express the reaction rate?

   (*a*) $-\frac{d[A]}{2dt}$ (*b*) $-\frac{d[C]}{3dt}$

   (*c*) $-\frac{d[B]}{dt}$ (*d*) $\frac{d[D]}{dt}$

6. Consider the reaction; $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

   The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is

   (*a*) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$

   (*b*) $\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$

   (*c*) $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

   (*d*) $+\frac{d[NH_3]}{dt} = -\frac{3}{2}\frac{d[H_2]}{dt}$

7. For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$, if $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol $L^{-1}\ s^{-1}$, the value of $\frac{-d[H_2]}{dt}$ would be

   (*a*) 4×10^{-4} mol $L^{-1}\ s^{-1}$ (*b*) 6×10^{-4} mol $L^{-1}\ s^{-1}$

   (*c*) 1×10^{-4} mol $L^{-1}s^{-1}$ (*d*) 3×10^{-4} mol $L^{-1}s^{-1}$

8. In the reaction

   $BrO_3^-(aq) + 5Br^-(aq) + 6H^+ \rightarrow 3Br_2(l) + 3H_2O(l)$

   The rate of appearance of bromine (Br_2) is related to the rate of disappearance of bromide ions as

   (*a*) $\frac{d[Br_2]}{dt} = -\frac{5}{3}\frac{d[Br^-]}{dt}$ (*b*) $\frac{d[Br_2]}{dt} = \frac{5}{3}\frac{d[Br^-]}{dt}$

   (*c*) $\frac{d[Br_2]}{dt} = \frac{3}{5}\frac{d[Br^-]}{dt}$ (*d*) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

9. For the reaction A + B $\longrightarrow$ products, it is observed that

   (*i*) on doubling the initial concentration of A only, the rate of reaction is also doubled and

   (*ii*) on doubling the initial concentration of both A and B, there is a change by a factor of 8 in the rate of the reaction.

   The rate of this reaction is given by

   (*a*) rate = $k[A][B]^2$ (*b*) rate = $k[A]^2[B]^2$

   (*c*) rate = $k[A][B]$ (*d*) rate = $k[A]^2[B]$

10. During the kinetic study of the reaction, $2A + B \rightarrow C + D$, following results were obtained.

Run	*[A]/mol L^{-1}*	*[B]/mol L^{-1}*	*Initial rate of formation of D/mol L^{-1} min^{-1}*
I.	0.1	0.1	6.0×10^{-3}
II.	0.3	0.2	7.2×10^{-2}
III.	0.3	0.4	2.88×10^{-1}
IV.	0.4	0.1	2.40×10^{-2}

   Based on the above data which one of the following is correct?

   (*a*) rate = $k[A]^2[B]$ (*b*) rate = $k[A][B]$

   (*c*) rate = $k[A]^2[B]^2$ (*d*) rate = $k[A][B]^2$

11. Consider the reaction:

   $Cl_2(aq) + H_2S(aq) \longrightarrow S(s) + 2H^+(aq) + 2Cl^-(aq)$

   The rate of reaction for this reaction is

   rate = $k[Cl_2][H_2S]$

   Which of these mechanism is/are consistent with this rate equation?

   A. $Cl_2 + H_2S \longrightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)

   $Cl^+ + HS^- \longrightarrow H^+ + Cl^- + S$ (fast)

   B. $H_2S \longrightarrow H^+ + HS^-$ (fast equilibrium)

   $Cl_2 + HS^- \longrightarrow 2Cl^- + H^+ + S$ (slow)

   (*a*) A only (*b*) B only

   (*c*) Both A and B (*d*) Neither A nor B

12. For the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + 1/2O_2(g)$ the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol L^{-1}s^{-1}. The rate of formation of NO_2 and O_2 is given respectively as

   (*a*) 6.25×10^{-3} mol L^{-1}s^{-1}and
   6.25×10^{-3} mol L^{-1}s^{-1}

   (*b*) 1.25×10^{-2} mol L^{-1}s^{-1}and
   3.125×10^{-3} mol L^{-1}s^{-1}

   (*c*) 6.25×10^{-3} mol L^{-1}s^{-1}and
   3.125×10^{-3} mol L^{-1}s^{-1}

   (*d*) 1.25×10^{-2} mol L^{-1}s^{-1}and
   6.25×10^{-3} mol L^{-1}s^{-1}

(B) Fill in the Blanks

Fill in the blank spaces:

1. Rate of a chemical reaction is measured by the _______ in the amount of the reactants or _______ in the amount of products per unit time.
2. For the decomposition of nitrogen pentoxide, rate of decomposition of N_2O_5 is represented as _______ and rate of formation of oxygen is represented as _______.
3. Rate of a chemical reaction increases by about _______ times for every _______ rise in temperature.
4. In the reaction $aA + bB \rightarrow$ Products, the molecularity of the reaction is given by _______ .
5. If the rate of a reaction is found to be proportional to $[A]^{\alpha}\ [B]^{\beta}$, then $\alpha + \beta$ represents the _______ of the reaction.
6. A series of step reactions or elementary processes proposed to account for overall reaction is called the _______of the _______ .

(C) True/False Statements

Write T for true and F for false statements:

1. Rate of the reaction, $A + 2B \rightarrow$ Product, can be given as:
   rate of the reaction = $\dfrac{-d[B]}{dt}$.
2. Rate of a reaction increases with temperature because the fraction of molecules possessing energies greater than the threshold energy increases.
3. A catalyst changes the equilibrium point in the reaction.
4. Rate constant is equal to the rate of a reaction when the concentration of all the reactants is unity.
5. Inversion of cane sugar in water in the presence of an acid is a unimolecular reaction.
6. One gram of pulverised wood burns faster than one gram of piece of wood.

(D) Assertion-Reason Type Questions

*In each question given below, there are two statements, **Assertion (A)** and **Reason (R)**. Answer the questions as instructed below:*

(*a*) If both **A** and **R** are correct, and **R** is the correct reason for **A**.

(*b*) If both **A** and **R** are correct, but **R** is not the correct reason of **A**.

(*c*) If **A** is correct but **R** is wrong.

(*d*) If both **A** and **R** are incorrect.

1. ***Assertion (A)*** : Reactions which take place in the presence of light are called photochemical reactions.

Reason (R) : In the case of reversible reaction, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.

2. ***Assertion (A)*** : The units of the rate of reaction are moles litre^{-1} time^{-1}.

Reason (R) : Molecularity is the sum of molecules of different reactants as represented by balanced chemical equation.

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. The role of a catalyst is to change ___________.
   (*a*) Gibbs energy of reaction.
   (*b*) enthalpy of reaction.
   (*c*) activation energy of reaction.
   (*d*) equilibrium constant.

2. In the presence of a catalyst, the heat evolved or absorbed during the reaction ___________.
   (*a*) increases.
   (*b*) decreases.
   (*c*) remains unchanged.
   (*d*) may increase or decrease.

3. Activation energy of a chemical reaction can be determined by ___________.
   (*a*) determining the rate constant at standard temperature.
   (*b*) determining the rate constants at two temperatures.
   (*c*) determining probability of collision.
   (*d*) using catalyst.

4. Which of the following statements is **not** correct about order of a reaction?
   (*a*) The order of a reaction can be a fractional number.
   (*b*) Order of a reaction is experimentally determined quantity.
   (*c*) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.
   (*d*) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

5. Which of the following statements is correct?
   (*a*) The rate of a reaction decreases with the passage of time as the concentration of reactants decreases.
   (*b*) The rate of a reaction is same at any time during the reaction.
   (*c*) The rate of a reaction is independent of temperature change.
   (*d*) The rate of a reaction decreases with increase in concentration of the reactant(s).

6. Which of the following expressions is correct for the rate of reaction given below?

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

   (*a*) $\dfrac{\Delta[Br^-]}{\Delta t} = 5\dfrac{\Delta[H^+]}{\Delta t}$ (*b*) $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{6}{5}\dfrac{\Delta[H^+]}{\Delta t}$
   (*c*) $\dfrac{\Delta[Br^-]}{\Delta t} = \dfrac{5}{6}\dfrac{\Delta[H^+]}{\Delta t}$ (*d*) $\dfrac{\Delta[Br^-]}{\Delta t} = 6\dfrac{\Delta[H^+]}{\Delta t}$

7. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be

$$\text{Rate} = k\,[A]\,[B]$$

   Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of the rate constant will be _________.
   (*a*) the same (*b*) doubled
   (*c*) quadrupled (*d*) halved

8. Which of the following statements is **incorrect** about the collision theory of chemical reaction?
   (*a*) It considers reacting molecules or atoms to be hard spheres and ignores their structural features.
   (*b*) Number of effective collisions determines the rate of reaction.
   (*c*) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation.
   (*d*) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

9. Which of the following statement is **not** correct for the catalyst?
   (*a*) It catalyses the forward and backward reactions to the same extent.
   (*b*) It alters ΔG of the reaction.
   (*c*) It is a substance that does not change the equilibrium constant of a reaction.
   (*d*) It provides an alternate mechanism by reducing the activation energy between the reactants and the products.

10. Rate law cannot be determined from a balanced chemical equation if _________.
   (*a*) reverse reaction is involved.
   (*b*) it is an elementary reaction.
   (*c*) it is a sequence of elementary reactions.
   (*d*) any of the reactants is in excess.

11. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?
   (*a*) Order is same as molecularity.
   (*b*) Order is less than the molecularity.
   (*c*) Order is greater than the molecularity.
   (*d*) Molecularity can never be zero.

12. In any unimolecular reaction __________.
   (*a*) only one reacting species is involved in the rate determining step.
   (*b*) the order and the molecularity of the slowest step is equal to one.
   (*c*) the molecularity of the reaction is one and order is zero.
   (*d*) both molecularity and order of the reaction is one.

13. For a complex reaction __________.
   (*a*) order of overall reaction is same as molecularity of the slowest step.
   (*b*) order of overall reaction is less than the molecularity of the slowest step.
   (*c*) order of overall reaction is greater than the molecularity of the slowest step.
   (*d*) molecularity of the slowest step is never zero or non-integer.

14. Mark the **incorrect** statements.
   (*a*) Catalyst provides an alternative pathway to reaction mechanism.
   (*b*) Catalyst raises the activation energy.
   (*c*) Catalyst lowers the activation energy.
   (*d*) Catalyst alters enthalpy change of the reaction.

II. Matching Type Questions

Match the items of Column I with appropriate item given in Column II.

1. Match the items of Column I and Column II.

Column I	Column II
(*i*) Diamond	(*a*) short interval of time
(*ii*) Instantaneous rate	(*b*) ordinarily rate of conversion is imperceptible
(*iii*) Average rate	(*c*) long duration of time

2. Match the items of Column I and Column II

Column I	Column II
(*i*) Mathematical expression for the rate of reaction	(*a*) by lowering the activation energy
(*ii*) Catalyst alters the rate of reaction	(*b*) rate law
(*iii*) Molecularity	(*c*) order of slowest step
(*iv*) Order of a complex reaction is determined by	(*d*) cannot be fraction or zero

III. Assertion-Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reasons (R) is given. Choose the correct answer out of the following choices.

(*i*) Both assertion and reason are correct and the reason is correct explanation of assertion.
(*ii*) Both assertion and reason are correct but reason does not explain assertion.
(*iii*) Assertion is correct but reason is incorrect.
(*iv*) Both assertion and reason are incorrect.
(*v*) Assertion is incorrect but reason is correct.

1. ***Assertion* (*A*):** Order of the reaction can be zero or fractional.
   ***Reason* (*R*):** We cannot determine order from balanced chemical equation.
2. ***Assertion* (*A*):** Order and molecularity are same.
   Reason (R): Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.
3. ***Assertion* (*A*):** The enthalpy of reaction remains constant in the presence of a catalyst.
   ***Reason* (*R*):** A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.
4. ***Assertion* (*A*):** All collisions of reactant molecules lead to product formation.
   ***Reason* (*R*):** Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

IV. Short Answer Type Questions

1. How can you determine the rate law of the following reaction?

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

2. For which type of reactions, order and molecularity have the same value?
3. In a reaction if the concentration of the reactant A is tripled, the rate of reaction becomes twenty seven times. What is the order of the reaction?
4. For a reaction $A + B \longrightarrow$ Products, the rate law is — Rate $= k\,[A]\,[B]^{3/2}$. Can the reaction be an elementary reaction? Explain.
5. Why cannot molecularity of any reaction be equal to zero?

6. Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

7. Why we cannot determine the order of a reaction by taking into consideration the balanced chemical equation?

V. Long Answer Type Questions

1. All energetically effective collisions do not result in a chemical change. Explain with the help of an example.
2. What happens to most probable kinetic energy and the energy of activation with increase in temperature?
3. Explain the difference between instantaneous rate of a reaction and average rate of a reaction.

ANSWERS

(A) Multiple Choice Questions

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

(B) Fill in the Blanks

1. decrease, increase
2. $\frac{-d[N_2O_5]}{dt}, \frac{-d[O_2]}{dt}$
3. two, 10°
4. $a + b$
5. order
6. mechanism, reaction

(C) True/False Statements

1. False 2. True 3. False 4. True 5. False 6. True

(D) Assertion-Reason Type Questions

1. (*b*) 2. (*b*)

Some Additional Questions

I. Multiple Choice Questions

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

II. Matching Type Questions

1. (*i*) → (*b*), (*ii*) → (*a*), (*iii*) → (*c*),
2. (*i*) → (*b*), (*ii*) → (*a*), (*iii*) → (*d*), (*iv*) → (*c*)

III. Assertion-Reason Type Questions

1. (*ii*) 2. (*v*) 3. (*i*) 4. (*v*)

8
CHAPTER

Chemical Equilibria

LEARNING OBJECTIVES

- List examples of chemical reactions those are reversible.
- Explain the dynamic nature of a reaction in equilibrium as applied to states of matter, solutions and chemical reactions.
- Apply Le Chatelier's principle to predict the effects of changes in concentration, pressure and temperature on the position of equilibrium in homogenous reactions.
- Explain that a catalyst speeds up the attainment of an equilibrium but not its position.
- Deduce expressions for homogeneous and heterogeneous reactions for the equilibrium constant K_c and K_p from equilibrium concentrations or equilibrium partial pressures.
- Determine the values of K_c and K_p and state the units of K_c and K_p.
- Explain the effects of the changing temperature on the value of K_c and K_p for exothermic and endothermic reactions.
- Discuss how the value of K_c and K_p remains unaffected by the change in concentration, pressure or by the presence of a catalyst.
- Apply the concepts of equilibria, kinetics and economics to industrial processes like the Haber Process to explain that particular reaction conditions are adopted.

8.1 INTRODUCTION

If we add equal volumes of equimolar solutions of sodium chloride and silver nitrate, a precipitate of silver chloride is obtained quantitatively as expected. This is the basis of gravimetric and volumetric estimations. However, all the chemical reactions don't proceed to completion. After some time, we find that although there are still certain quantities of the reactants in the reaction mixture, the reaction seems to have stopped. This state is called the state of **equilibrium**. At a particular temperature and pressure, there is a fixed ratio between the concentrations of the reactants and the products for a reaction. Of course, the equilibrium point changes with the change of temperature, pressure and concentration. The objective of this chapter is to investigate the factors that influence the equilibrium point.

Equilibrium *represents the state of a process in which the properties like temperature, pressure, concentration of the system do not show any change with the passage of time.*

In all processes which attain equilibrium, two opposing processes are involved. Equilibrium is attained when the rates of the two opposing processes become equal.

If the opposing processes involve only physical changes, the equilibrium is called **physical equilibrium**. *If the opposing processes involve chemical changes, i.e., the opposing processes are chemical reactions, the equilibrium is called* **chemical equilibrium**.

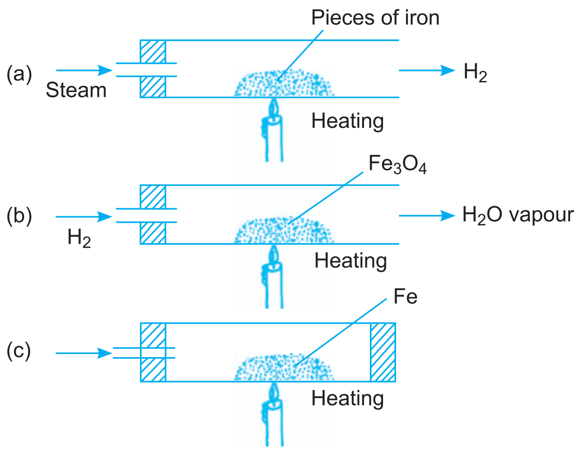


Fig. 8.1: *Reversible reaction occurring in a closed tube (c)*

Reversible and Irreversible Reactions: The concept of reversibility in a chemical reaction may be explained with the help of the following experiment.

Place pieces of iron in an *open glass tube* heated from below and pass steam from the other end [Fig. 8.1 (*a*)]. The following reaction takes place:

$$\underset{\text{Iron}}{3Fe\,(s)} + \underset{\text{Steam}}{4H_2O\,(g)} \rightarrow \underset{\text{Iron oxide}}{Fe_3O_4\,(s)} + \underset{\text{Hydrogen}}{4H_2\,(g)}$$

In another experiment, place iron oxide (Fe_3O_4) in the tube, heated from below and pass hydrogen over it [Fig. 8.1 (*b*)]. The following reaction takes place:

$$Fe_3O_4\,(s) + 4H_2\,(g) \rightarrow \underset{\text{Iron}}{3Fe\,(s)} + \underset{\text{Water vapour}}{4H_2O\,(g)}$$

As the tube was open, hydrogen in the first case and water vapour in the second case escape out. However, if the *tube is closed* [Fig. 8.1 (*c*)], both the reactions (forward and backward) take place simultaneously and hence, the reaction becomes reversible. It may be represented as:

$$3Fe\,(s) + 4H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s) + 4H_2\,(g)$$

Obviously, first two reactions can go to completion, *i.e.*, whole of iron can be converted into iron oxide in the first case and iron oxide into iron in the second case, but the last reaction, *viz.*, the reversible reaction does not go to completion.

A few more common examples of reversible reactions carried out in closed vessels are given below:

(*i*) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

(*ii*) $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

(*iii*) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$

(*iv*) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

It may be noted that reactions in the open glass tubes [Fig. 8.1 (*a*) and (*b*)] are irreversible reactions. They are progressing only in the forward direction. We cannot expect to get back Fe or Fe_3O_4. After sometime, the whole of Fe [Fig. 8.1 (*a*)] will react to give Fe_3O_4 and we cannot expect to get back some amount of Fe. But it is possible to retain some amount of Fe every time. Thus, reactions depicted in Fig. 8.1 (*a*) and (*b*) are irreversible and that depicted in Fig. 8.1 (*c*) is reversible.

8.2 IRREVERSIBLE REACTIONS

If a reaction cannot take place in the reverse direction, i.e., the products formed do not react to give back the reactants under the same conditions, it is called an **irreversible reaction**.

It is represented by putting a single arrow between the reactants and the products pointing from reactants towards products, *i.e.*,

$$A + B \rightarrow C + D$$

A few examples of irreversible reactions are as follows:

(*i*) $AgNO_3\,(aq) + NaCl\,(aq) \rightarrow AgCl\,(s) + NaNO_3\,(aq)$

(*ii*) $BaCl_2\,(aq) + Na_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + 2NaCl\,(aq)$

It may be noted that a reversible reaction becomes irreversible if one of the products (which is gaseous) is allowed to escape out. It is for this reason that the reaction between iron and steam is irreversible if carried out in the open tube because hydrogen gas formed escapes out.

8.3 EQUILIBRIA INVOLVING PHYSICAL CHANGES

The characteristics of systems at equilibrium are more easily understood if we examine some physical changes in a state of equilibrium. The most familiar examples involve changes of state such as

(*a*) *Solid-liquid equilibrium, e.g.,* ice $\rightleftharpoons$ liquid water.
(*b*) *Liquid-gas equilibrium, e.g.,* water $\rightleftharpoons$ water vapour.
(*c*) *Equilibrium of solute in two phases of solution, e.g.,*
  (*i*) Sugar (*s*) $\rightleftharpoons$ Sugar in saturated solution in water
  (*ii*) CO_2 (*g*) $\rightleftharpoons$ CO_2 (in solution), *i.e.*, dissolved in water

(*a*) **Solid-Liquid Equilibrium.** This is a very familiar type of equilibrium which we come across in our daily life. If we put a block of ice in a cup and leave it open, we shall see that ice melts and after some time the whole of it is converted into water. If we place this cup containing water and ice inside a perfectly insulated thermos flask so that the heat from the surroundings is not allowed to enter the flask, we shall notice that

(*i*) The mass of ice and water does not change with time.
(*ii*) The temperature of the ice + water system does not change.
(*iii*) If we could observe the individual molecules of ice and water, we would notice that there is considerable activity in the molecules of ice and water in the sense that some molecules from the liquid water join on to the ice and that some molecules of ice pass on to the water. Since, there is no change in masses of the ice and water, so *the rate of transfer of molecules from ice into water must be equal to the rate of reverse transfer from water into ice.*

In terms of *free energy*, we say that for ice and water system, $\Delta G = 0$ at 273 K and one atmospheric pressure.

We know that at other temperatures for ice $\rightleftharpoons$ water or $H_2O\ (s) \rightleftharpoons H_2O\ (l)$

$\Delta G > 0$ at temperatures greater than 273 K, and $\Delta G > 0$ at temperatures less than 273 K.

From this, we can infer that ice and water are at equilibrium only at a particular temperature. *For any pure substance at one atmospheric pressure, the temperature at which the solid and liquid phases are in equilibrium is known as the normal freezing point of the substance.* The equilibrium in this case is **dynamic equilibrium**.

We can infer from the above that in any system at dynamic equilibrium:

(*i*) Free energy change, $\Delta G = 0$ at T = 273 K, and P = 1 atm.
(*ii*) The two processes occur in both the directions simultaneously.
(*iii*) These two changes occur at the same rate, so that the masses on both sides of the equilibrium undergo no change.

(*b*) **Liquid-Gas Equilibrium.** It is of common experience that even though the temperature of Delhi and the temperature of Mumbai be the same on a particular day, we sweat more at Mumbai especially during summer months. We say that the humidity is greater in cities which are close to the sea. How can we explain this? Let us perform the following experiment to understand the reason.

A box without bottom fitted with a U-tube containing mercury (manometer), is made dry by putting some drying agent like anhydrous $CaCl_2$ or phosphorus pentoxide for a few hours under it [step (a) Fig. 8.2] and then removing the drying agent [step (b) Fig. 8.2]. By tilting the box on one side, a Petri dish containing water is quickly pushed into the box [step (c) Fig. 8.2]. We then look to the manometer. It is found that mercury level in the right limb of the manometer slowly rises and finally reaches a constant value which shows that the pressure inside the box has increased and reached a constant value [step (d) Fig. 8.2]. It would also be observed that the volume of water in the Petri dish has decreased. Repeat the experiment with different amounts of water in the Petri dish, caring that every time you start with a dried box.

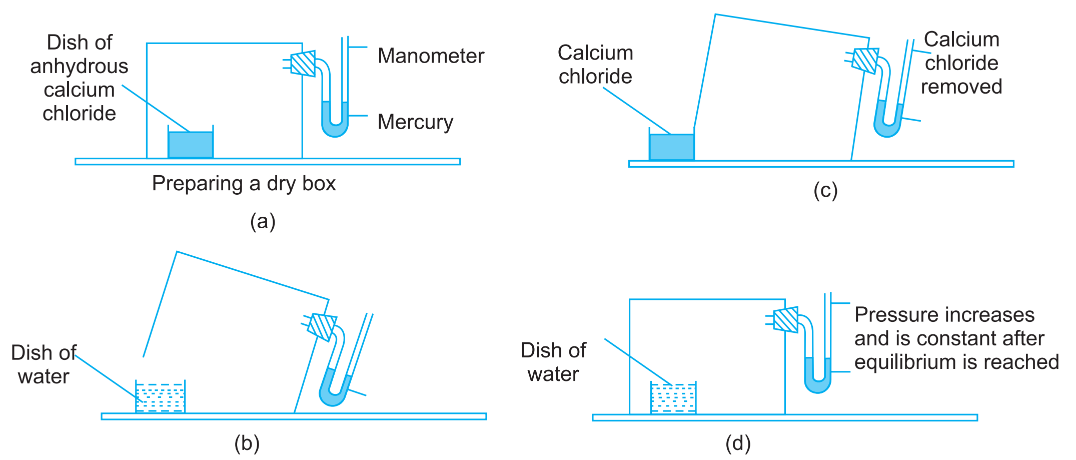


Fig. 8.2: *Measurement of vapour pressure of water*

In the beginning, there is no (or very little) water vapour inside the box and as the water evaporates the pressure in the box increases due to the addition of water molecules into the gaseous phase inside the box. Since the temperature is kept constant, the rate of evaporation will remain constant. However, the rate of increase of pressure decreases with time leading to a final situation or equilibrium condition, when there is no net evaporation. This shows that as the number of water molecules in the gaseous state increases, the rate of the return of water molecules from the gaseous state into the liquid state increases and when equilibrium is reached,

Rate of evaporation = Rate of condensation.

and the dynamic equilibrium can be written as:

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

When the equilibrium is attained, the pressure exerted by the water molecules remains constant and this is termed as Equilibrium Vapour Pressure of water or just vapour pressure of water and it will vary with temperature. When the temperature increases, the vapour pressure also increases. It is also observed that till there is adequate water in the Petri dish, the final equilibrium vapour pressure is independent of the amount of water in the Petri dish.

[In case, the same experiment is repeated in a room where the temperature is higher, the equilibrium pressure would be found to be higher. If the experiment is repeated with methyl alcohol, ethyl alcohol and acetone it would be found that different liquids exhibit different equilibrium vapour pressures at the same temperature, and the liquid which has a higher vapour pressure is more volatile.]

Let us expose three watch glasses having 1 cm^3 each of acetone, ethyl alcohol and water to air without box. Repeat the experiment in a warmer room.

We find that in these cases the liquid eventually disappears and the time taken for complete evaporation depends upon the nature of the liquid, the amount of the liquid and the temperature.

When the watch glass is open to the atmosphere, the rate of evaporation is still constant but since the molecules get dispersed into a large volume, *the rate of condensation from gas to liquid state can never equal the rate of evaporation.* Such systems are said to be *open* and the systems such as a closed box are called as *closed* systems. We cannot attain equilibrium in an open system. Thus, in a closed system there is a dynamic equilibrium between molecules in the gaseous state and the liquid state, *e.g.*,

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

The vapour pressure exerted by the molecules in the gaseous phase is constant at equilibrium. The equilibrium vapour pressure depends upon the nature of liquid and temperature and not on the amount of liquid present after equilibrium is reached. It is also independent of the volume of the container for the gaseous state.

Our atmosphere is a system and the water vapour in the air would depend on the amount of water in water bodies in the area, the wind velocity, temperature, etc. Near a sea or a lake, especially when the wind is not blowing the amount of water vapour in the air at a given temperature is high compared to a city in a desert.

(*c*) Equilibrium involving dissolution of solids in liquids or gases in liquids.

(*i*) *Solids in liquids.* It is a common experience that we cannot dissolve just any amount of salt or sugar in a given amount of water. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals will separate if we cool the syrup. A saturated solution is one in which more solute cannot dissolve. The concentration of the solute in a saturated solution depends upon the temperature. A dynamic equilibrium exists between the molecules in the solid state and the molecules in the solution of a saturated solution.

Sugar (*in solution*) $\rightleftharpoons$ *Sugar* (*solid*) and at equilibrium.

Rate of dissolution of sugar = Rate of precipitation of sugar.

Equality of the two rates and dynamic nature of the equilibrium can be demonstrated with the help of radioactive sugar (Fig. 8.3). If we drop radioactive sugar into a saturated solution of non-radioactive sugar, it will be observed that the solution and the rest of the sugar existing as solid will also become radioactive. It points to the dynamic nature of chemical equilibrium.

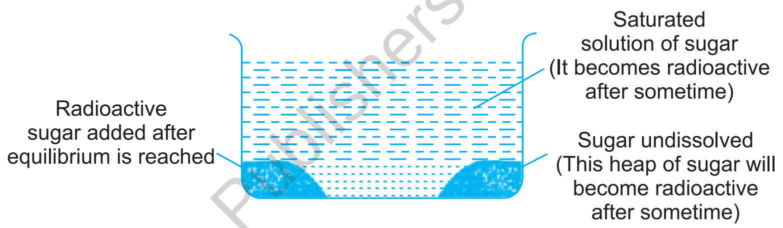


Fig. 8.3: *Demonstration for dynamic nature of chemical equilibrium*

(*ii*) *Solutions of gases in liquids.* Soda water is a solution of carbon dioxide in water. Water from the tap has some air dissolved in it. All gases are soluble in one solvent or the other to a certain extent. The solubility of the gas in a liquid depends on pressure, nature of the gas and liquid and the other soluble components present in the solution. The effect of pressure on the solubility of different gases was quantitatively studied by William Henry under various pressures. He gave a law known as *Henry's law* which states that:

The amount of a gas that dissolves in a given amount of a liquid at a constant temperature is proportional to the partial pressure of the gas provided the gas does not undergo any chemical change during the formation of solution. If a mixture of gases is in contact with the liquid, the solubility of each gas is proportional to its partial pressure. In simpler way, the law can also be written as

$$m \propto p$$

$$m = kp$$

$$\frac{m}{p} = k \text{ (a constant)}$$

where m is the mass of a gas dissolved in a given volume of the liquid at pressure p and at constant temperature T.

It implies that lower the pressure, smaller would be the amount of a gas dissolved in a given quantity of solvent. This explains why bubbles of gas (CO_2) from soda water bottle start coming out briskly as the cork is opened. The reason is that solubility of the gas dissolved at high pressure in the bottle becomes less on lowering the pressure and excess of it bubbles out on opening.

Example. *The solubility of a substance A (M = 120 g* mol^{-1}*) at 300 K at equilibrium is equal to 0.002 mol* dm^{-3}*. How much A will remain undissolved?*

(*i*) *If 0.5 g of it were taken with 200* cm^3 *of water till the equilibrium is reached?*

(*ii*) *How much of A will be dissolved if another 200* cm^3 *of water is added to the above mixture?*

Solution. At equilibrium the amount of A dissolved per dm^3 or 100 cm^3 of water = 0.002 mol.

Molar mass of A = 120 g mol^{-1}

∴ Mass of A dissolved in 1000 ml of water = 0.002 × 120 = 0.24 g

(*i*) Since in the first case volume of water taken = 200 ml.

$$\therefore \text{ Mass of A dissolved in 200 cm}^3 = \frac{200 \times 0.24}{1000} = 0.048 \text{ g}$$

Total mass of A taken = 0.5 g

Hence, mass of A left undissolved = 0.5 – 0.048 = 0.452 g.

(*ii*) In the second case, the total volume of water is 200 cm^3 (taken initially) + 200 cm^3 (added later) = 400 cm^3

$$\therefore \text{ Mass of A dissolved in second case} = \frac{400 \times 0.24}{1000} = 0.096 \text{ g.}$$

PROBLEMS FOR PRACTICE

1. 0.20 g of solid iodine was treated with 100 cm^3 of water at 288 K till equilibrium was established. Calculate:
   (*i*) How much iodine remained undissolved?
   (*ii*) How much iodine could remain undissolved if another 150 cm^3 of water is added to the solution?
   Given that the solubility of iodine = 0.0011 mole/litre at 288 K. [**Ans.** (*i*) 0.172 g (*ii*) 0.130 g]

2. 425 g of sugar was treated with 100 cm^3 of water at 293 K till equilibrium was established. Calculate:
   (*i*) How much sugar remain undissolved at equilibrium?
   (*ii*) How much sugar will remain undissolved when solution is diluted to make the volume 200 cm^3?
   Given that solubility of sugar is 5.9 moles/litre at 293 K. [**Ans.** (*i*) 223.22 g (*ii*) 21.44 g]

8.4 GENERAL CHARACTERISTICS OF EQUILIBRIA INVOLVING PHYSICAL PROCESSES

Following factors have come to light from the discussion of various processes involving physical equilibrium:

(*i*) In the case of liquid $\rightleftharpoons$ gas equilibrium, the pressure of the gas above the liquid was found to be constant at a given temperature.

(*ii*) In the case of solid $\rightleftharpoons$ liquid equilibrium, there is only one temperature called melting point, at which the system does not lose matter to the surroundings or gain matter from the surroundings. So, the mass of the two phases remains constant.

(*iii*) In case of dissolution of solids in liquids the solubility is constant at a given temperature.

(*iv*) In case of dissolution of gases in liquids the concentration of a gas in liquid is proportional to the pressure of the gas over the liquid or the concentration of the gas in the space above the liquid.

These four concentrations related findings are expressed in the Table 8.1.

Table 8.1

Process	Expression that states the findings above, the expression has a constant value for a given condition
(*i*) $H_2O\ (l) \rightleftharpoons H_2O\ (g)$	P_{H_2O} at constant temperature.
(*ii*) $H_2O\ (l) \rightleftharpoons H_2O\ (s)$	Melting point at constant pressure.
(*iii*) Sugar (*s*) $\rightleftharpoons$ Sugar (solution)	[Sugar (solution)] at constant temperature.
(*iv*) $CO_2\ (g) \rightleftharpoons CO_2\ (aq)$	$\dfrac{[CO_2(aq)]}{[CO_2(g)]}$ at constant temperature.

From the physical changes studied by us, we can state that the characteristics common to the systems at equilibrium are as given below:

(*i*) *The system has to be closed, i.e., exchange of matter from the surroundings to the system and vice-versa is not allowed.*

(*ii*) *The rate of forward reaction or process = Rate of reverse reaction or process.*

(*iii*) *The measurable properties of the system suffer no observable change even after the lapse of indefinite time, although individual molecules are moving from one phase to another.*

(*iv*) *After the attainment of equilibrium there exists an expression involving concentration of reacting substances which reaches a constant value at a given temperature.* The table given on the previous page provides the concentration related expressions for certain physical processes.

(*v*) *From the magnitude of the constant value of the concentration related term, we can determine how far the process has proceeded before reaching the equilibrium state.*

8.5 EQUILIBRIA IN CHEMICAL PROCESS: DYNAMIC EQUILIBRIUM

It has been observed that all the chemical reactions do not proceed to completion at all, just as in physical processes. We reach a state of equilibrium.

Actually, no reaction truly goes to completion. In some reaction in the final state of equilibrium, the concentration of reactants (those on the L.H.S. of an equation) is negligibly small as compared to the concentration of the products (those on the R.H.S. of an equation). For example,

$$AgNO_3\ (aq) + NaCl\ (aq) \rightarrow NaNO_3\ (aq) + AgCl\ (s)$$

Here we may add a small arrow in the reverse direction to indicate that at equilibrium the reaction proceeds far to the right. In the present unit we shall not make such distinction and presume that arrows $\rightleftharpoons$ indicate equilibria and do not speak anything about the relative concentrations of the species involved.

In order to understand the equilibrium in a chemical system, let us study the following reaction and perform the experiment

$$\underset{\text{(yellow)}}{Fe^{3+}\ (aq)} + \underset{\text{(colourless)}}{SCN^-\ (aq)} \rightleftharpoons \underset{\text{(deep red)}}{FeSCN^{2+}\ (aq)}$$

Experimental procedure. Add a few drops of ferric chloride solution (very light yellow colour) to water taken in a beaker. Add potassium thiocyanate solution (colourless) to this beaker. A red colour will be obtained. Go on adding potassium thiocyanate, drop by drop, till no increase in intensity of colour takes place. Now dilute the coloured solution by adding excess water. Blood red colour changes to brownish. If a precipitate of ferric hydroxide is formed due to hydrolysis, dissolve it by adding a few drops of dilute hydrochloric acid.

Now take 5 ml of this solution in each of the four test tubes and label them as 1, 2, 3 and 4.

(*i*) To test tube no. 1, add a few drops of concentrated ferric chloride solution.
(*ii*) To test tube no. 2, add a few drops of conc. potassium thiocyanate solution.
(*iii*) To test tube no. 3, add some solid ammonium chloride.
(*iv*) Leave the test tube no. 4 as such for reference. What do you observe?

It will be observed that in (*i*) and (*ii*) there is deepening of red colour, *i.e.*, formation of more of ferric thiocyanate complex, which is red in colour. It means, the equilibrium has shifted towards the right.

In test tube no. 3, the red colour disappears, thus showing that the equilibrium has shifted towards left.

From the above experiment we reach a conclusion that,

1. There exists a *chemical equilibrium* Fe^{3+} (*aq*) + SCN^- (*aq*) $\rightleftharpoons$ $FeSCN^{2+}$ (*aq*).
2. Addition of either Fe^{3+} or SCN^- brings about an increase in the concentration of $FeSCN^{2+}$ in the solution.

Effect of decrease of concentration on equilibrium. We have been observing the effect of increase of concentration of the reactants on the state of equilibrium. We have inferred that increase in concentration of either or any of the reactants results in the increase in the concentration of the products.

Now, let us study the effect of decrease of concentration of the reactants. In the experiment mentioned above, let us decrease the concentration of Fe^{3+} by addition of fluoride ions to the solution. Fluoride ions react with ferric ions to form a colourless complex ion.

$$Fe^{3+}\,(aq) + F^-\,(aq) \rightarrow FeF^{2+}\,(aq)$$

This way the concentration of ferric ions in the solution can be decreased.

To test tube no. 2 add a little of sodium fluoride and stir. It will be observed that the colour of the solution has dimmed in comparison to test tube no. 1.

We therefore, conclude that a decrease in the concentration of the reactant results into decrease in the concentration of the products.

8.6 CONCEPT OF CHEMICAL EQUILIBRIUM

Consider the general reversible reaction represented as under:

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

In the beginning (*i.e.*, at time $t = 0$), the concentrations of A and B are maximum and the concentrations of C and D are minimum (equal to zero, because no C and D are yet formed). As the reaction proceeds, the concentrations of A and B are decreasing with the passage of time, whereas the concentrations of C and D are increasing. Therefore, the rate of forward reaction is decreasing while the rate of backward reaction goes on increasing.

A stage comes, when the rate of forward reaction becomes equal to the rate of backward reaction. The reaction is then said to be in a *state of chemical equilibrium.*

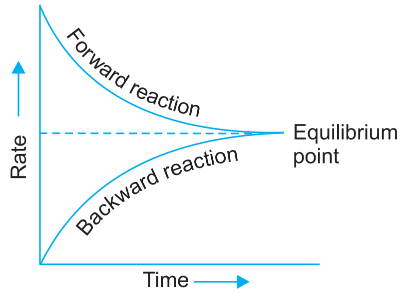


Fig. 8.4: *Variation in reaction rates for the forward and backward reaction with time*

The variation of the reaction rates with time and ultimately the attainment of chemical equilibrium may be represented as shown in Fig. 8.4.

Examples. The following processes are being described to illustrate how the equilibrium is attained:

1. **Combination of H_2 and I_2 to form HI.** It is a reversible reaction as represented below:

$$\underset{\text{(Colourless)}}{H_2\,(g)} + \underset{\text{(Purple)}}{(I_2)\,(g)} \rightleftharpoons \underset{\text{(Colourless)}}{2HI\,(g)}$$

If H_2 and I_2 in equimolar ratio are enclosed in a glass bulb at 500°C, the colour is deep purple in the beginning. As the time passes, the intensity of the colour decreases and then a stage comes when no further change in colour is observed. This indicates that the reaction has attained a state of equilibrium.

2. **Decomposition of calcium carbonate in a closed vessel.** If calcium carbonate is heated in a closed vessel, reversible reaction as shown below takes place

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

If the temperature of the furnace is kept constant (say at 500°C) and the vessel is connected to a manometer (Fig. 8.5), the pressure due to CO_2 gas first keeps on increasing and ultimately becomes constant. This is due to the fact that now as much of CO_2 is formed from $CaCO_3$, as the amount of CO_2 reacts with CaO to give back $CaCO_3$. In other words, the rates of forward reaction and backward reaction have become equal. Hence, the reaction has attained chemical equilibrium.

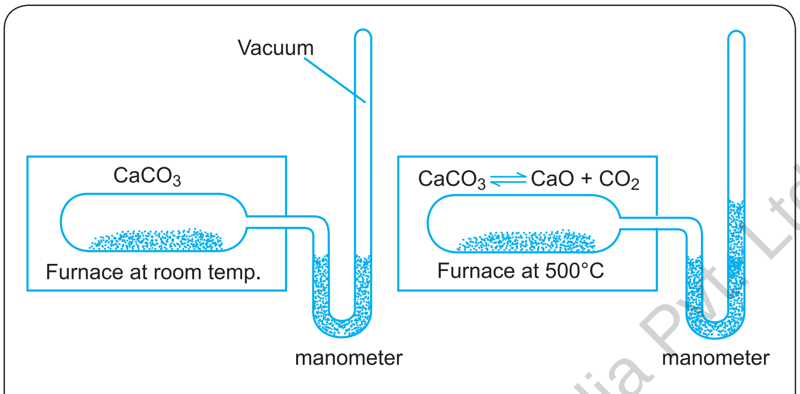


Fig. 8.5: *Equilibrium in the decomposition of* $CaCO_3$

3. **Decomposition of N_2O_4 in a closed vessel.** The decomposition of N_2O_4 in a closed vessel is a reversible reaction given by the following equation:

$$\underset{\text{(Colourless)}}{N_2O_4\ (g)} \rightleftharpoons \underset{\text{(Reddish brown)}}{2NO_2\ (g)}$$

N_2O_4 is stable at 0°C and is colourless. If N_2O_4 is taken in a glass bulb which is then sealed and placed in ice, it is almost colourless. Now, if the sealed glass bulb is placed into a vessel containing water at 25°C, the bulb starts acquiring brown colour which first deepens and then becomes constant. This indicates a state of equilibrium in which the concentrations of N_2O_4 and NO_2 have become constant. Both N_2O_4 and NO_2 are present in the reaction mixture. This can be tested by increasing the temperature of the bulb further when brown colour deepens indicating the formation of more NO_2. On cooling the bulb down from 25°C, the brown colour fades indicating formation of more of N_2O_4.

Dynamic nature of chemical equilibrium. At the point of equilibrium the reaction does not stop but appears to have stopped. Actually, both the reactions are still going on with equal speed without changing the concentrations of the various species.

At equilibrium the concentrations of all the species are not same, they may be different. *It is the two rates of the reactions which are equal,* that is why the equilibrium is said to be *dynamic* in nature. In other words, every reaction comes to a state of *dynamic equilibrium* after some time.

The state of equilibrium can be compared to that of a water reservoir provided with an inlet and outlet for water. Let some water be filled in the reservoir up to a level as shown in the Fig. 8.6. If the rate of flow-in and flow-out remains the same, the reservoir will maintain the same water level.

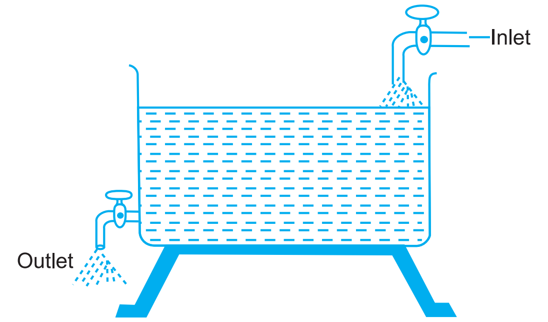


Fig. 8.6: *Water keeping its level constant in the reservoir*

8.6.1 Main Features (Characteristics) of Chemical Equilibrium

1. *It is* **dynamic**. *It is a permanent situation maintained by the equality of the rates of two opposing chemical reactions.*
2. *The amounts of reactants and products remain constant so long as the factor like concentration, temperature, pressure, etc. remain unchanged.*
3. *It can be attained from either direction. The nature and properties of equilibrium state are the same, regardless of the direction from which it is reached.*

   (*a*) Let us consider the example of $CaCO_3$, CaO, CO_2 system. It is observed that at each temperature there is a fixed value of the equilibrium CO_2 pressure when the rate of evolution of CO_2 equals the rate of its conversion to $CaCO_3$. It does not matter if this pressure is attained by allowing $CaCO_3$ to decompose.

   $$CaCO_3 \rightarrow CaO + CO_2$$

   or by allowing CO_2 to react with pure CaO

   $$CO_2 + CaO \rightarrow CaCO_3$$

   The rates of forward and reverse reactions become equal and the net reaction stops when the equilibrium pressure of CO_2 is reached, whether this pressure is approached from above or below the equilibrium value.

   (*b*) **Dissociation of N_2O_4**

   $$\underset{\text{Colourless}}{N_2O_4} \rightleftharpoons \underset{\text{Reddish brown}}{2NO_2\,(g)}$$

   The approach of equilibrium in this case can be made by observing the colour change of the reaction mixture.

   Take two bulbs A and B filled with NO_2 gas (Fig. 8.7). Place the bulb A in an ice bath at 273 K and B in a boiling water bath at 373 K. After some time the gas in the bulb A will become colourless. The gas in it will be mostly N_2O_4 (colourless). And thus, the equilibrium will shift towards the left. In bulb B the gas will be dark brown. Obviously, there is NO_2 in B. The equilibrium will shift towards right.

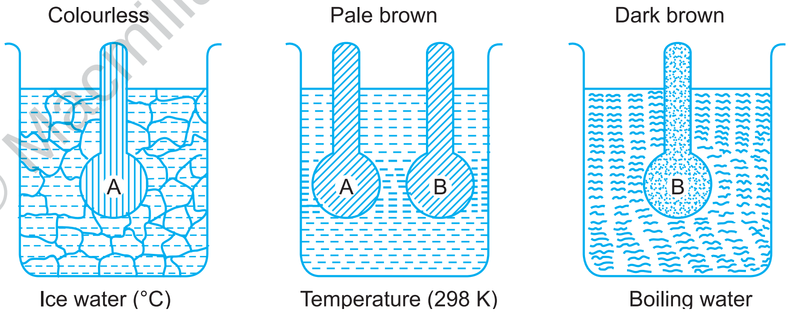


Fig. 8.7: *$N_2O_4 \rightleftharpoons 2NO_2$ equilibrium*

Now, place both the bulbs in a water bath at 298 K. After some time the colour in both the bulbs will be pale brown and this will continue to be so as long as the temperature of both remains the same. This shows that the system has attained the state of equilibrium. In the bulb A the equilibrium has been approached starting from N_2O_4 and in bulb B it has been attained starting from NO_2. This indicates that composition of the reaction mixture is the same regardless the direction from which it is reached. This also proves the dynamic nature of chemical equilibrium.

4. *System moves towards an equilibrium state spontaneously. A system can be removed from equilibrium only by some outside influence.*
5. *A catalyst does not alter the state of equilibrium, but it can bring about equilibrium in less time.*
6. *It can take place in a closed system only.*

8.7 LAW OF CHEMICAL EQUILIBRIUM FROM LAW OF MASS ACTION

In 1867, **Guldberg** and **Waage** enunciated the generalization, known as the *law of mass action.* It expresses quantitatively the effect of mass or concentration on the rate of a chemical reaction.

Let us consider a reaction between two substances A and B to form the products.

$$A + B \rightarrow \text{Products}$$

According to the law of mass action,

Rate of reaction $\propto [A]\,[B] = k\,[A]\,[B]$,

where [A] and [B] stand for the molar concentrations (active masses) of A and B respectively and k is a constant of proportionality known as velocity constant or rate constant.

Guldberg and Waage

Now, if $[A] = [B] = 1$

Then,

Rate of reaction $= k \times 1 \times 1$

or Rate of reaction $= k$

Thus, **velocity constant *k*** *is defined as the rate of a reaction when the activities of the reactants are unity each.*

For a general reaction, $xA + yB + zC \rightarrow \text{Products}$

The law of mass action may be written as: Rate of reaction $= k[A]^x\,[B]^y\,[C]^z$

Thus, the law of mass action may be restated as:

The **rate of reaction** *is proportional to the product of the molar concentrations (active masses) of reactants raised to the powers equal to the number of its molecules taking part in the reaction.*

By applying the law of mass action to a reversible reaction, we can derive a mathematical expression known as the *law of chemical equilibrium.*

Let us consider a homogeneous reversible reaction taking place in a gas or liquid phase, at a constant temperature.

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

According to the law of mass action,

Rate of forward reaction $\propto [A]\,[B]$

or Rate of forward reaction $= k_1\,[A]\,[B]$ ...(*i*)

Similarly, Rate of backward reaction $= k_2\,[C]\,[D]$ ...(*ii*)

[A], [B], [C] and [D] represent the active masses (molar concentration) of A, B, C and D respectively.

and k_1 = Velocity constant of the forward reaction.

k_2 = Velocity constant of the backward reaction.

Since, at equilibrium, the rate of forward reaction is equal to the rate of backward reaction, it follows from (*i*) and (*ii*) that

$$k_1\,[A]\,[B] = k_2\,[C]\,[D]$$

or $$\frac{k_1}{k_2} = K_c = \frac{[C][D]}{[A][B]}$$

K_c is known as the *equilibrium constant.* It is the ratio of velocity constants of two opposing reactions. The value of K_c for any given reaction is a constant at a given temperature. The above equation is known as the *law of chemical equilibrium.*

Physical significance of velocity constant: k_1 and k_2 are called *velocity constants* or *velocity coefficients* or *specific reaction rates* of forward and backward reactions respectively. The value of velocity constant is independent of the concentrations of the reactants but varies with temperature.

The numerical value of velocity constant of a reaction indicates whether the reaction is fast or slow. In other words, if the value is more, the reaction is fast and if value is less, the reaction is slow. Thus, by knowing the value of velocity constant, we can compare the rates of the reactions.

The simple reaction that we have considered above, *i.e.,*

$$A + B \leftrightharpoons C + D$$

involves a single molecule of each of the substances concerned.

Consider the general reaction, $aA + bB \leftrightharpoons lL + mM$

where a, b represent the number of molecules of the reactants A, B and l, m the number of molecules of the products L, M, then

$$K = \frac{[L]^l\,[M]^m}{[A]^a\,[B]^b}$$

This expression is known as **the law of chemical equilibrium**. The equilibrium constant is defined as *the product of the concentrations or active masses of the substances produced at equilibrium divided by the product of the concentrations or active masses of the reacting substances, each concentration term raised to the power equal to the number of its molecules taking part in the reaction as represented by the balanced chemical equations.*

For gaseous reactions, the partial pressure of a substance is proportional to its concentration in the gaseous phase. The general mass law equation for such reactions can be written as:

$$K_p = \frac{P_L^l \times P_M^m}{P_A^a \times P_B^b}$$

where K_p is the *equilibrium constant* expressed in terms of partial pressures, P_A, P_B, P_L and P_M.

For example, let us consider the formation of hydrogen iodide from H_2 and I_2.

$$H_2 + I_2 \leftrightharpoons 2HI$$

Applying the law of chemical equilibrium, we have

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

K for this reaction can be given as

$$K_p = \frac{[P_{HI}]^2}{[P_{H_2}] \times [P_{I_2}]}$$

K_p is related to K_c as $K_p = K_c(RT)^{\Delta n}$, where Δn is the difference in the number of moles of products and reactants taking part in the reaction. R is a gas constant and T is the temperature in Kelvin.

Predicting the direction of reaction. For the reaction, $aA + bB \leftrightharpoons xX + yY$, at any stage of the reaction, other than the stage of chemical equilibrium, concentration ratio is called concentration quotient. It is usually represented by Q. Thus,

$$\text{Concentration quotient, } Q = \frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b}$$

(*i*) If Q = K, the reaction is in equilibrium.

(*ii*) If Q > K, Q will tend to decrease so as to become equal to K. As a result the reaction will proceed in the backward direction.

(*iii*) If Q < K, Q will tend to increase. As a result the reaction will proceed in the forward direction.

8.7.1 Relationship Between K_p and K_c

Consider the general reversible reaction

$$aA + bB \leftrightharpoons xX + yY$$

If the equilibrium constant for this reaction is expressed in terms of concentrations, we may write

$$K_c = \frac{[X]^x\,[Y]^y}{[A]^a\,[B]^b}$$

or simply as,

$$K_c = \frac{C_X^x \cdot C_Y^y}{C_A^a \cdot C_B^b} \qquad \text{...}(i)$$

where C_A, C_B, C_X and C_Y represent the molar concentration of A, B, X and Y respectively.

If A, B, X and Y are gaseous, the equilibrium constant for the above reaction may be expressed in terms of pressure as:

$$K_p = \frac{P_X^x \cdot P_Y^y}{P_A^a \cdot P_B^b} \qquad \text{...}(ii)$$

If the gas behaves ideally then we can apply the ideal gas equation, viz.

$$PV = nRT$$

or

$$P = \frac{n}{V}RT \qquad \left[\because \frac{n}{V} = \text{no. of moles/litre} = C \text{ (molar concentration)}\right]$$

$$= CRT$$

∴ For the gases A, B, X and Y, we may write,

$$P_A = C_A\,RT, \qquad P_B = C_B\,RT,$$

$$P_X = C_X\,RT \quad \text{and} \quad P_Y = C_Y\,RT$$

Putting these values in equation (*ii*), we get

$$K_p = \frac{(C_X RT)^x \cdot (C_Y RT)^y}{(C_A RT)^a \cdot (C_B RT)^b} = \frac{C_X^x \cdot C_Y^y (RT)^{x+y}}{C_A^a \cdot C_B^b (RT)^{a+b}}$$

$$= \frac{C_X^x \cdot C_Y^y}{C_A^a \cdot C_B^b}(RT)^{(x+y)-(a+b)} = K_c.(RT)^{\Delta n}$$

where $$K_c = \frac{C_X^x \cdot C_Y^y}{C_A^a \cdot C_B^b} \text{ according to equation } (i)$$

and $$\Delta n = (x + y) - (a + b)$$

$$= \text{No. of moles of products} - \text{No. of moles of reactants}$$

$$= \text{Change in the number of moles}$$

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

As the partial pressures are taken in atmospheres, the value of R to be used in the above equation will be 0.0821 litre atmospheres/degree/mole. Temperature T will be in degree Kelvin (°K). If pressure is taken in k Pa, R is taken as 8.314 JK^{-1} mol^{-1}. Conversion factor being 1 atm = 101325 pa = 101.3 k pa.

Example. *At 700 K, the equilibrium constant K_p for the reaction $2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$ is 1.80×10^{-3} k Pa. What is the numerical value in moles per litre of K_c for this reaction at the same temperature?*

Solution. Here $$n_p = 3 \text{ moles}, \; n_r = 2 \text{ moles}$$

∴ $$\Delta n = n_p - n_r = 3 - 2 = 1 \text{ mole}$$

$$K_p = 1.80 \times 10^{-3} \text{ k Pa}$$

$$T = 700 \text{ K}$$

Use the relation, $$K_p = K_c\,(RT)^{\Delta n}$$

As, $$\Delta n = 1$$

$$K_p = K_c\,RT$$

$$K_p = 1.80 \times 10^{-3} \text{ k Pa}$$

$$= \frac{1.80 \times 10^{-3}}{101.3} \text{atm}$$

$$R = 0.0821 \text{ litre atm } K^{-1} \text{ mol}^{-1}$$

∴ $$K_c = \frac{K_p}{RT} = \frac{1.80 \times 10^{-3}/101.3}{0.0821 \times 700} = 3.09 \times 10^{-7} \text{ mol } L^{-1}.$$

8.8 CHARACTERISTICS OF EQUILIBRIUM CONSTANT

Some of the important characteristics of equilibrium constant are as follows:

(*i*) *The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start or the direction from which the equilibrium is approached.*

(*ii*) *If the reaction is reversed, the value of the equilibrium constant is inversed.*

For example, for the reaction between acetic acid and ethyl alcohol at 25°C, the value of the equilibrium constant is found to be 4.0, *i.e.*, for the reaction

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O}$$

$$K_c \text{ at } 25°C = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} = 4.0$$

If the above reaction is written in the reverse manner, *i.e.*, as:

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

the value of the equilibrium constant will be

$$K'_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_5][H_2O]} = \frac{1}{K_c}$$

$$= \frac{1}{4} = 0.25 \text{ at } 25°C$$

(*iii*) *If the equation (having equilibrium constant K) is written in two steps (having equilibrium constant K_1 and K_2) then, $K_1 \times K_2 = K$.*

For example, consider the reaction

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

For this reaction, $K = \frac{[NO_2]^2}{[N_2][O_2]^2}$

Imagine the above reaction taking place in the following two steps.

$$N_2 + O_2 \rightleftharpoons 2NO$$
$$2NO + O_2 \rightleftharpoons 2NO_2$$

For the 1st step, $K_1 = \frac{[NO]^2}{[N_2][O_2]}$

For the 2nd step, $K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$

$$\therefore \quad K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K$$ [according to equation (*i*)]

(*iv*) *If the equation (having equilibrium constant K) is divided by 2, the equilibrium constant for the new equation is the square root of K (i.e.,* $\sqrt{K}$ *).*

For example, if K is the equilibrium constant for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad ...(i)$$

then for the reaction, $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ ...(*ii*)

the value of equilibrium constant, $K' = \sqrt{K}$

This can be understood as under

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad K' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \sqrt{K}$$

[For reaction (*i*)] [For reaction (*ii*)]

(*v*) *If the equation (having equilibrium constant K) is multiplied by 2, the equilibrium constant for the new equation is the square of K (i.e., K^2).* Equilibrium constant for the new reaction can be computed as in the above case.

(*vi*) *The magnitude of the equilibrium constant gives an idea of the relative amounts of the reactants and the products.*

Large value of K indicates that large amounts of products are present at equilibrium. Small values of K indicate the opposite, *i.e.*, greater amount of reactants at equilibrium. Further, for $K < 1$, the amounts of reactants > amounts of products and for $K > 1$, the amounts of reactants < amounts of products.

(*vii*) *The value of the equilibrium constant is not affected by the addition of a catalyst to the reaction.*

The addition or removal of a catalyst does not shift the equilibrium point in either direction. A catalyst is a substance that affects the rate of the reaction, but is not consumed in the reaction. The catalyst provides an alternative reaction pathway or mechanism of lower activation energy. It therefore changes the rate of approach of equilibrium and so affects the forward and backward reaction rates equally. The composition of the equilibrium mixture remains constant. We can therefore conclude that the value of equilibrium constant is not affected by the addition of a catalyst.

(*viii*) *The value of equilibrium constant (K_c or K_p) depends only upon the temperature of the system. It is independent of concentration or pressure of the system.*

Effect of Temperature on the Equilibrium Constant. It is well known that the rate of a chemical reaction increases with the increase in temperature. Extent of this increase in rate depends upon the energy of activation of the reaction. Now, since the energies of activation for the forward and backward reactions are different, so a given increase in temperature will increase the rates of the forward and backward reactions to different extents. In other words, the values of the velocity constants for forward and backward reactions, *i.e.*, k_f and k_b will change differently with a given rise or fall in temperature. Further, since $K = k_f/k_b$, therefore, the value of the equilibrium constant (K) will change. Further, it has been found that the value of the equilibrium constant of an endothermic reaction increases (k_f increases more than k_b) and that of an exothermic reaction decreases (k_b increase more than k_f) with rise in temperature. For reactions having zero heat of reaction, temperature has no effect on the value of K.

Quantitatively, the effect of temperature on the equilibrium constant is given by **Van't Hoff** equation, which has been derived from Arrhenius equation.

$$\log \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

where $(K_p)_1$ = equilibrium constant at temperature T_1

$(K_p)_2$ = equilibrium constant at temperature T_2

ΔH = average enthalpy change in the temperature range T_1 to T_2

R = gas constant

8.9 TYPES OF CHEMICAL EQUILIBRIA

There are two types of chemical equilibria, depending upon the phases (physical states) of the reactants and products:

(*i*) **Homogeneous Equilibria.** *When all the reactants and the products are present in the same phase (i.e. gaseous or liquid) in a reaction at equilibrium, it is called a* **homogeneous equilibrium**.

This is further sub-divided into two types.

Type I: In which the number of moles of products is equal to the number of moles of reactants.

$$N_2 + O_2 \rightleftharpoons 2NO$$

$$2CO + 2H_2O \rightleftharpoons 2CO_2 + 2H_2$$

Type II: In which the number of moles of products is not equal to the number of moles of reactants.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Reactions in liquid phase

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

$$Fe^{3+}\ (aq) + SCN^-\ (aq) \rightleftharpoons FeSCN^{2+}\ (aq)$$

(*ii*) **Heterogeneous Equilibria.** *When the reactants and the products are present in two or more than two phases at equilibrium, it is called a* **heterogeneous equilibrium**.

A few common examples are given below:

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

$$3Fe\ (s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$$

Equilibrium Constant Expressions. In writing the equilibrium constant expressions the following two conventions must be followed.

(*i*) The active mass of every solid is taken as 1, *i.e.*, [Solid] = 1.

(*ii*) If a pure liquid is present in excess (*e.g.*, a solvent), its concentration remains almost constant and this constant is included into the equilibrium constant, *i.e.*, for liquid present in excess, [Liquid] = 1.

Equilibrium constant expressions for a few homogeneous and heterogeneous reactions are computed as under:

(A) For Homogeneous Equilibrium

(*i*) For the reaction $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3},\ K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}}$$

(*ii*) For the reaction $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

$$K_c = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]},\ K_p = \frac{P_{Cl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

(*iii*) For the reaction $CH_3COOH\ (l) + C_2H_2OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$

Here no liquid is present in excess, hence

$$K = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

(*iv*) For the reaction $NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$

$$K = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)][H_2O(l)]}$$

As H_2O is present in excess (being the solvent) therefore, by convention $[H_2O]$ is constant and put equal to 1. Hence we write,

$$K = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]}$$

(B) For Heterogeneous Equilibrium

(*i*) For the reaction $3Fe\ (s) + 4H_2O\ (g) \rightleftharpoons Fe_3O_4\ (s) + 4H_2\ (g)$

Applying the law of chemical equilibrium, we have

$$K_c = \frac{[Fe_3O_4(s)][H_2(g)]^4}{[Fe(s)]^3\ [H_2O(g)]^4}$$

But by convention, we put $[Fe_3O_4\ (s)] = 1$ and $[Fe\ (s)] = 1$

Hence, $K_c = \dfrac{[H_2(g)]^4}{[H_2O(g)]^4}$ or in terms of pressure, $K_p = \dfrac{P^4_{H_2}}{P^4_{H_2O}}$

Taking the 4th root of both the sides $K_p = \frac{P_{H_2}}{P_{H_2O}}$

(*ii*) For the reaction $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

Applying the law of chemical equilibrium, we have

$$K = \frac{[CaO(s)]\,[CO_2(g)]}{[CaCO_3(s)]}$$

But by convention we put [CaO (s)] = 1 and [$CaCO_3$ (s)] = 1

Hence, $K = [CO_2\ (g)]$

Since, the concentration of a gas is usually expressed in terms of partial pressures, hence we better write

$$K_p = P_{CO_2}$$

This explains why pressure of CO_2 becomes constant when equilibrium is attained in the decomposition of $CaCO_3$ in a closed vessel.

Units of Equilibrium Constant (K). The units of equilibrium constant vary from reaction to reaction.

(*i*) K_c has no units, when there is no change in the number of reactants and products in a reaction. For example, for the reaction

$$N_2\ (g) + O_2\ (g) \rightleftharpoons 2\ NO\ (g)$$

$$K_c = \frac{[NO]^2}{[N_2]\,[O_2]} = \frac{[mol/L]^2}{[mol/L]\,[mol/L]}$$

The units in the numerator and denominator will cancel.

(*ii*) K_c has some units when the number of moles of the reactants and products are different. For example, for the reaction

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

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{[mol/L]^2}{[mol/L]\,[mol/L]^3} = L^2\ mol^{-2}.$$

Thus, K_c has the units of $L^2\ mol^{-2}$.

However, it is customary not to mention the units of K for any type of reaction.

8.10 EQUILIBRIUM STUDIES OF SOME WELL-KNOWN REACTIONS

(*i*) *Dissociation of N_2O_4 into NO_2. ($N_2O_4 \rightleftharpoons 2NO_2$)*

Suppose *a* moles of N_2O_4 are heated in a closed vessel of volume V litres and *x* moles of it are dissociated at equilibrium into NO_2. Since, 1 mole of N_2O_4, on dissociation, gives 2 moles of NO_2, *x* moles of N_2O_4 on decomposition will give 2*x* moles of NO_2.

Substances	N_2O_4	$2NO_2$
Initial amounts (moles):	a	0
Equilibrium amounts (moles):	$(a - x)$	$2x$
Equilibrium concentrations (moles/litres):	$\frac{a-x}{V}$	$\frac{2x}{V}$

Substituting these values in the equilibrium constant expression, we get

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x/V)^2}{(a-x)/V}$$

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

(*a*) *Effect of changing pressure.* The expression for K_c given above has V in the denominator. When pressure is increased, the volume V decreases and since K_c remains constant at a given temperature, x also decreases. Thus, an increase in pressure suppresses the degree of dissociation of N_2O_4.

(*b*) *Effect of adding NO_2.* If an additional quantity of NO_2 is added without changing the volume and temperature $[NO_2]$ increases. Hence, in order to keep the value of K_c constant $[N_2O_4]$ must decrease, *i.e.*, one NO_2 is converted into N_2O_4. In other words, *the addition of NO_2 suppresses the dissociation of* N_2O_4.

(*ii*) *Dissociation of HI into H_2 and I_2:*

$$2HI \rightleftharpoons H_2 + I_2$$

Suppose a moles of HI are heated in a closed vessel of volume V litres and x moles of it are dissociated at equilibrium into H_2 and 1 mole of I_2 or 1 mole of HI gives $\frac{1}{2}$ mole of H_2 and $\frac{1}{2}$ mole of I_2, x moles of HI will give $x/2$ mole of H_2 and $x/2$ moles of I_2. Initial and equilibrium amounts of substances may be written as under:

	2HI	H_2	I_2
Initial amounts (moles):	a	0	0
Equilibrium amounts (moles):	$(a-x)$	$\frac{x}{2}$	$\frac{x}{2}$
Equilibrium concentrations (moles/litre):	$\frac{a-x}{V}$	$\frac{x}{2V}$	$\frac{x}{2V}$

Substituting these values in the equilibrium constant expression, we get

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(x/2V)(x/2V)}{(a-x/V)^2}$$

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

(*a*) *Effect of changing pressure.* From the above expression we find that K_c is independent of volume. Thus, volume has no effect on K_c. Now variation in pressure changes the volume of equilibrium mixture but volume has no effect on K_c. Consequently, changes in pressure does not affect the final state of equilibrium.

(*b*) *Effect of changing temperature.* Equilibrium constant $K_c = K_1/K_2$ where K_1 is the velocity constant for the forward reaction and K_2 is the velocity constant for the backward reaction. K_1 and K_2 change differently with the increase or decrease of temperature. It has been observed that K_1 increases more rapidly than K_2 with rise of temperature. *Thus, high temperature favours dissociation of HI.*

(*c*) *Effect of adding H_2 or I_2.* On addition of, say, H_2 to the equilibrium mixture, the value of K_c increases. Hence, in order to keep the value of K_c constant.

$[I_2]$ must decrease and [HI] must increase. Thus, some I_2 combines with H_2 to produce more HI. In other words, *the addition of any of the products* (H_2 or I_2) *suppresses the dissociation of HI.*

(*d*) *Effect of adding an inert gas.* On adding an inert gas, volume of the mixture and the number of moles of the individual species do not change. Thus, the molar concentrations $[H_2]$, $[I_2]$ and [HI] do not change. The value of K_c therefore, does not change.

(*iii*) *Synthesis of SO_3 by Contact process:*

$$2SO_2 + O_2 \rightleftharpoons SO_3$$

Suppose *a* moles of SO_2 react with *b* moles of O_2 in a closed vessel of V litres and that *x* moles of O_2 are used up at equilibrium. Since, 1 mole of O_2 combines with 2 moles of SO_2 to produce 2 moles of SO_3, $2x$ moles of SO_2 will combine with *x* moles of O_2 and $2x$ moles of SO_3 will be formed. Thus, the quantities of SO_2 and O_2 at equilibrium will be $(a - 2x)$ moles and $(b - x)$ moles respectively as shown below.

Substances	$2SO_2$	O_2	$2SO_3$
Initial amounts (moles):	a	b	0
Equilibrium amounts (moles):	$(a - 2x)$	$(b - x)$	$2x$
Equilibrium concentrations (moles/litres):	$\frac{a-2x}{V}$	$\frac{b-x}{V}$	$\frac{2x}{V}$

Substituting these values in the equilibrium constant expression, we have

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

or

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

(*a*) *Effect of changing pressure.* When pressure is increased, the volume V decreases. Hence, in order to keep the value of K_c constant, *x* must increase, *i.e.*, increase in pressure favours the combination of SO_2 and O_2 to form SO_3.

(*b*) *Effect of adding SO_2 or O_2.* Adding of SO_2 or O_2 to the equilibrium mixture will increase the denominator in the equilibrium constant expression.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

Thus, in order to keep the value of K_c constant, the numerator, *i.e.*, $[SO_3]$ increases. This indicates that more of the reactants are converted into SO_3. In actual practice and excess of O_2 (air) is used to convert the whole of SO_2 into SO_3.

(*iv*) *Synthesis of NH_3 by Haber process:*

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Suppose *a* moles of N_2 react with *b* moles of H_2 in a closed vessel of volume V litres and that *x* moles of N_2 are used up at equilibrium. Since, 1 mole of N_2 combines with 3 moles of H_2 to produce 2 moles of NH_3. *x* mole of N_2 will combine with $3x$ moles of H_2 to produce $2x$ moles of NH_3 at equilibrium. Then we have:

Substances	N_2	$3H_2$	$2NH_3$
Initial amounts (moles):	a	b	0
Equilibrium amounts (moles):	$(a - x)$	$(b - 3x)$	$2x$
Equilibrium concentrations (moles/litre):	$\frac{a-x}{V}$	$\frac{b-3x}{V}$	$\frac{2x}{V}$

Substituting these values in the equilibrium constant expression; we obtain

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

or $$K_c = \frac{(2x/V)^2}{(a - x/V)(b - 3x/V)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

(*a*) *Effect of changing pressure.* If pressure is increased, the volume V decreases. Hence in order to maintain the value of K_c constant, x must increase. Thus, increase in pressure favours the conversion of N_2 and H_2 into NH_3. In other words, high pressure is favourable for the formation of NH_3 from the combination of N_2 and H_2.

(*b*) *Effect of adding N_2 or H_2.* Addition of N_2 or H_2 to the equilibrium mixture will increase the denominator in the expression

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

So, in order to keep the value of K_c constant, the numerator (*i.e.* the concentration of NH_3) increases. Consequently more of the reactants are converted into NH_3. In practice N_2 is used in excess.

(*v*) *Hydrolysis of ethyl acetate:*

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

Suppose a moles of $CH_3COOC_2H_5$ react with b moles of H_2O in volume V litres and that x moles of $CH_3COOC_2H_5$ and x moles of water react to produce x moles each of acetic acid and ethyl alcohol. At equilibrium, we have

Substances	$CH_3COOC_2H_5$	H_2O	CH_3COOH	C_2H_5OH
Equilibrium concentrations (moles/litres)	$\frac{a-x}{V}$	$\frac{b-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

Substituting these values in the equilibrium constant expression:

$$K_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_5][H_2O]}, \text{ we get}$$

$$K_c = \frac{(x/V)(x/V)}{(a - x/V)(b - x/V)} = \frac{x^2}{(a-x)(b-x)}$$

(*a*) *Effect of changing pressure.* Since the volume term V does not appear in the expression for K_c the equilibrium is not affected by a change in volume or pressure.

(*b*) *Effect of adding H_2O.* Increase in concentration of H_2O will favour the hydrolysis of $CH_3COOC_2H_5$ as it will lead to an increase in the concentration of CH_3COOH and C_2H_5OH to keep the value of K_c constant in the expression

$$K_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_5][H_2O]}$$

(*vi*) *Dissociation of PCl_5:*

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Let us suppose that we heat a moles of PCl_5 in a closed vessel of volume V litres. Let x moles of it dissociate into PCl_3 and Cl_2. Since, 1 mole of PCl_5 dissociates to give 1 mole each of PCl_3 and Cl_2, x moles of PCl_5 dissociate to give x moles of both PCl_3 and Cl_2. Thus, at equilibrium we have

Substances	PCl_5	PCl_3	Cl_2
Initial amounts (moles):	a	0	0
Equilibrium amounts (moles):	$(a-x)$	x	x

Now applying equilibrium law, we have

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

Substituting for various quantities, we have

$$K_c = \frac{(x/V)(x/V)}{(a-x)/V} = \frac{x^2}{(a-x)V}$$

Here, since V appears in the denominator, the equilibrium state is affected by volume changes and pressure changes.

Example 1. *In a reaction between H_2 and I_2, 6.34 moles of H_2 and 4.02 moles of iodine are found to be present in equilibrium with 42.85 moles of HI in one litre vessel at 623 K. Calculate the equilibrium constant.*

Solution. The given reaction is represented as

$$\begin{array}{ccccccl} H_2 & + & I_2 & \rightleftharpoons & 2HI & & \\ 6.34 & & 4.02 & & 42.85 & & \text{Concentrations at equilibrium} \end{array}$$

The equilibrium constant,

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left[\frac{42.85}{1}\right]^2}{\left[\frac{6.34}{1}\right]\left[\frac{4.02}{1}\right]}$$

$$K = 72.04.$$

Example 2. *If 1 mole of H_2O and 1 mole of CO are taken in 10 litres vessel and heated to 1259 K, 40% of water reacts with CO according to the equation.*

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

Calculate the equilibrium constant K for the reaction.

Solution. The given reaction is represented as:

$$\begin{array}{ccccccccl} H_2O & + & CO & \rightleftharpoons & H_2 & + & CO_2 & & \\ 1 \text{ mole} & & 1 \text{ mole} & & 0 & & 0 & & \text{Initial concentration} \\ (1-x) & & (1-x) & & x & & x & & \text{Concentrations at equilibrium} \end{array}$$

where x is the no. of moles of water which has reacted at equilibrium.

Now $x = a\alpha$, where α = degree of reaction

a = initial concentration

Here $a = 1$ mole and $\alpha = \frac{40}{100}$

$\therefore$ $x = 1 \times \frac{40}{100} = 0.4$

Volume of the vessel = 10 litres.

$\therefore$ Molar concentrations at equilibrium are

$$[H_2O] = \frac{1-x}{10}; \ [CO] = \frac{1-x}{10};$$

$$[H_2] = \frac{x}{10} : [CO_2] = \frac{x}{10}$$

∴ Applying the law of chemical equilibrium

$$K = \frac{\left[\frac{x}{10}\right]^1 \left[\frac{x}{10}\right]^1}{\left[\frac{1-x}{10}\right]^1 \left[\frac{1-x}{10}\right]^1} = \frac{x^2}{(1-x)(1-x)}$$

Putting the value of $x = 0.4$, we get

$$K = \frac{(0.04)^2}{(1-0.4)(1-0.4)} = \frac{0.4 \times 0.4}{0.6 \times 0.6} = 0.44$$

Hence, the value of equilibrium constant is 0.44.

Example 3. *In an experiment, 2 moles of HI is taken into a 5 litres container. At 717 K, the equilibrium constant equals to 0.0156 for the gaseous reaction.*

$$2HI \rightleftharpoons H_2\,(g) + I_2\,(g)$$

Calculate the equilibrium concentrations of HI, H_2 and I_2. What is the fraction of HI which decomposes?

Solution. The given reaction is represented as

$$\begin{array}{cccccl} 2HI & \rightleftharpoons & H_2\,(g) & + & I_2\,(g) & \\ 2 & & 0 & & 0 & \text{Initial concentrations} \\ (2-x) & & \frac{x}{2} & & \frac{x}{2} & \text{Concentrations at equilibrium} \end{array}$$

where x moles of HI have decomposed at equilibrium.

Given V = 5 litres, K = 0.0156

Molar concentrations at equilibrium for various substances are as follows:

$$[HI] = \frac{2-x}{5};\quad [H_2] = \frac{x/2}{5};\quad [I_2] = \frac{x/2}{5}$$

∴ Applying the Law of mass action

$$K = \frac{\left[\frac{x/2}{5}\right]^1 \left[\frac{x/2}{5}\right]^1}{\left[\frac{2-x}{5}\right]^2} = \frac{x}{10} \times \frac{x}{10} \times \frac{25}{(2-x)^2}$$

$$K = \frac{x^2}{4(2-x)^2}\text{, substituting the value of K}$$

$$0.0156 = \frac{x^2}{4(2-x)^2}$$

or

$$\sqrt{0.0156} = \frac{x}{2(2-x)}$$

$$0.125 = \frac{x}{2(2-x)} \quad \text{or } x = 0.4$$

Thus, at equilibrium,

$$\text{No. of moles of HI} = 2 - x = 2 - 0.4 = 1.6 \text{ moles}$$

$$\text{No. of moles of } H_2 = \frac{x}{2} = \frac{0.4}{2} = 0.2 \text{ mole}$$

$$\text{No. of moles of } I_2 = \frac{x}{2} = \frac{0.4}{2} = 0.2 \text{ mole}$$

Now $x = a \times \alpha$

x = Amount that decomposes

a = Initial concentration

α = Degree of dissociation

Putting the values of x and α in the above relation, we get

$$0.4 = 2 \times \alpha$$

$$\therefore \quad \alpha = \frac{0.4}{2} = 0.2 \text{ mole}$$

$\therefore$ Fraction of HI decomposed = 0.2 × 100 = 20%

Example 4. *The equilibrium constant in the reaction between ethyl acetate and water to form ethyl alcohol and acetic acid is 0.25 at 298 K. What weight of ethyl acetate will be obtained from 92 grams of alcohol and 120 grams of acetic acid, the reaction being carried out in a closed vessel?*

Solution. The equilibrium constant for the reaction $CH_3COOC_2H_5 + H_2O \rightleftharpoons C_2H_5OH + CH_3COOH$ is 0.25

$\therefore$ The equilibrium constant for the reaction

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

will be reciprocal of the 0.25, *i.e.*, $\frac{1}{0.25} = 4$

$$\text{Moles of } C_2H_5OH \text{ taken} = \frac{92}{\text{Molecular wt. of } C_2H_5OH} = \frac{92}{46} = 2$$

$$\text{Moles of } CH_3COOH = \frac{120}{\text{Molecular wt. of } CH_3COOH} = \frac{120}{60} = 2$$

Let x moles each of the alcohol and acetic acid be converted into the ester and water at equilibrium. The concentration at equilibrium will be as

$$\begin{array}{ccccl} C_2H_5OH + & CH_3COOH \rightleftharpoons & CH_3COOC_2H_5 + & H_2O & \\ 2 & 2 & 0 & 0 & \text{Initial concentration} \\ (2-x) & (2-x) & x & x & \text{No. of moles at equilibrium} \end{array}$$

If V is the volume of the reaction mixture then,

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

or

$$4 = \frac{x^2}{(2-x)(2-x)}$$

$$x = \frac{4}{3} \text{ or } 1.33$$

The value 4 for x is obviously not possible because we start with 2 moles of each of the alcohol and the acid.

$$\therefore \quad x = 1.33$$

$\therefore$ No. of moles of ethyl acetate at equilibrium = 1.33 moles

$\therefore$ Weight of ester present at equilibrium = 1.33 × Molecular wt. of ester

= 1.33 × 88 = 117.04 grams.

Example 5. *10 moles of HI were produced by the interaction of 15 moles of H_2 and 5.2 moles of I_2 vapour at 717 K. Calculate the equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$.*

Solution.

$$\begin{array}{cccl} H_2 & + \; I_2 & \rightleftharpoons 2HI & \\ a & b & 0 & \text{Initial concentrations} \\ (a-x) & (b-x) & 2x & \text{Concentrations at equilibrium} \end{array}$$

Let the volume of the vessel in which reaction is taking place = V

∴ Molar concentration of the various species at equilibrium are

$$[H_2] = \left[\frac{a-x}{V}\right]\text{mole}^{-1}$$

$$[I_2] = \left[\frac{b-x}{V}\right]\text{mole}^{-1}$$

$$[HI] = \left[\frac{2x}{V}\right]\text{mole}^{-1}$$

Here a = 15 moles, b = 5.2 moles, $2x$ = 10 moles, x = 5 moles.

$$K = \frac{\left[\frac{2x}{V}\right]^2}{\left[\frac{a-x}{V}\right]\left[\frac{b-x}{V}\right]} = \frac{4x^2}{(a-x)(b-x)}$$

$$= \frac{4 \times (5)^2}{(15-5)(5.2-5)} = \frac{100}{(10)(0.2)} = 50.$$

Hence, the equilibrium constant for the reaction is 50.

Example 6. *For an equilibrium reaction, the rate constants for the forward and the backward reaction are 2.38×10^{-4} and 8.15×10^{-5} respectively. Calculate the equilibrium constant for the reaction.*

Solution.

$$\text{Equilibrium constant } K = \frac{K_f}{K_b} = \frac{2.38 \times 10^{-4}}{8.15 \times 10^{-5}}$$

$$= 2.92$$

Example 7. *For the reaction, N_2O_4 (g) $\rightleftharpoons$ $2NO_2$ (g) the concentrations of an equilibrium mixture of 298 K are N_2O_4 = 4.50×10^{-2} moles/litre and NO_2 = 1.61×10^{-2} moles/litre. What is the value of equilibrium constant?*

Solution.

$$K = \frac{[NO_2]^2}{[N_2O_2]}$$

$$= \frac{(1.61 \times 10^{-2})^2\,(\text{moles/litre})^2}{(4.50 \times 10^{-2})\,(\text{moles/litre})^2}$$

$$= 5.76 \times 10^{-3} \text{ moles/litre.}$$

Example 8. *For the reaction, N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$(g), the partial pressures of N_2 and H_2 are 0.80 and 0.40 atmosphere respectively at equilibrium. The total pressure of the system is 2.80 atmospheres. What is K_p for the above reaction?*

Solution. The reaction is

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

We are given that at equilibrium

$$P_{N_2} = 0.80 \text{ atmosphere}$$

$$P_{H_2} = 0.40 \text{ atmosphere}$$

$$P_{N_2} + P_{H_2} + P_{NH_3} = 2.80 \text{ atmosphere}$$

$$\therefore \quad P_{NH_3} = 2.80 - (0.80 + 0.40)$$

$$= 1.60 \text{ atmosphere.}$$

Applying the law of chemical equilibrium, we get

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}} = \frac{(1.60)^2}{0.80 \times (0.40)^3}$$

$$= 50.0 \text{ atm}^{-2}.$$

Example 9. *Two moles of PCl_5 were heated to 327°C in a closed two litres vessel and when equilibrium was achieved, PCl_5 was found to be 40% dissociated into PCl_3 and Cl_2. Calculate the equilibrium constants, K_p and K_c for this reaction.*

Solution. PCl_5 dissociates at $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Initial amount of PCl_5 = 2 moles (Given)

Percentage dissociation at equilibrium = 40%

$$\therefore \; PCl_5 \text{ dissociated at equilibrium} = \frac{40}{100} \times 2 = 0.8 \text{ mole}$$

∴ Amounts of PCl_5, PCl_3 and Cl_2 at equilibrium will be

$$PCl_5 = 2 - 0.8 = 1.2 \text{ moles}$$

$$PCl_3 = 0.8 \text{ mole}$$

$$Cl_2 = 0.8 \text{ mole}$$

[∵ 1 mole of PCl_5 on dissociation gives 1 mole of PCl_3 and 1 mole of Cl_2]

As the volume of the vessel is 2 litres, the molar concentrations at equilibrium will be

$$[PCl_5] = \frac{1.2}{2} = 0.6 \text{ mol L}^{-1}$$

$$[PCl_3] = \frac{0.8}{2} = 0.4 \text{ mol L}^{-1}$$

and

$$[Cl_2] = \frac{0.8}{2} = 0.4 \text{ mol L}^{-1}$$

Applying the law of chemical equilibrium to the dissociation equilibrium, we get

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.4 \times 0.4}{0.6}$$

$$= 0.267 \text{ mol L}^{-1}$$

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

Here $\quad \Delta n = n_p - n_r = 2 - 1 = 1$

$$\therefore \quad K_p = K_c (RT)$$

But $\quad T = 327 + 273 = 600 \text{ K (Given)}$

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

$$\therefore \quad K_p = 0.267 \times 0.0821 \times 600$$

$$= 13.15 \text{ atmosphere}$$

Example 10. *The equilibrium constant for the reaction* $CH_3COOH + C_2H_5OH \leftrightharpoons CH_3COOC_2H_5 + H_2O$ *is 4.0 at 25°C. Calculate the weight of ethyl acetate that will be obtained when 120 g of acetic acid is reacted with 92 g of alcohol.*

Solution. The given reaction is $CH_3COOH + C_2H_5OH \leftrightharpoons CH_3COOC_2H_5 + H_2O$

Applying the law of chemical equilibrium, we get

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} \qquad ...(i)$$

Here we are given that $K_c = 4.0$

Initial amount of acetic acid (CH_3COOH) = 120.0 g

$$= \frac{120.0}{60} \text{ moles} = 2 \text{ moles} \qquad (\because \text{ Mol. wt. of } CH_3COOH = 60)$$

Initial amount of ethyl alcohol (C_2H_5OH) = $92 \text{ g} = \frac{92}{46} = 2$ moles $(\because \text{ Mol. wt. of } C_2H_5OH = 46)$

Suppose ethyl acetate ($CH_3COOC_2H_5$) obtained at equilibrium = x moles and the volume of the reaction mixture at equilibrium is V litres. Then we will have

$$CH_3COOH + C_2H_5OH \leftrightharpoons CH_3COOC_2H_5 + H_2O$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial amounts	2 moles	2 moles	0	0
Amounts at eqm.	$(2 - x)$	$(2 - x)$	x	x (moles)
Molar concs. at eqm.	$(2 - x)/V$	$(2 - x)/V$	x/V	x/V

Putting the values in equation (i) above, we get

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

Taking the square root of both sides, we get

$$2 = \frac{x}{(2-x)}$$

or $$4 - 2x = x$$

or $$3x = 4 \text{ or } x = \frac{4}{3} = 1.33 \text{ moles.}$$

Hence, the amount of ethyl acetate present at equilibrium = 1.33 moles.

Amount in grams = 1.33 × 88 g = 117.04 g.

Example 11. *0.1 mole of* PCl_5 *is vaporised in a litre vessel at 260°C. Calculate the concentration of* Cl_2 *at equilibrium, if the equilibrium constant for the dissociation of* PCl_5 *is 0.0414.*

Solution. Suppose the concentration of Cl_2 at equilibrium is x moles/litre. Then we will have

$$PCl_5 \leftrightharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2
Initial conc.	0.1 mole	0	0
Conc. at eqm. (moles/litre)	$(0.1 - x)$	x	x

Applying the law of chemical equilibrium, we get

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

Here $$K_c = 0.0414$$

∴ $$0.0414 = \frac{x \times x}{(0.1 - x)}$$

or $$\frac{x^2}{0.1 - x} = 0.0414$$

or $x^2 + 0.0414x - 0.00414 = 0$

$$x = \frac{-0.04140 \pm \sqrt{(0.0414)^2 - 4 \times 1\,(-0.00414)}}{2} \qquad \left[\text{Using the formula } x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right]$$

$$= \frac{-0.0414 \pm \sqrt{0.0017 + 0.01656}}{2}$$

$$= \frac{-0.0414 \pm \sqrt{0.01826}}{2} = \frac{-0.0414 \pm 0.135}{2}$$

$$= 0.0468 \text{ mol L}^{-1}.$$

(The negative value of x is meaningless and rejected)

Thus, the concentration of Cl_2 at equilibrium will be 0.0468 mol L^{-1}.

Example 12. *At 448°C, the equilibrium constant (K_c) for the reaction: $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$ is 50.5. Predict the direction in which the reaction will proceed to reach equilibrium at 448°C, if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2 and 3.0×10^{-2} mol of I_2 in a 2.0 L container.*

Solution. The initial concentrations are computed as under:

$$[HI] = \frac{2.0 \times 10^{-2}}{2} \text{ mol L}^{-1} = 1.0 \times 10^{-2} \text{ mol L}^{-1}$$

$$[H_2] = \frac{1.0 \times 10^{-2}}{2} \text{ mol L}^{-1} = 0.5 \times 10^{-2} \text{ mol L}^{-1}$$

$$[I_2] = \frac{3.0 \times 10^{-2}}{2} \text{ mol L}^{-1} = 1.5 \times 10^{-2} \text{ mol L}^{-1}$$

Concentration quotient,

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

$$= \frac{(1.0 \times 10^{-2} \text{ mol L}^{-1})^2}{(0.5 \times 10^{-2} \text{mol L}^{-1})\,(1.5 \times 10^{-2} \text{ mol L}^{-1})}$$

$$= 1.33$$

Since, Q < K, the reaction will proceed in the forward direction to attain equilibrium so that Q becomes equal to K.

Example 13. *AB_2 dissociates as: $AB_2\ (g) \rightleftharpoons AB\ (g) + B\ (g)$. If the initial pressure is 500 mm of Hg and the total pressure at equilibrium is 700 mm of Hg, calculate K_p for the reaction.*

Solution. After dissociation, suppose the decrease in the pressure of AB_2 at equilibrium is P mm. Then

	$AB_2\ (g)$	$\rightleftharpoons$	$AB\ (g)$ +	$B\ (g)$
Initial pressures:	500 nm		0	0
Pressure at eqm:	(500 – P) mm		P mm	P mm

$\therefore$ Total pressure at equilibrium = 500 – P + P + P

$$= 500 + P \text{ mm}$$

$$500 + P = 700 \text{ (Given) or } P = 200 \text{ mm}$$

Hence, at equilibrium $P_{AB_2} = (500 - 200)$ mm = 300 mm,

$$P_{AB} = 200 \text{ mm}, \; P_B = 200 \text{ mm}$$

$$\therefore \qquad K_p = \frac{P_{AB} \times P_B}{P_{AB_2}} = \frac{200 \times 200}{300} = 133.3 \text{ mm}$$

Example 14. *Under what pressure must an equimolar mixture of PCl_3 and Cl_2 be placed at 250°C in order to obtain PCl_5 at 1 atm? (K_p for dissociation of $PCl_5 = 1.78$).*

Solution.

Suppose partial pressure of PCl_3 at equilibrium = P atm

Then partial pressure of Cl_2 at equilibrium = P atm

Partial pressure of PCl_5 at equilibrium = 1 atm

For dissociation of PCl_5, $PCl_5 \leftrightharpoons PCl_3 + Cl_2$

$$K_p = 1.78 = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{P \times P}{1} = P^2$$

$$\therefore \quad P = \sqrt{1.78} = 1.33 \text{ atm}$$

$$\therefore \quad \text{Total pressure} = P_{PCl_5} + P_{PCl_3} + P_{Cl_2}$$

$$= 1 + 1.33 + 1.33 = 3.66 \text{ atm}$$

PROBLEMS FOR PRACTICE

1. How much PCl_5 must be added to a one litre vessel at 250°C in order to obtain a concentration of 0.1 mole of chlorine? Equilibrium constant for the dissociation of PCl_5 at 250°C is 0.0414.

[**Ans.** 0.3415 mole]

2. If 1 mole of acetic acid and 1 mole of ethyl alcohol are mixed and the reaction proceeds to equilibrium, the concentrations of acetic acid and water are found to be 1/3 and 2/3 mole respectively. If 1 mole of ethyl acetate and 3 moles of water are mixed, how much ester is present when equilibrium is reached?

[**Ans.** 0.47 mole]

3. The equilibrium composition for the reaction is

$$\underset{0.20}{PCl_3} + \underset{0.10}{Cl_2} \leftrightharpoons \underset{0.40 \text{ mole/litre}}{PCl_5}$$

What will be the equilibrium concentration of PCl_5 on adding 0.10 mole of Cl_2 at the same temperature?

[**Hint.** First calculate $K_c = \dfrac{4}{0.20 \times 0.10}$

New initial conc. of $Cl_2 = 0.10 + 0.10$

$= 0.20$ mole

New initial concs. of PCl_3 and PCl_5 remain the same.

Suppose x mole of PCl_3 reacts, the new equilibrium concs. will be $[PCl_3] = 0.20 - x$, $[Cl_2] = 0.20 - x$ and $[PCl_5] = 0.40 + x$.

Put the values in $K_c = \dfrac{[PCl_5]}{[PCl_3][Cl_2]}$ and calculate x.] [**Ans.** 0.45 mol L^{-1}]

4. Calculate the equilibrium constants K_p and K_c for the reaction

$CO\,(g) + 1/2\, O_2\,(g) \leftrightharpoons CO_2\,(g)$

Given that the partial pressures at equilibrium in a vessel at 3000 K are $P_{CO} = 0.4$ atm, $P_{CO_2} = 0.6$ atm and $P_{O_2} = 0.2$ atm. [**Ans.** $K_p = 3.356 \text{ atm}^{-1/2}$, $K_c = 52.67$]

5. Calculate the degree of dissociation of HI at 450°C, if the equilibrium constant for the dissociation reaction is 0.263.

   [**Hint.** Suppose we start with 1 mole of HI and x is the degree of dissociation. Then at equilibrium $[HI] = (1 - x)/V$, $[H_2] = x/2V$, $[I_2] = x/2V$ moles per litre. Put the values in the equation $K_c = \dfrac{[H_2][I_2]}{[HI]^2}$ and calculate x.]

   [**Ans.** 0.506]

6. One mole of pure ammonia was injected into a one litre flask at a certain temperature. The equilibrium mixture was then analysed and found to contain 0.30 mole of H_2. Calculate (*i*) the concentration of N_2 and (*ii*) the concentration of NH_3 at equilibrium. [**Ans.** (*i*) 0.10 mole, (*ii*) 0.80 mole]

7. 1.5 moles of PCl_5 are heated at constant temperature in a closed vessel of 4 litres capacity. At the equilibrium point, PCl_5 is 35% dissociated into PCl_3 and Cl_2. Calculate the equilibrium constant.

   [**Ans.** 0.071]

8.11 FACTORS AFFECTING THE STATE OF EQUILIBRIUM

Le Chatelier's Principle. A chemical equilibrium is governed by the following factors:

(*i*) Concentration
(*ii*) Temperature
(*iii*) Pressure

Le Chatelier

The equilibrium is disturbed when the conditions under which it is occurring are altered. The combined effect of all the above factors is studied by one principle known as *Le Chatelier's Principle.* It is stated as:

If a system at equilibrium is subjected to a change in concentration, pressure or temperature the equilibrium shifts in such a direction so as to minimise or undo the effect of the change imposed.

This principle helps us to predict qualitatively the effect of change in the concentration of the reactants or products, temperature and pressure on any reversible reaction in equilibrium.

Let us apply the Le Chatelier's principle to study a few important equilibria.

1. **Effect of change in concentration.** The effect of change in concentration may be illustrated by the following reaction in equilibrium.

$$\underset{\text{Pale yellow}}{FeCl_3\,(aq)} + \underset{\text{Colourless}}{3NH_4CNS\,(aq)} \rightleftharpoons \underset{\text{Dark red}}{Fe(CNS)_3\,(aq)} + \underset{\text{Colourless}}{3NH_4Cl\,(aq)}$$

Suppose, we add a few drops of concentrated ferric chloride solution to this equilibrium. Then equilibrium is disturbed and is under stress.

According to Le Chatelier's principle the equilibrium is displaced in that direction which tends to minimise the effect of added $FeCl_3$. And this can be minimised when Fe^{+++} ion starts combining with thiocyanate ion, thus, the added $FeCl_3$ will shift the equilibrium towards right hand side forming the coloured complex ion. This is indicated by the dark red colour due to the formation of more of ferric thiocyanate.

Similarly, if we add a few drops of concentrated ammonium thiocyanate solution to the above equation the colour again deepens owing to the formation of more ferric thiocyanate. This change is in accordance with Le Chatelier's principle.

Now, suppose a small amount of solid ammonium chloride is added to the above equilibrium. The equilibrium is disturbed, i.e, it is under stress or strain. According to the Le Chatelier's principle, the equilibrium is shifted in that direction which tends to minimise the effect. And this can be minimised if NH_4Cl starts combining with ferric thiocyanate to form ammonium thiocyanate (colourless) and $FeCl_3$ (pale yellow). Thus, added NH_4Cl will shift the equilibrium towards left. This is indicated by the colour of the solution, which becomes less dark.

Thus, we see that the system gets displaced towards the right or towards the left accordingly as the concentration of a substance occurring on the left hand side or the right hand side is increased.

Some examples from everyday life. If the concentration in any one part of a system in equilibrium is disturbed, it no longer remains in equilibrium and re-adjusts its concentration to re-establish the equilibrium. The following examples illustrate this point.

(*i*) *We sweat more on a humid day but it evaporates when we sit under the fan*. More sweating takes place because the surrounding air has large amount of water vapour and our skin cannot lose more to it. The fan removes the humid air and evaporation starts from the skin.

(*ii*) *Clothes dry quicker when there is a breeze or we keep on shaking it.* This is because water vapour of the nearby air is removed and cloth loses more water vapour to re-establish equilibrium with the surrounding air.

(*iii*) *Transport of oxygen by haemoglobin in blood*. Oxygen breathed in combines with the haemoglobin in the lungs according to the equilibrium.

$$Hb\ (s) + O_2\ (g) \rightleftharpoons HbO_2\ (s)$$

When it reaches the tissues, the pressure of oxygen there is low. To re-adjust the equilibrium, oxyhaemoglobin gives up oxygen. When it returns to lungs where the pressure of oxygen is high, more of oxyhaemoglobin is formed.

(*iv*) *Tooth decay by sweets*. Our teeth are coated with an enamel of an insoluble substance known as hydroxypatite, $Ca_5(PO_4)_3(OH)$. It exists in equilbrium with its ions as follows:

$$Ca_5(PO_4)_3(OH)\ (s) \xrightleftharpoons[\text{Remineralisation}]{\text{Demineralisation}} 5Ca^{2+} + 3PO_4^{3-} + OH^-$$

The forward reaction involving dissociation is called demineralisation and the backward reaction involving formation is called remineralisation. If we do not brush our teeth after eating sweets, the sugar gets fermented on the teeth to produce H^+ ions which combine with the OH^- ions shifting the equilibrium in the forward direction thereby causing tooth decay.

Thus in general, *if in a reaction in equilibrium, the concentration of any reactant is increased, the equilibrium shifts in the forward direction. On the other hand, if the concentration of any product is increased, the equilibrium shifts in the backward direction.*

2. Effect of change in temperature. There are two opposing reactions in a chemical equilibrium in which one favours the formation of products and the other reactants. If in one of these reactions heat is evolved (exothermic) then, in other reaction heat is absorbed (endothermic). This is according to the law of conservation of energy.

For example, consider the equilibrium

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad \Delta H = +58.6\ \text{kJ}$$

It is clear from the above equilibrium that the reaction which favours the product (NO_2) is absorbing heat (endothermic). Therefore, the opposing reaction which favours the reactant (N_2O_4) must be exothermic. Let us suppose the temperature is increased in the above equilibrium. Then, the equilibrium is disturbed. Now according to Le Chatelier's principle, the equilibrium will shift in that direction which tends to undo or minimise the effect of heat. And this can be minimised by shifting in a direction where the heat is absorbed, *i.e.*, in the forward direction. Therefore, the equilibrium will shift in favour of NO_2. Hence, high temperature will favour the dissociation of N_2O_4 into NO_2.

If the temperature on the system is decreased (*i.e.*, cooled), the equilibrium will shift in the direction which tends to produce heat. This is in backward direction, *i.e.*, in the favour of N_2O_4. Therefore, low temperature will decrease the dissociation of N_2O_4.

Hence, in endothermic reactions, the forward reaction is favoured by high temperature and in exothermic reactions, the forward reaction is favoured by low temperature.

3. **Effect of change in pressure.** If a system in equilibrium involves only solids or only liquids, then pressure has no significant effect on the equilibrium.

   However, if a system in equilibrium involves gases then pressure plays an important role and the concentrations of all the components can be altered by changing the pressure.

   Let us consider the gaseous reaction:

$$\underbrace{\underset{\text{1 mole}}{N_2(g)} + \underset{\text{3 moles}}{3H_2(g)}}_{\text{4 moles}} \rightleftharpoons \underset{\text{2 moles}}{2NH_3(g)} \qquad \Delta H = -93.6 \text{ kJ}$$

   It is clear from the above reaction that the formation of NH_3 (forward reaction) is accompanied by a decrease in the number of moles.

   Let us increase pressure in the above equilibrium. According to Le Chatelier's principle, the equilibrium will shift in that direction which tends to minimise the effect of pressure. This can be minimised only if volume, *i.e.*, number of moles decrease and decrease in volume is in forward direction. Thus, high pressure will favour the formation of NH_3.

   Low pressure always favours those reactions which occur with increase in total number of moles but high pressure favours those reactions which occur with decrease in total number of moles. Pressure has no effect on equilibrium reactions which take place with no change in total number of moles.

4. **Effect of addition of inert gas.** If an inert gas is added to a system in equilibrium at constant volume, the concentration of each species will remain unchanged. Similarly, the partial pressures of gaseous species will remain unchanged (although total pressure will increase). Thus, the equilibrium will not be affected. But the situation is different when the reaction is at equilibrium at constant pressure. On adding an inert gas, total volume of the system will increase. This will decrease the concentrations and the equilibrium point will be shifted in such a case so as to increase the number of moles per unit volume.

5. **Effect of catalyst.** A catalyst increases the rates of forward and the backward reaction equally by lowering the activation energies of the two reactions to the same extent. Since the ratio of the two rates remains the same on addition of a catalyst, no net change occurs in the relative amounts of the reactants and products present at the equilibrium. *Thus, the addition of a catalyst only enables the system to achieve equilibrium in the shorter period of time but does not affect the position of the equilibrium.*

8.11.1 Application of Le Chatelier's Principle to Reactions of Industrial Importance

1. **Formation of SO_3** (Contact process for H_2SO_4)

$$\underbrace{\underset{\text{2 vols}}{2SO_2\ (g)} + \underset{\text{1 vol}}{O_2\ (g)}}_{\text{3 vols}} \rightleftharpoons \underset{\text{2 vols}}{2SO_3\ (g)} \qquad \Delta H = -98 \text{ kJ}$$

   The formation of SO_3 from SO_2 and O_2 is an exothermic reaction. It is accompanied by a decrease in volume. The reverse reaction must be endothermic.

   (*i*) *Effect of Temperature.* If temperature is raised (by applying heat to the system) then system will be under stress. According to the Le Chatelier's principle, the equilibrium will shift in that direction which tends to minimise the effect of increased heat. And this can be reduced in the direction of the reaction that proceeds with absorption of heat. But a reaction that lowers temperature is endothermic, it is the reverse of the above exothermic reaction, *i.e.*,

$$2SO_3 \rightarrow 2SO_2 + O_2 - \text{heat energy.}$$

   In other words, the effect of raising the temperature on the above equilibrium is to **diminish** the yield of SO_2 and to **increase** the concentration of the reactants ($SO_2 + O_2$).

(*ii*) *Effect of Concentration.* If the concentration of SO_2 or O_2 or both on the system is increased, it imposes a stress. According to Le Chatelier's principle to minimise or to counteract this stress more SO_3 will be formed. Thus, the equilibrium is shifted towards the products.

(*iii*) *Effect of Pressure.* The formation of SO_3 is accompanied by decrease in volume. If the pressure on the system is increased the equilibrium will shift in that direction which tends to minimise the effect of increased pressure. This stress is due to increased pressure and can be relieved if volume is decreased. In this, equilibrium volume is decreased in the forward direction. Hence, equilibrium will shift towards the right side which results in lower volume. Thus, the formation of SO_3 is favoured by high pressure.

2. Formation of nitric oxide. Consider the formation of nitric oxide by direct combination of nitrogen and oxygen. The thermochemical equation for this reaction is

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g) \qquad \Delta H = +180.7 \text{ kJ}$$

(*i*) *Effect of Temperature.* The forward reaction resulting in the formation of NO is endothermic. If the temperature of the system is increased, then according to Le Chatelier's principle, the equilibrium will shift in that direction in which absorption of heat occurs *i.e.*, in the forward direction. Therefore, the formation of NO will be favoured by high temperature. Usually, a temperature of 2773 K is employed.

(*ii*) *Effect of Pressure.* In this equilibrium reaction, no change in the number of moles takes place since one mole of N_2 combines with one mole of O_2 to produce 2 moles of NO. Hence, pressure has no effect on this equilibrium reaction.

(*iii*) *Effect of Concentration.* A high concentration of N_2 and O_2 will favour the formation of nitric oxide.

3. Formation of ammonia (Haber process). The chemical equilibrium taking place in this process is

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \qquad \Delta H = -92.5 \text{ kJ}$$

(*i*) *Effect of Temperature.* Lower the temperature, greater would be the yield of ammonia. However, if the temperature is kept low the reaction will take a long time to attain equilibrium state. Therefore, a compromise is to be made for economical process. Usually, a temperature of 75 K is employed. At this temperature, the yield of NH_3, of course, is less than that at a lower temperature. But from industry point of view, it is rather advisable to get a poorer yield than to waste time unnecessarily. Finely divided iron is used as a catalyst to achieve the equilibrium rapidly, molybdenum (promoter) is used to increase the efficiency of the catalyst.

(*ii*) *Effect of Pressure.* Higher the pressure, greater would be yield of ammonia. Usually a pressure of 350 atmospheres is employed.

(*iii*) *Effect of Concentration.* According to Le Chatelier's principle, an increase in the concentration of reactants (N_2 and H_2) would shift the equilibrium in that direction in which the reactants are consumed, *i.e.*, in the forward direction. In other words, formation of NH_3 would be favoured. Moreover, NH_3 formed should be continuously removed by liquefaction so that equilibrium shifts in the forward direction.

4. Bosch process for the manufacture of hydrogen. In this process, H_2 is produced from water gas and steam according to the following equilibrium reaction:

$$\underbrace{\underset{\text{Water gas}}{H_2\,(g) + CO\,(g)} + \underset{\text{Steam}}{H_2O\,(g)}}_{\text{3 moles}} \rightleftharpoons \underbrace{2H_2\,(g)}_{\text{3 moles}} + CO_2\,(g);\ \Delta H = +42.0 \text{ kJ}$$

Effects of change in temperature, pressure and concentration are described as under:

(*i*) *Effect of Temperature.* The forward reaction being endothermic is favoured by high temperature. Usually a temperature of 673–723 K is used.

(*ii*) *Effect of Pressure.* Since there is no change in the total number of moles in this reversible reaction, pressure has no effect on this equilibrium reaction.

(*iii*) *Effect of Concentration.* Formation of CO_2 and H_2 is favoured by high concentration of water gas as well as steam.

Physical equilibria. Some applications of the Le Chatelier's principle to physical equilibria are discussed below:

(*i*) **Water-Vapour equilibrium – Vaporisation of water**

$$\underset{\text{Less volume}}{\text{Water}} + \text{Heat} \rightleftharpoons \underset{\text{More volume}}{\text{Water vapour}}$$

(*ii*) **Ice-Water equilibrium – Melting ice**

$$\underset{\text{More volume}}{\text{Ice}} + \text{Heat} \rightleftharpoons \underset{\text{Less volume}}{\text{Water}}$$

The change of ice into water is an endothermic and reversible process. The reaction involves decrease in volume, *i.e.*, when ice melts into water, volume decreases. Hence,

(*a*) On increasing the pressure on this system, the equilibrium tends to shift in a direction in which volume decreases, *i.e.*, equilibrium shifts to the right. Thus, increasing pressure favours change of ice into water, *i.e.*, more of ice melts.

(*b*) Since the change of ice into water is an endothermic process, increase in temperature tends to shift the equilibrium to the right, *i.e.*, on increasing the temperature more ice melts into water.

QUICK SCAN (FOR REVISION)

1. Reactions which can proceed in both the directions are called reversible reactions.
2. A state in which the rate of reversible reaction in one direction equals the rate in the other direction is called chemical equilibrium.
3. A reversible reaction never goes to completion in any one direction if performed in a closed vessel.
4. After equilibrium is attained, the concentrations of the different reactants and products remain constant (temperature and pressure remaining constant).
5. The vapour pressure of a liquid is constant at a constant temperature because it is measured at equilibrium when the rate of evaporation is equal to the rate of condensation.
6. According to Henry's law, the mass of a gas dissolved in a given mass of a solvent is directly proportional to the pressure of the gas above the solvent, *i.e.*, $m \propto p$ or $m = kp$, where k is Henry's constant.
7. Equilibrium is dynamic in nature and not static, *i.e.*, after attainment of equilibrium, the process does not stop but the rate of forward reaction = the rate of backward reaction.
8. Magnitude of equilibrium constant represents the extent to which the forward reaction proceeds before equilibrium is attained.
9. Equilibrium cannot be established if:
   (*i*) a product is gaseous and escapes *e.g.*,
   $CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g)$ in an open vessel.
   (*ii*) a product separates out as a solid *e.g.*,
   $AgNO_3\ (aq) + KCl\ (aq) \rightarrow AgCl\ (s) \downarrow + KNO_3$
10. NO_2 is colourless at 0°C (273 K) but has brown colour at higher temperature because at 0°C, it exists as N_2O_4 but at higher temperature as
    $$N_2O_4 \rightleftharpoons 2NO_2$$
11. A catalyst does not alter the state of equilibrium. It increases the speed of forward and backward reaction to the same extent and helps to attain the equilibrium quickly.
12. Law of mass action was put forward by Guldberg and Waage.
13. Active mass is the same thing as molar concentration. Active mass of a solid is always taken as unity irrespective of the quantity.

14. Equilibrium constant in terms of pressure (K_p) and in terms of concentration (K_c) are related as $K_p = K_c(RT)^{\Delta n}$ where $\Delta n = (n_p - n_r)$.

15. The ratio of velocity constants of forward and backward reactions is called the equilibrium constant.

16. For the equilibrium $xA + yB \rightleftharpoons pC + qD$, expression for equilibrium constant can be written as

$$K_c = \frac{[C]^p\,[D]^q}{[A]^x\,[B]^y}$$

17. In terms of partial pressures, the expression for equilibrium constant is

$$K_p = \frac{P_C^p\,P_D^q}{P_A^x\,P_B^x}$$

18. Larger is the value of K, greater is the reaction towards the product side.

19. Equilibrium constant is constant for a particular reaction at constant temperature and does not depend upon the concentration of the reactants.

20. If the equilibrium constant for the reaction

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

is 4, then for the reverse reaction its value is 1/4.

21. If the equilibrium constant for the reaction

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ is K, then for

$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$, it is $\sqrt{K}$ and for

$2N_2 + 6H_2 \rightleftharpoons 4NH_3$, it is K^2.

22. The value of equilibrium constant for endothermic reaction increases with increase in temperature whereas for exothermic reaction, it decreases with increase of temperature.

23. Effect of temperature on equilibrium constant is given by van't Hoff equation, viz.,

$$\log \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H}{2.303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

24. The expression for equilibrium constant, K_p for the reaction

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

is $K_p = P_{CO_2}$ $\quad$ ($\because$ active mass of a solid = 1)

25. The unit of equilibrium constant depends upon the nature of reaction. For the reaction $aA + bB \rightleftharpoons xX + yY$, K_c has the unit $(mol\ L^{-1})^{(x+y)-(a+b)}$ and K_p has the unit $(atm)^{(x+y)-(a+b)}$. Strictly speaking K is dimensionless.

EXERCISES

Very Short Answer Type Questions

1. A crystal of common salt of a given mass is kept in its aqueous solution. After 24 hours, its mass remains the same. Is the crystal in equilibrium with the solution?
2. Why don't the chemical reactions go to completion?
3. What is meant by homogeneous and heterogeneous equilibria?
4. What is meant by a reversible reaction?
5. State Le Chatelier's principle.
6. Which of the following are at equilibrium?
   (*i*) Bhakra dam and the lake behind it. (Water level is constant, though a river flows into lake).
   (*ii*) Mercury and mercury vapour in a thermometer at constant temperature.
7. State the law of mass action.
8. How does the magnitude of equilibrium constant tell about the extent of reaction?
9. What is meant by equilibrium?
10. What is the relation between K_p and K_c?
11. Define equilibrium constant.
12. Write the expression for equilibrium constant K_p for the reaction
    $3Fe\,(s) + 4H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s) + 4H_2\,(g)$
13. Give the example from everyday life in which there is gas-solution equilibrium.
14. What is the effect of increasing pressure on the following equilibrium: $N_2 + 3H_2 \rightleftharpoons 2NH_3$
15. Does the value of equilibrium constant change on adding catalyst?
16. Which measurable property becomes constant in water-vapour equilibrium at a constant temperature?
17. What are the conditions for getting maximum yield of NH_3 by Haber process?

Short Answer Type Questions

1. A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.
   (*i*) What is the initial effect of the change on vapour pressure?
   (*ii*) How do the rates of evaporation and condensation change initially?
   (*iii*) What happens when equilibrium is restored finally and what will be the final vapour pressure?
2. Explain the term chemical equilibrium.
3. Briefly discuss an experiment to show that equilibrium can be approached from either direction.

4. How will you show that the chemical equilibrium is of dynamic nature?
5. Enlist the general characteristics of an equilibrium involving a physical process.
6. What are the characteristics associated with equilibrium state?
7. For the reaction:

$$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g):$$

$$\Delta H = -198 \text{ kJ},\ K_p = 40.5 \text{ atm}^{-1} \text{ at } 900 \text{ K}$$

   (*i*) What is the expression for the equilibrium constant for the reaction?

   (*ii*) At 300 K, will K_p be greater than, less than or equal to K_p at 900 K?
8. What are the characteristics of chemical equilibrium?
9. Discuss the role of a catalyst in influencing the equilibrium state of a chemical reaction.
10. Why are chemical equilibria called dynamic equilibria?

Long Answer Type Questions

1. State Le Chatelier's principle. Discuss its application in the manufacture of NH_3 by Haber process.
2. State the law of mass action. Derive the expression for K, the equilibrium constant for the reaction:

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

3. Derive the relationship between K_p and K_c.
4. (*i*) The Haber process for the manufacture of ammonia is based on the equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (\Delta H \text{ negative})$$

   How is composition of equilibrium mixture affected by:

   (*a*) a change in temperature?

   (*b*) a change in pressure?

   (*c*) the presence of catalyst?

   (*d*) a change in concentration of one of the reactants?

   (*ii*) Write an expression for the equilibrium constant for the above reaction in terms of partial pressure.
5. Write the expression showing the equilibrium constant for the dissociation of N_2O_4.
6. Synthesis of ammonia by the Haber process is an exothermic reaction:

   (*i*) Write the equation for the formation of ammonia from hydrogen and nitrogen.

   (*ii*) What is meant by the equilibrium constant of the reaction? Write an expression for the equilibrium constant for the synthesis of ammonia.

   (*iii*) What is the effect of temperature and pressure on the yield of ammonia? Give reasons for your answer.
7. The following equation represents the reaction between N_2 and H_2:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 22.4 \text{ kcals}$$

   (*i*) What type of chemical reaction is this?

   (*ii*) Is it endothermic or exothermic?

   (*iii*) Write an expression for the equilibrium constant in terms of pressure.

   (*iv*) State the law on which your answer to (*iii*) is based.

   (*v*) What catalyst is generally used in the manufacture of NH_3 in the above process?

   (*vi*) Is it homogenous or heterogeneous?

   (*vii*) Why the catalyst used is in a finely divided state?
8. How is the solubility of a gas in a liquid affected by pressure? Explain it in terms of Le Chatelier's principle.
9. Sulphur trioxide gas is obtained as shown by the reaction:

$$2SO_2\ (g) + O_2\ (g) \rightleftharpoons 2SO_3\ (g)$$

   (*i*) Write the equation of equilibrium constant for the reaction using concentration terms. Explain all the terms involved.

   (*ii*) State Le Chatelier's principle.

   (*iii*) Predict the changes in the composition of the equilibrium mixture resulting from:

   (*a*) An increase in the total pressure.

   (*b*) The removal of some of the SO_3.

   (*c*) A rise in temperature.
10. (*i*) In a chemical reaction at equilibrium what can be said of the rates of the opposing reactions?

   (*ii*) If 'α' is the degree of dissociation of HI at equilibrium, what will be the total number of moles present at equilibrium in terms of 'α'?

   (*iii*) For the synthesis of ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

   When equilibrium is reached, the total pressure is increased by adding helium gas without altering temperature and volume of the reaction system. What will be the value of new equilibrium constant? What will happen to the relative values of $[NH_3]$, $[N_2]$ and $[H_2]$? Why?

ANSWERS TO SELECTED QUESTIONS

Very Short Answers Type Questions

1. Yes
6. (*ii*)
8. Greater value of K indicates the greater extent of reaction in the forward direction.
10. $K_p = K_c(RT)^{\Delta n(g)}$
12. $K_p = P_{H2O}/P_{H2}$
14. Equilibrium will shift in the forward direction forming more ammonia.
15. No
16. Vapour pressure
17. High concentration of N_2 and H_2, low temperature, high pressure.

COMPETITION FILE

SUBJECTIVE PROBLEMS

Problem 1. *What is the role of catalyst in case of reversible reactions?*

Solution. A catalyst does not change the equilibrium point of the reaction. It affects the forward and backward reactions to the same extent. But it is helpful in the quick attainment of the equilibrium point. If the product formed is removed regularly, the equilibrium is attained in shorter time and the yield increases.

Problem 2. *What is the effect of addition of an inert gas on the position of equilibrium at: (i) constant volume, (ii) constant pressure?*

Solution.

(*i*) Addition of an inert gas at constant volume does not affect the position of equilibrium.

(*ii*) Addition of an inert gas at constant pressure will favour the direction of reaction where there is increase in the number of moles.

Problem 3. *In which of the following cases equilibrium can be attained in an open vessel? Explain your answer.*

(*i*) *Decomposition of* $CaCO_3$.

(*ii*) *Formation of an ester.*

(*iii*) *Formation of HI from* H_2 *and* I_2.

Solution.

(*i*) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

Equilibrium can be attained only in a closed vessel. In an open vessel, one of the product (CO_2) escapes and the reverse reaction cannot take place.

(*ii*) $CH_3COOH\,(l) + C_2H_5OH\,(l) \rightarrow CH_3COOC_2H_5\,(l) + H_2O\,(l)$

The reactants (acetic acid and ethyl alcohol) as well as the products (ethyl acetate and water) are all liquids. So, the equilibrium can be attained in the open vessel.

(*iii*) $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$

Since the reactants and product are all gaseous, equilibrium cannot be attained in an open vessel.

Problem 4. *Discuss the effect of addition of inert gas on the position of equilibrium.*

Solution. The addition of inert gas will cause a decrease in the partial pressure of gaseous reactants and products, so that the total pressure due to the reacting gases will decrease. To maintain a constant pressure, the reaction will proceed in a direction where the number of moles is increased. Thus, the addition of inert gas will favour the reaction that results in an increase in the number of moles. For any general reaction

$$aA + bB \rightleftharpoons mM + nN$$

(*i*) If $(m + n) > (a + b)$, the addition of inert gas will favour the formation of products, *i.e.*, forward reaction.

(*ii*) If $(m + n) < (a + b)$, the addition of inert gas will favour the formation of the reactants, i..e, backward reaction.

(*iii*) If $(m + n) = (a + b)$, the addition of an inert gas will have no effect on the position of equilibrium.

Problem 5. *How will you predict the direction of a reaction from the known value of its concentration quotient (Q) and equilibrium constant (K)?*

Solution.

(*i*) When Q < K, the reaction will proceed in the forward direction till the state of equilibrium is reached.

(*ii*) When Q > K, the reaction will proceed in the backward direction till the state of equilibrium is reached.

(*iii*) When Q = K, the reaction is in a state of equilibrium. It will proceed with the same rate in both forward and the backward directions.

Problem 6. *An equilibrium mixture at 300 K contains* N_2O_4 *and* NO_2 *at 0.28 and 1.1 atm pressure respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the two gases.*

Solution. $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

$$P_{NO_2} = 1.1 \text{ atm},\ P_{N_2O_4} = 0.28 \text{ atm}$$

$$P_{Total} = 1.1 + 0.28 = 1.38 \text{ atm}$$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(1.1)^2}{0.28} = \frac{121}{28}$$

At constant temperature, when volume is doubled, the pressure is reduced to one half.

Therefore, new pressure $= \dfrac{1.38}{2} = 0.69$ atm.

Let the new partial pressure of N_2O_4 be P atm.

∴ Partial pressure of NO_2, $P_{NO_2} = (0.69 - P)$ atm

$$\therefore \qquad K_p = \frac{(0.69-P)^2}{P} = \frac{121}{28}$$

or $\quad (0.4761 + P^2 - 1.38P)\,28 = 121\,P$

or $\quad 28\,P^2 - 38.64\,P + 13.33 = 121\,P$

or $\quad 28\,P^2 - 159.64\,P + 13.33 = 0$

On solving, we get P = 0.04 atm and partial pressure of N_2O_4 = 0.65 atm.

Problem 7. *A vessel at 1000 K contains carbon dioxide with a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K, if total pressure at equilibrium is 0.8 atm.*

Solution. Reaction involved is:

	$CO_2\,(g) + C\,(s)$	$\rightleftharpoons 2\,CO\,(g)$
Initial pressure:	0.5	0 atm
Final pressure at equilibrium:	$0.5 - x$ atm	$2x$ atm

where x is the change in pressure due to the reduction of CO_2 to CO.

Total pressure at equilibrium $= P_{CO_2} + P_{CO}$

$= 0.5 - x + 2x = 0.5 + x$

Total pressure at equilibrium = 0.8 atm

$\therefore \qquad 0.8 = 0.5 + x$

or $\qquad x = 0.3$ atm

$$K_p = \frac{\left[P_{CO_{(g)}}\right]^2}{P_{CO_{2(g)}}} = \frac{(2\times 0.3)^2}{0.5-0.3} = \frac{0.36}{0.2} = 1.80 \text{ atm.}$$

Problem 8. *0.15 mole of CO taken in 2.51 litres flask is maintained at 750 K along with a catalyst so that the following reaction can take place*

$$CO\,(g) + 2H_2\,(g) \rightleftharpoons CH_3OH\,(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atmospheres at equilibrium and 0.08 mole of methanol is formed. Calculate

(i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used but with no catalyst so that the reaction does not take place.

Solution. (*i*)

	$CO + 2H_2$	$\rightleftharpoons CH_3OH$
Initially:	0.15 mole	
At. eq.:	(0.15 – 0.08) mole = 0.017 mole	0.08 mole

Total volume, V = 2.5 L, total pressure P = 8.5 atm, T = 750 K

Applying general gas equation, PV = nRT,

we get $\quad 8.5 \times 2.5 = n \times 0.0821 \times 750$

or $\qquad n = 0.345$ mole

∴ No. of moles of H_2 at equilibrium

= 0.345 – (0.017 + 0.08) = 0.248 mol.

$$P_{CO} = \frac{0.017}{0.345} \times 8.5 \text{ atm} = 0.42 \text{ atm}$$

$$P_{H_2} = \frac{0.248}{0.345} \times 8.5 \text{ atm} = 6.11 \text{ atm}$$

$$P_{CH_3OH} = \frac{0.248}{0.345} \times 8.5 \text{ atm} = 1.97 \text{ atm}$$

$$K_p = \frac{P_{CH_3OH}}{P_{CO} \times P_{H_2}} = \frac{1.97}{0.42 \times (6.11)^2}$$

$$= 0.1256$$

$$K_c = \frac{[CH_3OH]}{[CO]\,[H_2]^2}$$

$$= \frac{0.08 \times 2.5}{(0.017 \times 2.5)\,(0.248 \times 2.5)^2}$$

$$= 478.2$$

(*ii*) No. of moles of H_2 taken initially

= 0.248 + 2 × 0.08 = 0.308

No. of moles of CO taken initially = 0.15

∴ Total no. of moles = 0.308 + 0.15 = 0.458

Applying general gas equation, PV = nRT

P × 2.5 = 0.458 × 0.0821 × 750

or $\qquad$ P = 11.28 atm

Problem 9. *One mole of H_2 and three moles of HI are injected in a litre flask. What will be the concentration of H_2, I_2 and HI at equilibrium at 490°C? The equilibrium constant for the reaction at 490°C is 45.9.*

Solution. $[I_2] = 1.316 \text{ mol L}^{-1}$, $[HI] = 4.368 \text{ mol L}^{-1}$

	H_2	$+\ I_2$	$\rightleftharpoons 2HI$
Initial conc.:	1	2	3 moles L^{-1}
Conc. at eqm.:	$(1 - x)$	$(2 - x)$	$(3 + 2x)$ mole L^{-1}

$$K = \frac{(3+2x)^2}{(1-x)(2-x)}$$

$$= \frac{9+4x^2+12x}{2+x^2-3x}$$

$$= 45.9 \qquad \text{(Given)}$$

$$\therefore \quad 9 + 4x^2 + 12x = 91.8 + 45.9x^2 - 137.7\,x$$

or $41.9x^2 - 149.7x + 82.8 = 0$, solving for x,

$$x = \frac{149.7 \pm \sqrt{(149.7)^2 - 4\times 41.9\times 82.8}}{2\times 41.9}$$

$$= \frac{149.7 \pm \sqrt{22410.99 - 13877.28}}{83.8}$$

$$= \frac{149.7 \pm 92.4}{83.8} = 2.89 \text{ and } 0.68$$

Ignoring $x = 2.89$, $x = 0.684$

∴ Concentrations at equilibrium will be

$$[H_2] = 1 - x = 1 - 0.684 = 0.316 \text{ mol L}^{-1}$$

$$[I_2] = 2 - x = 2 - 0.684 = 1.316 \text{ mol L}^{-1}$$

$$[HI] = 3 + 2x = 3 + 2 \times 0.684 = 4.368 \text{ mol L}^{-1}.$$

Problem 10. *20% of N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of the equilibrium mixture.*

Solution.

	$N_2O_4\,(g)$	$\rightleftharpoons 2NO_2\,(g)$
Initial conc.:	1 mole	
At eqm.:	1 − 0.2	0.4 mole
	= 0.8 mole	

Total = 1.2 moles

If V is the volume of the vapour per mole, volume of vapour before dissociation = V

Hence, density (D) $\propto \frac{1}{V}$

But density before dissociation

$$D = \frac{\text{Mol. wt. of } N_2O_4}{2}$$

$$= \frac{92}{2} = 46 \quad \text{(Theoretical density)}$$

Volume after dissociation = 1.2V

$$\therefore \quad \text{Density } (d) \propto \frac{1}{12\text{ V}}$$

$$\therefore \quad \frac{D}{d} = \frac{1}{V} \times 1.2V = 1.2$$

$$\text{or} \quad d = \frac{D}{1.2} = \frac{46}{1.2} = 38.2$$

Alternatively, use the formula directly, $\alpha = \frac{D-d}{d}$.

Problem 11. *A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO(g)$ was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium the mole % of NO was 1.8. Estimate the initial composition of the air in mole fraction of N_2 and O_2.*

Solution. In the given reaction, there is no change in the number of moles. Suppose total no. of moles initially present in the air = 100. The no. of moles after attainment of equilibrium = 100. We have

	$N_2\,(g)$	$+\ O_2\,(g)$	$\rightleftharpoons 2NO$
Initial conc.:	a	b	0
At eqm.:	$a - x$	$b - x$	$2x$

$$a + b = 100 \qquad \text{...}(i)$$

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

In the question we are given that $2x = 1.8$

or $\quad x = 0.9$ and $K_c = 2.1 \times 10^{-3}$

$$\therefore \quad 2.1 \times 10^{-3} = \frac{(1.8)^2}{(a-0.9)(b-0.9)}$$

or $\quad ab - 0.9a - 0.9b + 0.81 = 1542$

or $\quad ab - 0.9(a + b) + 0.81 = 1542$

or $\quad ab - 0.9 \times 100 + 0.81 = 1542$

or $\quad ab = 1632$

Now, $\quad (a - b)^2 = (a + b)^2 - 4ab$

$\quad = (100)^2 - 4 \times 1632 = 3472$

or $\quad a - b = \sqrt{3472} = 58.9 \qquad \text{...}(ii)$

Solving (*i*) and (*ii*), a = 79.46 moles

$$\text{Mole fraction of } N_2 = \frac{79.46}{100} = 0.79$$

$$\text{Mole fraction of } O_2 = 1 - 0.79 = 0.21.$$

Problem 12. *A mixture of H_2 and I_2 (vapour) in molecular proportion of 2 : 3 was heated at 440°C till the reaction $H_2 + I_2 \rightleftharpoons 2HI$ reached equilibrium state. Calculate the percentage of iodine converted into HI (K_c at 440°C is 0.02).*

Solution.

	$H_2\,(g)$	$+\ I_2\,(g)$	$\rightleftharpoons 2HI\,(g)$
Initial conc.:	2	3	0 moles
At eqm.:	$2 - x$	$3 - x$	$2x$
Molar conc.:	$\frac{2-x}{V}$	$\frac{3-x}{V}$	$\frac{2x}{V}$

$$K_c = \frac{(2x/V)^2}{[(2-x)/V]\,[(3-x)/V]}$$

$$= \frac{4x^2}{(2-x)(3-x)}$$

$$= 0.02 \text{ (Given)}$$

This on solving gives $\quad x = 0.1615$

$$\therefore \text{ \% of iodine converted into HI } = \frac{0.1615}{3} \times 100$$

$$= 5.38\%$$

Problem 13. *The K_p for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is 640 mm at 775 K. Calculate the percentage dissociation of N_2O_4 at equilibrium pressure of 160 mm. At what pressure the dissociation will be 50%?*

Solution. Suppose initially N_2O_4 taken = 1 mole and its degree of dissociation = α.

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Initial conc.:	1 mole	
At eqm.:	$1 - \alpha$	2α

Total no. of moles = $1 - \alpha + 2\alpha = 1 + \alpha$

If P is the total pressure at equilibrium, then

$$P_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times P$$

and
$$P_{NO_2} = \frac{2\alpha}{1+\alpha} \times P$$

Now,
$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha} \cdot P\right)^2}{\frac{1-\alpha}{1+\alpha} \cdot P} \times P$$

$$= \frac{4\alpha^2}{(1+\alpha)(1-\alpha)} = \frac{4\alpha^2}{1-\alpha^2} \times P$$

Putting K_p = 640 mm (given) and equilibrium pressure, P = 160 mm, we get

$$640 = \frac{4\alpha^2}{1-\alpha^2} \times 160$$

or
$$\frac{\alpha^2}{1-\alpha^2} = 1$$

or $\alpha^2 = 1 - \alpha^2$

or $2\alpha^2 = 1$ or $\alpha^2 = 0.5$

or $\alpha = 0.707 = 70.7\%$

For dissociation to be 50%, α = 0.50, K_p = 640 mm (constant)

∴
$$640 = \frac{4(0.5)^2}{1-(0.5)^2} \times P$$

or
$$640 = \frac{1}{1-\frac{1}{4}} P = \frac{4}{3} P$$

or P = 480 mm.

Problem 14. *The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of the equilibrium mixture at 400 K and 1.0 atmosphere. (Atomic mass of P = 31.0 and Cl = 35.5).*

Solution.	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
At. eqm.:	0.6	0.4	0.4 mole

Average molecular weight of the mixture

$$= \frac{0.6(31+5\times35.5)+0.4(31+3\times35.5)+0.4(2\times35.5)}{0.6+0.4+0.4}$$

$$= \frac{125.1+55+42.6}{1.4} = 148.92$$

For ideal gases, $PV = nRT = \frac{w}{M} RT$

or
$$PM = \frac{w}{V} RT = d\ RT$$

∴
$$d = \frac{PM}{RT} = \frac{1 \times 148.92}{0.08205 \times 400}$$

$$= 4.5374 \text{ g L}^{-1}.$$

Problem 15. *At 540 K, 0.10 mol of PCl_5 is heated in a 8.0 L flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.*

Solution.	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
Initial conc.:	0.1 mol		
At eqm.:	$0.1 - x$	x	x

Total no. of moles at eqm. = $0.1 + x$

$$PV = nRT$$

i.e.,
$$n = \frac{PV}{RT} = \frac{1 \times 8}{0.0821 \times 540} = 0.18$$

∴ $0.1 + x = 0.18$

or $x = 0.08$

∴
$$K_c = \frac{(0.08/8)(0.08/8)}{(0.02/8)} = 0.04$$

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

$$= 0.04\ (0.0821 \times 540)^1 = 1.77$$

Problem 16. *When 3.06 g of solid NH_4HS is introduced into a two-litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_c and K_p for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?*

Solution. The reaction along with the given data is

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

No. of moles initially

$NH_4HS\ (s)$	$NH_3\ (g)$	$H_2S\ (g)$
= 03.06 g	0	0
= (3.06/51) mol		
= 0.06 mol		

No. of moles at eqm.

$NH_4HS\ (s)$	$NH_3\ (g)$	$H_2S\ (g)$
0.7 × 0.06	0.3 × 0.06	0.3 × 0.06
= 0.042 mol	= 0.018 mol	= 0.018 mol

(*i*) The equilibrium constant K_c is

$$K_c = [NH_3][H_2S]$$

(Conc. of solids is taken as constant)

$$= \left(\frac{0.018 \text{ mol}}{2L}\right)\left(\frac{0.018 \text{ mol}}{2L}\right)$$

$$= 8.1 \times 10^{-5}\ (\text{mol/L})^2$$

The equilibrium constant K_p is

$$\begin{aligned} K_p &= K_c(RT)^{\Delta n(g)} \\ &= (8.1 \times 10^{-5}\ \text{mol}^2/\text{L}^2) \\ &\qquad [(0.082\ \text{atm L mol}^{-1}\ \text{K}^{-1})(300\ \text{K})]^2 \\ &= 4.90 \times 10^{-2}\ \text{atm}^2 \end{aligned}$$

(*ii*) There will be no effect on the equilibrium by introducing more of solid NH_4HS as the equilibrium constant is independent of the quantity of solid.

Problem 17. *$3H_2 + N_2 \rightleftharpoons 2NH_3$, $K_c = 61$*

$N_2 = 1 \times 10^{-3}$; $H_2 = 3 \times 10^{-3}$

$NH_3 = 3 \times 10^{-3}$

State whether the concentration of NH_3 will increase or decrease.

Solution. Apply the following relation and substitute given values

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(3\times10^{-3})^2}{(1\times10^{-3})(3\times10^{-3})^3}$$

$$= \frac{1}{3} \times 10^6$$

As Q_c is greater than K_c, reaction proceeds in backward direction. Thus, concentration of NH_3 decreases.

Problem 18. *For 0.5 M H_2SO_3 solution,*

$K_{a1} = 1.3 \times 10^{-2}$ and $K_{a2} = 6.5 \times 10^{-8}$.

Find the concentration of H^+, HSO_3^-, SO_3^{2-}.

Solution. Given

Concentration of $H_2SO_3 = 0.5$ M

$$K_{a_1} = 1.3 \times 10^{-2};\ K_{a_2} = 6.5 \times 10^{-8}$$

In first step: $H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$

$$[H^+] = [HSO_3^-]$$

$$= \sqrt{K_{a_1}C} = \sqrt{1.3\times10^{-2}\times0.5}$$

$$[H^+] = [HSO_3^-] = 8.07 \times 10^{-2}$$

In second step: $[HSO_3^-] \rightleftharpoons H^+ + SO_3^{2-}$

$$K_{a_2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$$

$$6.5 \times 10^{-8} = \frac{8.07\times10^{-2}[SO_3^{2-}]}{[8.07\times10^{-2}]}$$

$$[SO_3^{2-}] = 6.5 \times 10^{-8}$$

Problem 19. *Degree of dissociation of N_2O_4 is 40%. If dissociation constant is K_x in the form of mole and K_p in the form of pressure then what will be the relation in between K_p and K_x if pressure is 1 atm?*

Solution. $N_2O_4 \rightleftharpoons 2NO_2$, $\alpha = 40\%$, P = 1 atm

1 0 Initial conc.

$1 - 0.4$ 2×0.4 conc. at equilibrium

$= 0.6$ $= 0.8$

Total moles at equilibrium = 1.4

$$P_{N_2O_4} = \frac{1.6}{1.4}\times1;\ P_{NO_2} = \frac{0.8}{1.4}\times1$$

$$K_p = \frac{[P_{NO_2}]^2}{[P_{N_2O_4}]} = \frac{\left(\frac{0.8}{1.4}\times1\right)^2}{\left(\frac{0.6}{1.4}\times1\right)^2} = 0.76$$

Mole fraction is calculated as under:

$$X_{N_2O_4} = \frac{0.6}{1.4},\ X_{NO_2} = \frac{0.8}{1.4}$$

$$K_x = \frac{\left(\frac{0.8}{1.4}\right)^2}{\left(\frac{0.6}{1.4}\right)} = 0.76$$

Partial pressure = mole fraction × total pressure (P = 1)

Partial pressure = mole fraction

or $K_p = K_x$.

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. The reaction, $SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$ is exothermic and reversible. A mixture of SO_2 (*g*), Cl (*g*) and SO_2Cl_2(*l*) is at equilibrium in a closed container. Now a certain quantity of extra SO_2 is introduced into the container, the volume remaining the same. Which of the following is/are true?
   - (*a*) The pressure inside the container will not change.
   - (*b*) The temperature will not change.
   - (*c*) The temperature will increase.
   - (*d*) The temperature will decrease.
2. Steam reacts with iron at high temperature to give hydrogen gas and Fe_3O_4 (*s*). The correct expression for the equilibrium constant is
   - (*a*) $\frac{(P_{H_2})^2}{(P_{H_2O})^2}$ (*b*) $\frac{(P_{H_2})^4}{(P_{H_2O})^4}$
   - (*c*) $\frac{(P_{H_2})^4[Fe_3O_4]}{(P_{H_2O})^4[Fe]}$ (*d*) $\frac{[Fe_3O_4]}{[Fe]}$
3. In which of the following reaction $K_p > K_c$?
   - (*a*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (*b*) $H_2 + I_2 \rightleftharpoons 2HI$
   - (*c*) $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ (*d*) $2SO_3 \rightleftharpoons O_2 + 2SO_2$
4. If the equilibrium constant of the reaction $2HI \rightleftharpoons H_2 + I_2$ is 0.25, then the equilibrium constant for the reaction $H_2 + I_2 \leftrightharpoons 2HI$ would be
   - (*a*) 1 (*b*) 2
   - (*c*) 3 (*d*) 4

5. The equilibrium constant (K_p) for the reaction $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$ is 16. If the volume of the container is reduced to one-half of its original volume, the value of K_p for the reaction at the same temperature will be
   (*a*) 32 (*b*) 64
   (*c*) 16 (*d*) 4

6. In a reaction, $A + 2B \rightleftharpoons 2C$, 2.0 moles of A, 3.0 moles of B and 2.0 moles of C are placed in 2.0 L flask and the equilibrium concentration of C is 0.5 mole/L. The equilibrium constant (K) for the reaction is
   (*a*) 0.073 (*b*) 0.147
   (*c*) 0.05 (*d*) 0.026

7. One mole of N_2O_4 (g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_4\ (g)$ decomposes to $NO_2\ (g)$. The resultant pressure is
   (*a*) 1.2 atm (*b*) 2.4 atm
   (*c*) 2.0 atm (*d*) 1.0 atm

8. Which one is true?
   (*a*) $K_c = K_p(RT)^{\Delta n(g)}$ (*b*) $K_p = K_c(RT)^{\Delta n(g)}$
   (*c*) $\frac{K_c}{RT} = (KP)^{\Delta n(g)}$ (*d*) $\frac{K_p}{RT} = (KC)^{\Delta n(g)}$

9. $\frac{K_p}{K_c}$ for the reaction $CO\ (g) + \frac{1}{2}\ O_2\ (g) \rightleftharpoons CO_2\ (g)$ is
   (*a*) 1 (*b*) RT
   (*c*) $\frac{1}{\sqrt{RT}}$ (*d*) $(RT)^{1/2}$

10. If the equilibrium constant at 298 K for the reactions $A\ (g) + B\ (g) \rightleftharpoons AB\ (g)$ and $BC \rightleftharpoons B\ (g) + C\ (g)$ are K_1 and K_2 respectively, then the equilibrium constant K_3 for the reaction $A\ (g) + BC\ (g) \rightleftharpoons AB\ (g) + C\ (g)$ at 298 K would be
   (*a*) $K_1 \times K_2$ (*b*) K_1/K_2
   (*c*) $K_1 - K_2$ (*d*) $K_1 + K_2$

11. For the reaction $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$ at a given temperature, the equilibrium amount of $CO_2\ (g)$ can be increased by
   (*a*) adding a suitable catalyst
   (*b*) adding an inert gas
   (*c*) decreasing the volume of the container
   (*d*) increasing the amount of CO (*g*)

12. If K_1 and K_2 are the respective equilibrium constants for the two reactions,
   $XeF_6\ (g) + H_2O\ (g) \rightleftharpoons XeOF_4\ (g) + 2HF\ (g)$
   $XeO_4\ (g) + XeF_6\ (g) \rightleftharpoons XeOF_4\ (g) + XeO_3F_2\ (g)$
   then the equilibrium constant of the reaction
   $XeO_4\ (g) + 2HF\ (g) \rightleftharpoons XeO_3F_2\ (g) + H_2O\ (g)$ will be
   (*a*) $K_1 + K_2$ (*b*) $K_1.K_1$
   (*c*) K_1/K_2 (*d*) $K_2 - K_1$

13. For the chemical reaction $3X\ (g) + Y\ (g) \rightleftharpoons X_3Y\ (g)$, the amount of X_3Y at equilibrium is affected by
   (*a*) temperature and pressure
   (*b*) temperature only
   (*c*) pressure only
   (*d*) temperature, pressure and catalyst.

14. For the reversible reaction, $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$ at 500°C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c, with concentration in mol L^{-1}, is
   (*a*) $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$
   (*b*) $1.44 \times 10^{-5}/(8.314 \times 773)^{-2}$
   (*c*) $1.44 \times 10^{-5}/(0.082 \times 773)^{2}$
   (*d*) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

15. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = (4x^2\ P/1 - x^2)$, where P = pressure, x = extent of decomposition. Which one of the following statements is true?
   (*a*) K_p increases with increase in P.
   (*b*) K_p increases with increase in x.
   (*c*) K_p increases with decrease in x.
   (*d*) K_p remains constant with change in P and x.

16. For a sparingly soluble salt A_pB_q, the relationship of the solubility product (L_s) with its solubility is
   (*a*) $L_s = S^{p+q}\ .\ p^p.q^q$ (*b*) $L_s = S^{p+q}\ .\ p^q.q^p$
   (*c*) $L_s = S^{pq}\ .\ p^p\ .\ q^q$ (*d*) $L_s = S^{pq}\ .\ (pq)^{p+q}$

17. Consider the following equilibrium in a closed container:
   $$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$
   At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?
   (*a*) Neither K_p nor α changes.
   (*b*) Both K_p and α change.
   (*c*) K_p changes, but α does not change.
   (*d*) K_p does not change, but α changes.

18. What is the equilibrium expression for the reaction
   $$P_4\ (s) + 5O_2\ (g) \rightleftharpoons P_4O_{10}\ (s)?$$
   (*a*) $K_c = [P_4O_{10}]/[P_4][O_2]^5$ (*b*) $K_c = [P_4O_{10}]/5[P_4][O_2]$
   (*c*) $K_c = [O_2]^5$ (*d*) $K_c = 1/[O_2]^5$

19. For the reaction, $CO\ (g) + Cl_2\ (g) \rightleftharpoons COCl_2\ (g)$ the K_p/K_c is equal to
   (*a*) 1/RT (*b*) RT
   (*c*) $\sqrt{RT}$ (*d*) 1.0

20. The equilibrium constant for the reaction $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction $NO\,(g) \rightleftharpoons 1/2N_2\,(g) + 1/2O_2\,(g)$ at the same temperature is

(*a*) 2.5×10^{2} (*b*) 50

(*c*) 4×10^{-4} (*d*) 0.02

21. For the reaction:

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

$\Delta H_r = -170.8$ kJ mol^{-1}. Which of the following statements is not true?

(*a*) The reaction is exothermic.

(*b*) At equilibrium, the concentrations of $CO_2\,(g)$ and $H_2O\,(l)$ are not equal.

(*c*) The equilibrium constant for the reaction is given by

$$K_p = \frac{[CO_2]}{[CH_4][O_2]}$$

(*d*) Addition of $CH_4\,(g)$ or $O_2\,(g)$ at equilibrium will cause a shift to the right.

22. The equilibrium constant for the reaction

$$SO_3\,(g) \rightleftharpoons SO_2\,(g) + \frac{1}{2}\,O_2\,(g)$$

is $K_c = 4.9 \times 10^{-2}$. The value of K_c for the reaction $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$ will be

(*a*) 416 (*b*) 2.40×10^{-3}

(*c*) 9.8×10^{-2} (*d*) 4.9×10^{-2}

23. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+]$; $K_1 = 6.8 \times 10^{-3}$

$[Ag\,(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $k_2 = 1.6 \times 10^{-3}$

then the formation constant of $[Ag(NH_3)_2]^+$ is

(*a*) 1.08×10^{-7} (*b*) 1.08×10^{-5}

(*c*) 1.08×10^{-9} (*d*) None of these

(B) Fill in the Blanks

Fill in the blank spaces:

1. If an inert gas is added to the equilibrium mixture of the dissociation of PCl_5 at constant pressure, the dissociation of PCl_5 will ....
2. The equilibrium constant for a given reaction remains constant at ....
3. The rate at which a substance reacts is proportional to its ....
4. The value of equilibrium constant of an endothermic reaction .... with rise in temperature.
5. The value of equilibrium constant is constant at constant ....
6. Increase in concentration of the reactants favours .... reaction.
7. For a given reaction at a fixed temperature, equilibrium constants K_p and K_c are related as ....
8. Partial pressure of a gaseous substance is proportional to its .... at a given temperature.
9. The forward reaction is favoured by low temperature in case of ....
10. On increasing the concentration of reactants, the value of K_c .... at a given temperature.
11. A ten-fold increase in pressure on the reaction $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$ at equilibrium results in .... in K_p.
12. For a gaseous reaction $2B \rightarrow A$, the equilibrium K_p is .... than K_c.

(C) True/False Statements

Write T for true and F for false statements:

1. K_w increases with increase in temperature.
2. Equilibrium is disturbed if catalyst is added to it.
3. A weak acid has a strong conjugate base.
4. Burning of magnesium to form MgO is an irreversible process.
5. Solubility of a gas is increased at high pressure.

(D) Assertion-Reason Type Questions

The questions below (1 to 2) consist of an 'Assertion' in column 1 and the 'Reason' in column 2. Use the following key to choose the appropriate answer.

(*a*) Both Assertion and Reason are correct, and Reason is the correct explanation of the Assertion.

(*b*) Both Assertion and Reason are correct but Reason is not the correct explanation of the Assertion.

(*c*) The Assertion is correct, but Reason is incorrect.

(*d*) The Assertion is incorrect, but Reason is correct.

Assertion (Column 1)	**Reason (Column 2)**
1. Reactions which proceed in one direction only are called irreversible reactions.	1. Chemical equilibrium can be attained from the reactant's side or product's side.
2. For the equilibrium $xA + yB \rightleftharpoons pC + qD$, The expression for the equilibrium constant can be written as $K_c = \frac{[C]^p[D]^q}{[A]^x[B]^y}$	2. Relation between K_c and K_p is given by $K_c = K_p\,(RT)^{\Delta n}$ where Δn is the difference between the no. of moles of gaseous products and reactants.

(E) Matching Questions

Match the items in Column A with appropriate items of Column B.

Column A	Column B
1. Guldberg and Waage	*a*. Principle of equilibrium.
2. Le-Chatelier	*b*. pH scale.
3. Sorenson	*c*. Law of mass action.
4. Henderson	*d*. Theory of ionisation.
5. Arrhenius	*e*. Buffers.

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. We know that the relationship between K_p and K_c is
   $K_p = K_c\ (RT)^{\Delta n}$
   What would be the value of Δn for the reaction
   $$NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$$
   (*a*) 1 (*b*) 0.5
   (*c*) 1.5 (*d*) 2
2. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the standard free energy is $\Delta G\ \ > 0$. The equilibrium constant (K) would be _________.
   (*a*) $K = 0$ (*b*) $K > 1$
   (*c*) $K = 1$ (*d*) $K < 1$
3. Which of the following is **not** a general characteristic of equilibria involving physical processes?
   (*a*) Equilibrium is possible only in a closed system at a given temperature.
   (*b*) All measurable properties of the system remain constant.
   (*c*) All the physical processes stop at equilibrium.
   (*d*) The opposing processes occur at the same rate and there is dynamic but stable condition.
4. PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K in a closed container and their concentrations are 0.8×10^{-3} mol L^{-1}, 1.2×10^{-3} mol L^{-1} and 1.2×10^{-3} mol L^{-1} respectively. The value of K_c for the reaction $PCl_5\ (g) \rightleftharpoons PC1_3\ (g) + C1_2\ (g)$ will be
   (*a*) 1.8×10^3 mol L^{-1} (*b*) 1.8×10^{-3}
   (*c*) 1.8×10^{-3} L mol^{-1} (*d*) 0.55×10^4
5. K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions.
   $$H_2S \rightleftharpoons H^+ + HS^-$$
   $$H_2S^- \rightleftharpoons H^+ + S^{2-}$$
   $$H_2S \rightleftharpoons 2H^+ + S^{2-}$$
   The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is
   (*a*) $K_{a_3} = K_{a_1} \times K_{a_2}$ (*b*) $K_{a_3} = K_{a_1} + K_{a_2}$
   (*c*) $K_{a_3} = K_{a_1} - K_{a_2}$ (*d*) $K_{a_3} = K_{a_1}/K_{a_2}$
6. Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$?
   (*a*) $\Delta G\ \ = 0$ (*b*) $\Delta G\ \ > 0$
   (*c*) $\Delta G\ \ < 0$ (*d*) $\Delta G\ \ = -RT \ln 2$
7. On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction.
   $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$
   Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?
   (*a*) K will remain same
   (*b*) K will decrease
   (*c*) K will increase
   (*d*) K will increase initially and decrease when pressure is very high
8. At 500 K, equilibrium constant, K_c, for the following reaction is 5.
   $$\frac{1}{2} H_2(g) + \frac{1}{2} I_2\ (g) \rightleftharpoons HI\ (g)$$
   What would be the equilibrium constant K_c for the reaction $2HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$?
   (*a*) 0.04 (*b*) 0.4
   (*c*) 25 (*d*) 2.5
9. Le Chatelier principle is applicable only at
   (*a*) physical equilibrium.
   (*b*) system not in equilibrium.
   (*c*) homogeneous equilibrium.
   (*d*) heterogeneous equilibrium.
10. The change in pressure will affect the equilibrium for
    (*a*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
    (*b*) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
    (*c*) $H_2 + I_2 \rightleftharpoons 2HI$
    (*d*) all the above three reactions
11. Methyl orange can be used as the most suitable indicator for the titration of
    (*a*) $CH_3COOH + NH_4OH$
    (*b*) $CH_3COOH + NaOH$
    (*c*) $HCl + NH_4OH$
    (*d*) $HCl + NaOH$
12. For the reaction $C_2H_4 + H_2 \rightleftharpoons C_2H_6\ (g)$; $\Delta H = -119.7$ kJ, carried out in a closed vessel, the equilibrium concentration of C_2H_4 can be raised by
    (*a*) Decreasing temp.
    (*b*) Adding some C_2H_6
    (*c*) Removing some H_2
    (*d*) Decreasing the pressure
13. Find out the correct statements:
    (*a*) Equilibrium constant for endothermic reaction increases with rise in temperature.
    (*b*) Equilibrium constant of a reaction depends upon the balancing coefficients of a reaction.
    (*c*) Equilibrium constant for a reaction is independent of concentration of reactants.
    (*d*) If equations of two reactions are added to get an equation of third reaction the equilibrium constant of two reactions are to be multiplied to get the equilibrium constant of the third reaction.

14. The relation between K_c and K_p is

(*a*) $K_c = K_p(RT)^{\Delta n(g)}$ (*b*) $K_c = K_p \times \left(\frac{1}{RT}\right)^{\Delta n(g)}$

(*c*) $K_p = K_c(RT)^{\Delta n(g)}$ (*d*) $K_p/K_c = (RT)^{\Delta n(g)}$

II. Assertion-Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

1. **Assertion (A):** For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason (R): Equilibrium constant is independent of temperature.

(*i*) Both A and R are true and R is correct explanation of A.
(*ii*) Both A and R are true but R is not correct explanation of A.
(*iii*) A is true but R is false.
(*iv*) Both A and R are false.

2. **Assertion (A):** In the dissociation of PCl_5 at constant pressure and temperature addition of helium at equilibrium increases the dissociation of PCl_5.

Reason (R): Helium removes Cl_2 from the field of action.

(*i*) Both A and R are true and R is correct explanation of A.
(*ii*) Both A and R are true but R is not correct explanation of A.
(*iii*) A is true but R is false.
(*iv*) Both A and R are false.

ANSWERS

(A) Multiple Choice Questions

1. (*c*) 2. (*b*) 3. (*d*) 4. (*d*) 5. (*c*) 6. (*c*) 7. (*b*) 8. (*b*)
9. (*d*) 10. (*b*) 11. (*d*) 12. (*c*) 13. (*a*) 14. (*d*) 15. (*d*) 16. (*a*)
17. (*d*) 18. (*d*) 19. (*a*) 20. (*b*) 21. (*c*) 22. (*a*) 23. (*a*)

(B) Fill in the Blanks

1. increase 2. constant temperature 3. active mass 4. increases
5. temperature 6. forward 7. $K_p = K_c\ (RT)^{\Delta n}$ 8. molar concentration
9. exothermic reaction 10. remains unchanged 11. no change 12. less

(C) True/False Statements

1. F 2. F 3. T 4. T 5. T

(D) Assertion-Reason Type Questions

1. (*b*) 2. (*c*)

(E) Matching Questions

1. (*c*) 2. (*a*) 3. (*b*) 4. (*d*) 5. (*f*)

Some Additional Questions

I. Multiple Choice Questions

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

II. Assertion-Reason Type Questions

1. (*iii*) 2. (*iv*)

9
CHAPTER
Phase Equilibria

LEARNING OBJECTIVES

- Explain the terms —phase, components and degrees of freedom.
- Define the term equilibrium.
- Discuss the criteria for phase equilibrium.
- Create phase diagram.
- Compare evaporation with condensation.
- Explain Raoult's law.
- Discuss Dalton's law of partial pressure.
- Compare ideal solution with non-ideal solutions.
- Define azeotropes.
- Design the method for fractional distillation.

9.1 INTRODUCTION

Phase equilibrium is relevant to heterogeneous systems. A heterogeneous system is defined as a system consisting of a number of phases in equilibrium. The number of phases that can exist together at equilibrium depends upon the conditions of temperature, pressure and concentration of different phases. A relationship governing all heterogeneous equilibria was first given by Willard Gibbs. It is known as phase rule.


Willard Gibbs
(1839-1903)

Gibb's phase rule cannot be expressed in words. It is described by a mathematical equation as given:

For a heterogeneous system in equilibrium

$$F = C - P + 2$$

where F = No. of degrees of freedom

C = No. of components

P = No. of phases

9.2 EXPLANATION OF THE TERMS

9.2.1 Phase

A phase may be defined as any part of a system which is

(*a*) *homogeneous and separated from other parts of the system by a distinct boundary,*
(*b*) *physically and chemically different from other parts of the same system,*
(*c*) *mechanically separable from other parts of the system.*

Examples illustrating phases are given below:

	System	Phases
(i)	Ice and water.	2 phases: 1 solid and 1 liquid.
(ii)	Water and water vapour.	2 phases: 1 liquid and 1 gaseous.
(iii)	Ice, water and water vapour.	3 phases: 1 solid, 1 liquid and 1 gaseous.
(iv)	Two immiscible liquids, *e.g.*, CS_2/H_2O, CCl_4/H_2O, etc.	2 phases: both liquids.
(v)	Two miscible liquids, *i.e.*, water/alcohol	1 phase: only liquid.
(vi)	$CaCO_3$, CaO and CO_2	3 phase: 2 solids and 1 gaseous.
(vii)	Monoclinic and rhombic sulphur.	2 phases: both solids.

Miscible gases and miscible liquids constitute a *single* phase.

Solid + liquid, solid + gas, liquid + gas, two solids and two immiscible liquids constitute *two* phase.

Different solids are regarded as different phases, however intimately they may be mixed.

9.2.2 Components

The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed either directly or in the form of a chemical equation, negative and zero signs being permitted.

Example: (*i*) Water system consists of the equilibrium

$$\underset{\text{(Solid)}}{\text{Ice}} \rightleftharpoons \underset{\text{(Liquid)}}{\text{Water}} \rightleftharpoons \underset{\text{(Gaseous)}}{\text{Vapour}}$$

This system consists of one component only, *i.e., it is a one component system* because the composition of each of the three phases present can be directly expressed as H_2O.

(*ii*) **Sulphur system.** It consists of four phases—Monoclinic(*s*), Rhombic(*s*), Liquid(*l*) and vapour(*g*). It is also one component system because the composition of each phases can be expressed in terms of one constituent—sulphur.

(*iii*) Decomposition of $CaCO_3$ by heat can be expressed according to the equilibrium

$$\underset{\text{(Solid)}}{CaCO_3} \rightleftharpoons \underset{\text{(Solid)}}{CaO} + \underset{\text{(Gas)}}{CO_2}$$

There are three different constituents forming three different phases. But the composition of each phase can be expressed in terms of any two of the constituents. For example,

(a) If the constituents chosen are CaO and CO_2, then

Phase		*Composition*
$CaCO_3$	$\longrightarrow$	$CaO + CO_2$
CaO	$\longrightarrow$	$CaO + 0\ CO_2$
CO_2	$\longrightarrow$	$0\ CaO + CO_2$

(b) If the constituents chosen are $CaCO_3$ and CO_2, then

Phase *Composition*

$$\begin{array}{rcl} CaCO_3 & \longrightarrow & CaCO_3 + 0\ CO_2 \\ CaO & \longrightarrow & CaCO_3 - CO_2 \\ CO_2 & \longrightarrow & 0\ CaCO_3 + CO_2 \end{array}$$

Likewise composition of the three phases can be expressed in terms of $CaCO_3$ and CaO. Thus *the dissociation of* $CaCO_3$ *by heat is a two component system.*

(*iv*) **Sodium sulphate–water system.** This system at equilibrium contains a number of phases like $Na_2SO_4.10H_2O$, $Na_2SO_4.7H_2O$, Na_2SO_4 solution, ice, water and vapour, but the composition of each phase can be expressed by a chemical equation, in terms of only anhydrous sodium sulphate (Na_2SO_4) and water (H_2O) as follows:

Phase *Composition*

$$\begin{array}{rcl} Na_2SO_4.10H_2O & \longrightarrow & Na_2SO_4 + 10H_2O \\ Na_2SO_4.7H_2O & \longrightarrow & Na_2SO_4 + 7H_2O \\ Na_2SO_4 & \longrightarrow & Na_2SO_4 + 0\ H_2O \\ Na_2SO_4\ \text{Solution} & \longrightarrow & x\ Na_2SO_4 + y\ H_2O \\ \text{Ice} & \longrightarrow & 0\ Na_2SO_4 + H_2O \\ \text{Water} & \longrightarrow & 0\ Na_2SO_4 + H_2O \\ \text{Vapour} & \longrightarrow & 0\ Na_2SO_4 + H_2O \end{array}$$

Thus the *smallest number* of independently variable constituents by which the composition of the phases present at equilibrium can be expressed is two—Na_2SO_4 and H_2O. Hence it is also a *two component system*.

9.2.3 Degrees of Freedom

Degrees of freedom of a system is the smallest number of variable factors, i.e., temperature, pressure and concentration of the components which must be arbitrarily fixed in order that the conditions of the system may be completely defined.

Example:

(*i*) **Ice–water–vapour system:** In this system, there are three phases of one component (H_2O). These three phases can co-exist in equilibrium only at one particular temperature and under one particular pressure. Any variation in these factors will make one or more of the phases disappear and, therefore, will destroy the system. Hence, this system has no degree of freedom or in other words, it is *invariant*. The same result follows from Phase Rule *i.e.*,

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

(*ii*) **Water-vapour system:** This system consists of two phases of one component. As the vapour pressure of water is definite at a definite temperature, independent of the amount of water present, it follows that if the temperature is fixed, the vapour pressure is also fixed and conversely, fixing the pressure fixes the temperature. Thus, the system has only one degree of freedom or in other words, it is *univariant*.

(*iii*) **For a gas:** The temperature, pressure and concentration (volume) are related according to the equation PV = RT. Thus, in order to completely define the system any two factors out of P, V and T must be fixed. Hence it follows that a gas has two degrees of freedom or it is *bivariant*.

Example. Write the number of components, phases and degrees of freedom in the following equilibrium system.

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

Solution. No. of components = 2

No. of phases = 3 (2 solid + 1 gas)

Degrees of freedom F = C – P + 2 or F = 2 – 3 + 2 or F = 1

9.3 EQUILIBRIUM

A system is said to be in equilibrium if the properties such as temperature, composition, etc. of the various phases do not undergo any change with time. This is of the following two types:

(*i*) **True Equilibrium:** *A system is said to be in a state of true equilibrium if the same state can be achieved by approach from either direction*. For example, the equilibrium between ice and water at 1 atm. pressure and 0°C is a true equilibrium, because it can be attained by melting of ice or by freezing of water.

(*ii*) **Metastable Equilibrium:** *If the state of a system can be attained only from one direction and that too by very careful change of conditions, it is called a state of* **metastable equilibrium**. For example, water at – 2°C can be obtained only by very careful cooling of liquid water but not by melting of ice. Hence, – 2°C is said to be in a state of metastable equilibrium.

9.4 CRITERIA FOR PHASE EQUILIBRIUM

The following three equilibria must exist in phase equilibria in a multi-component system.

(*i*) **Thermal Equilibrium:** The temperature in every part of the system must be same as otherwise heat may flow from one part of the system to another.

(*ii*) **Mechanical Equilibrium:** The pressure in every part of the system must be same as otherwise matter may flow from one part of the system to another.

(*iii*) **Chemical Equilibrium:** At equilibrium, the chemical potential of any component in all the phases must be same. This is called **thermodynamic criteria for phase equilibrium**.

For a solution (or a phase) containing a number of constituents, the ***chemical potential*** *of any component is the increase or decrease of free energy that takes place, at constant temperature and pressure, for the addition or removal of one mole of that component, keeping the amount of all other components constant. It is usually represented by 'μ'.*

For a multiphase equilibria containing a number of components distributed among them, the chemical potential of any component is the same in all the phases.

9.4.1 Criteria for Two-phase Equilibria for One-component System

If a system consists of one substance only which may exist in two different phases in equilibrium, *e.g.*, liquid water $\rightleftharpoons$ water vapour or ice $\rightleftharpoons$ liquid water or sulphur (monoclinic) $\rightleftharpoons$ sulphur (rhombic), etc., the criterion is obtained in a simple manner in terms of *free energy* instead of chemical potential. Evidently, in such a case, if a certain amount of the substance is transferred from one phase to the other, the molar free energy of one phase decreases while that of the other phase increases by an equal amount. Hence the net result is that there is no change in free energy, *i.e.,*

$$\Delta G = 0$$

This implies that if at equilibrium, G_1 is the molar free energy of phase I and G_2 that of the phase II, we have

$$G_2 - G_1 = 0 \qquad \text{or} \qquad G_1 = G_2$$

Whenever two phases of the same substance in a one component system are in equilibrium at a given temperature and pressure, the molar free energy is the same for each phase.

9.5 PHASE DIAGRAM

The number of phases that exists together when the system is in equilibrium are studied under the following variable conditions:

(*i*) Temperature and pressure (*ii*) Temperature and composition (pressure being constant).

The variable temperature and pressure (or composition) governing the existence of various phases are obtained from the experiment. Then the temperature-pressure or temperature-composition diagrams are constructed for the different values of the variables.

The diagram which gives the conditions of equilibria between different phases of the system is called **phase diagram**. Such diagram contains a number of lines, points of intersection of lines and areas. Each of these has a significance attached to it.

9.5.1 One Component System

Phase rule as applied to one component system.

(*i*) When the number of phases in a one component system is 1, then C = 1 and P = 1. Substituting the values in the phase rule equation F = C – P + 2, we get F = 2.

Thus, the degree of freedom is 2. It is known as **bivariant system**. Hence we can completely describe the system graphically with the help of two variables *viz* temperature and pressure on X and Y axes.

(*ii*) When the number of phases in a one component system is 2, the degree of freedom is given by

$$F = C - P + 2 \quad \text{or} \quad F = 1 - 2 + 2 \quad \text{or} \quad F = 1$$

The system possess one degree of freedom. Such systems are called **univariant systems**. We need to mention only one variable in such a case. The other variable is automatically defined.

(*iii*) When the number of phases in a one component system is 3, the degree of freedom is given by

$$F = C - P + 2 \quad \text{or} \quad F = 1 - 3 + 2 \quad \text{or} \quad F = 0$$

Such a system having no degree of freedom is called **non-variant system**. Univariant system is represented by lines, bivariant system is represented by areas and non-variant system is represented by points in a one-component system.

9.6 PHASE DIAGRAM OF WATER SYSTEM

The water system consists of three phases.

$$\underset{(s)}{\text{Ice}} \rightleftharpoons \underset{(l)}{\text{Water}} + \underset{(g)}{\text{Vapour}}$$

These three single phases may occur in four possible combinations in equilibrium as

(*i*) Liquid ⇌ Vapour

(*ii*) Solid ⇌ Vapour

(*iii*) Solid ⇌ Liquid

(*iv*) Solid ⇌ Liquid ⇌ Vapour.

The number of phases that can exist in equilibrium at any point depends upon the conditions of temperature and pressure. These conditions have been determined experimentally and a phase diagram is constructed by plotting pressure against temperature (Fig. 9.1). The phase diagram consists of:

(*i*) *Three stable curves OA, OB, OC and one metastable curve OA´,*

(*ii*) *Three areas,*

(*iii*) *Definite point, O.*

These are separately discussed as under:

9.6.1 Curves

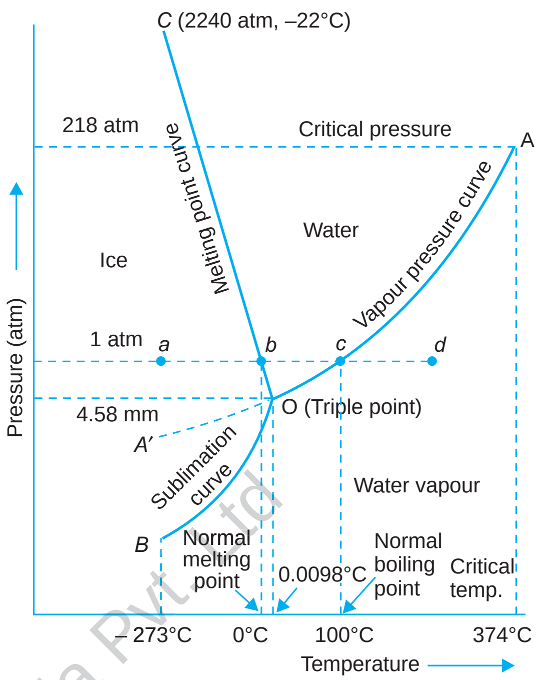


Fig. 9.1 *The water system (pressure and temperature indicated are not to scale)*

(i) OA: This is the *vapour pressure* curve of water. It represents the equilibrium between liquid water and vapour at different temperatures. At any point on the curve, the two phases are present. The curve starts from the point *O*, the freezing point of water and ends at *A*, the critical temperature (374 °C) beyond which the two phases merge into each other. Consider any point on the curve. For a fixed value of pressure, temperature has also a fixed value. If by keeping the pressure constant, an attempt is made to raise the temperature then the liquid phase will disappear and if the temperature is lowered then the vapour phase will disappear. Thus, to define the system completely at any time, it is necessary to mention either the temperature or the pressure. In other words, pressure being fixed, it is not necessary to mention temperature; it gets automatically fixed. Therefore, water-vapour system is univariant, or it has one degree of freedom. It also follows from the phase rule equation,

$$F = C - P + 2 \qquad \text{or} \qquad F = 1 - 2 + 2 = 1$$

(ii) OA: The dotted curve *OA*′, a continuation of curve *OA* represents the *vapour pressure curve of super cooled water*. It is a metastable curve. On being disturbed, the supercooled phase at once changes to solid ice and curve merges into *OB*.

(iii) OB: It is the *sublimation curve* or the vapour pressure curve of ice. It gives values of temperature and pressure at which ice and vapours can exist together. It is obtained by studying the effect of pressure on the freezing point of water. The curve starts from the point *O*, the freezing point of water and ends at *B* (– 273°C). As temperature decreases, the vapour pressure of ice tends to become negligible. We find that for a particular temperature, there can be only one pressure value and *vice versa*. In other words, ice-vapour system is univariant, or it has one degree of freedom.

(iv) OC: It is the *melting point curve* and represents the equilibrium between ice and liquid water at various pressures. In other words, it shows the effect of pressure on the melting point of ice. It should be noted that the line *OC* is inclined towards the pressure axis. The slope of the curve *OC* clearly indicates that melting point of ice is lowered by increase of pressure. There is, however, no limit for the curve *OC*. It goes up to a point corresponding to 2000 atmospheres and –20°C. At this point, one-type of ice changes into another solid modification but the solid-liquid equilibrium still remains.

At any point on the curve *OC*, two phases (ice and liquid water) are present in equilibrium. Hence the system is univariant, or its degree of freedom is one.

9.6.2 Areas

The areas, *i.e.* the regions bounded by two lines give the conditions of temperature and pressure under which the single phase *i.e.* ice or liquid water or vapour is capable for stable existence. Area below *AOB* has water vapour, area *BOC* has ice and area *COA* has liquid water. These areas are bivariant because to locate any point in the area, temperature as well as pressure must be fixed, thus indicating two degrees of freedom. This also follows from phase rule equation.

$$F = C - P + 2 \qquad \text{or} \qquad F = 1 - 1 + 2 = 2$$

9.6.3 Triple Point

It is a point where the three curves *OA, OB, OC* meet. At this point the three phases—ice, water and vapour are in equilibrium. It should be noted that it is only a point indicating that there is only one set of conditions under which it is possible for the three phases to exist together. The point *O* is a self-defined point corresponding to definite temperature of 0.0098°C and a definite pressure of 4.58 mm. If either pressure or temperature is changed, then one of the three phases will disappear therefore, the system at the point *O* has no degree of freedom, that is, it is invariant. The same result follows from phase rule equation.

$$F = C - P + 2 \qquad \text{or} \qquad F = 1 - 3 + 2 = 0$$

It may be mentioned that triple point is different from normal melting point of ice *i.e.* 0°C. At the normal melting point of ice at 0°C and 1 atmospheric pressure, only ice and water (no vapours) exist together.

Effect of change of temperature at constant pressure on water system. We shall study the effect of temperature on the water system at a constant pressure of one atom. Let us start from the point *a* where water exists as ice at a temperature lower than 0°C. Heat it slowly along the path *abcd* at constant pressure of one atmosphere. The system is bivariant at the point *a*. On reaching *b*, melting of ice commences. There are two phases now, ice and water, therefore the system becomes univariant, *i.e.* it has one degree of freedom. Further heating simply helps more ice to melt, temperature remaining constant and corresponding to point *b* till the melting of ice is completed. On further heating we follow the path *bc*. Now there is only water *i.e.* one phase and two degrees of freedom. The temperature of water keeps rising till we reach the point *c*. Further heating is used to convert water into vapours. Here we have two phases and one degree of freedom. The temperature remains constant till the whole of water has changed into vapour. Beyond the point *c*, further heating simply raises the temperature of vapour along the path *cd*.

Similarly, we can follow the effect of change of pressure on the water system at a constant temperature.

9.7 PHASE DIAGRAM OF SULPHUR SYSTEM

It is a one component system comprising **four phases**, *viz.*, (*i*) *Rhombic sulphur*, (*ii*) *Monoclinic sulphur*, (*iii*) *Sulphur liquid* and (*iv*) *Sulphur vapour*. This is a typical example of one component system exhibiting solid-solid transformation.

Sulphur exists in two well-known crystalline forms, namely rhombic sulphur and monoclinic sulphur. The two forms are in equilibrium with each other at 95.5°C, which is called its *transition temperature*. It is defined as the "*temperature at which one stable form of a solid is transformed into another stable solid form of it, without any change in temperature, pressure on the system being one atmosphere.*" Rhombic sulphur is stable below 95.5°C, whereas monoclinic is stable above this temperature.

According to phase rule equation, all the four phases cannot co-exist in equilibrium. This is because on substituting P = 4 and C = 1 in the phase rule equation, we get

$$F = C - P + 2 = 1 - 4 + 2 = -1$$

Thus, we get F = –1, which is meaningless. Hence for a system consisting of single component, it is not possible to have four phases together in equilibrium. However, three or fewer number of phases can exist together.

The phase diagram of the sulphur system as obtained experimentally by plotting pressure vs. temperature is shown in Fig. 9.2. The diagram consists of *six stable curves BO*, *OA*, *AE*, *OF*, *AC* and *CF* and *four metastable curves OD*, *OG*, *AD* and *CD*. The curves divide the diagram into *four areas, i.e.*, to the left of *BOCF*, below *BOAE*, to the right of *FCAE* and the one enclosed by *OCA*.

9.7.1 Areas

The areas are bivariant, that means to locate any point in the area, both temperature and pressure are to be specified. Each area represents the conditions for the stable existence of a single phase. In areas thus there are two degrees of freedom, which also follows from the phase rule equation F = C – P + 2; putting the values C = P = 1, we get F = 1 – 1 + 2 = 2.

In the area to the left of *BOCF* only S_R (rhombic sulphur) exists while in the area below *BOAE*, only S_V (sulphur vapour) exists; to the right of *FCAE*, S_L (liquid sulphur) is present and in the region enclosed by *OCA*, S_M, (monoclinic sulphur) exists.

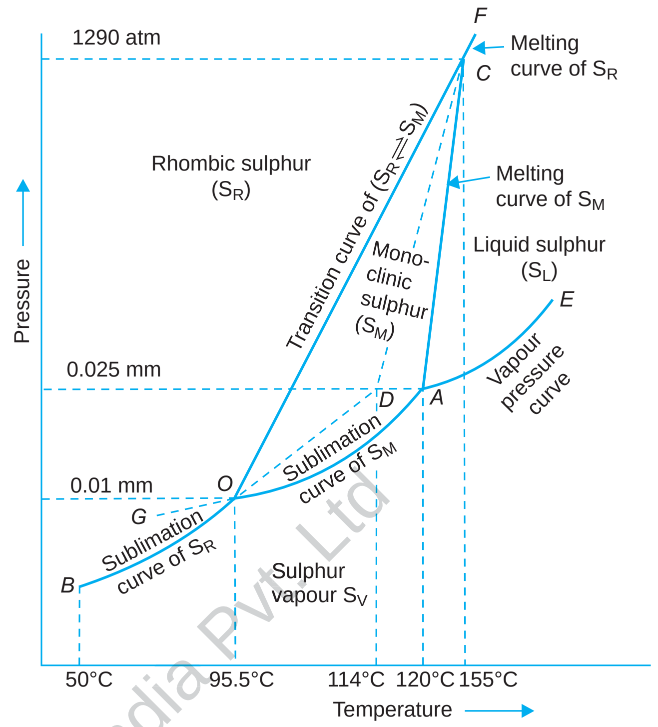


Fig. 9.2: *Phase diagram of the sulphur system*

9.7.2 Curves

(*i*) *OB*: It is the *sublimation curve of rhombic sulphur*. The phases present in equilibrium along this curve are S_R and S_V. The curve starts from the point *O*, the transition temperature of S_R to S_M, and ends at *B* (50°C) below which vapour-pressure of S_R cannot be measured. If heating is done rapidly, then it is possible to heat rhombic sulphur above the transition point along *OD*. *OD is the metastable curve*. On slight disturbance it merges into curve *OA*, which is the vapour pressure curve of monoclinic sulphur.

(*ii*) *OA*: It is the *sublimation curve of monoclinic sulphur*. The two phases present in equilibrium along this curve are S_M, and S_V. The curve starts from the point *A*, melting point of S_M (120°C) and ends at *O*, the transition temperature of S_R (95.5°C).

Except at the point *O*, where three phases S_R, S_M and S_V are in equilibrium, at any other point all along the curve only two phases S_V and S_M are in equilibrium. For a fixed value of temperature, pressure is automatically fixed. The degree of freedom, therefore, is one.

If the temperature of monoclinic sulphur is lowered, then it would change into rhombic sulphur at 95.5°C, but it is possible to prevent this conversion by a careful cooling. Then we will move along the curve *OG* which is a *metastable vapour pressure curve of monoclinic sulphur*.

(*iii*) *AE*: It is *the vapour pressure curve of liquid sulphur*. The two phases present in equilibrium along this curve are liquid sulphur, S_L, and vapour sulphur, S_V. The curve starts at *A*, the melting point of S_M, and ends at *E*, the critical point beyond which out of the two phases S_L and S_V, only S_V (vapour sulphur phase) can exist. For any point on the curve, for a fixed value of pressure, the temperature has a fixed value. Therefore, the system also has one degree of freedom. The extended curve *AD* represents the metastable vaporisation curve of liquid sulphur.

(*iv*) *OC*: It is *the transition curve* and represents the equilibrium between rhombic and monoclinic sulphur and is obtained from the effect of pressure on the transition temperature of rhombic sulphur. The slope of the curve *OC* is away from the vertical pressure axis, indicating that the transition point is raised by the rise of pressure. The curve ends at the point *C*, after which monoclinic sulphur phase disappears.

(*v*) *AC*: It is *the melting point curve of monoclinic sulphur*. It represents the equilibrium between monoclinic sulphur and liquid sulphur and results from the effect of pressure on the melting point of monoclinic sulphur. The curve is inclined away from the pressure axis showing that the melting point rises with the rise of pressure. The curve ends at C beyond which monoclinic sulphur does not exist in a stable condition. The system has degree of freedom equal to one.

(vi) ***CD*****:** This curve represents the equilibrium between rhombic and liquid sulphur and is the *metastable melting point curve of rhombic sulphur*. The curves *OC* and *AC* meet at C, at 155°C and 1290 atmospheres. Therefore, if liquid sulphur were cooled at a pressure higher than 1290 atmospheres, then rhombic sulphur would crystallised at once and no monoclinic sulphur being formed. The curve passes through the point C and beyond this point it becomes a stable melting point curve *CF* of rhombic sulphur.

9.7.3 Triple Points

There are three stable triple points *viz.*, *O*, *A* and *C* in this phase diagram. At the point *O*, three phases in equilibrium are sulphur rhombic, sulphur monoclinic and sulphur vapour. If one of the variables is changed, one of the phases disappears. Similarly, *A* is also a triple point between the monoclinic, vapour and liquid sulphur. The point is again invariant. Further, lines *OC* and *AC* intersect at *C* to yield a three phase equilibrium between rhombic, monoclinic and liquid sulphur. Since on changing one of the variables, either pressure or temperature, one of the phases disappears, therefore, the system at the triple point has no degree of freedom. We get the same result, from phase rule equation.

$$F = C - P + 2 \qquad \text{or} \qquad F = 1 - 3 + 2 = 0$$

D is a metastable triple point; the phases in equilibrium being S_R, S_L and S_V.

9.8 EVAPORATION AND CONDENSATION

According to kinetic theory of gases and liquids, the molecules are constantly moving in all possible directions and with all possible velocities. Some of the liquid molecules are moving with small velocities. They are associated with smaller kinetic energies. Such molecules continue moving in the liquid state. However, there are molecules moving faster. Such molecules possess higher kinetic energies and they have a tendency to leave the liquids phase and move into the space above the liquid. Such molecules constitute the vapour phase above the liquid phase. *This phenomenon of high-energy molecules leaving the liquid phase and moving into the vapour phase is called evaporation*.

The molecules in the vapour phase collide with one another and with the walls of the container. In this process, some of them lose a part of their energy and revert to the liquid state. *Transference of molecules from the vapour phase to the liquid phase is called condensation*.

At equilibrium, many molecules leave the liquid surface and move to the vapour phase as the molecules that move from vapour phase to liquid phase.

9.9 VAPOUR PRESSURE OF A LIQUID

Vapour pressure of a liquid at any temperature may be defined as the pressure exerted by the vapour present above the liquid in equilibrium with the liquid at that temperature. Vapour pressure exerted by the vapour obtained from the liquid may be illustrated as shown in Fig. 9.3.

Cooling Caused by Evaporation

When a liquid evaporates, the more energetic molecules leave the liquid. As a result, the average kinetic energy of the remaining liquid decreases and hence the temperature falls.

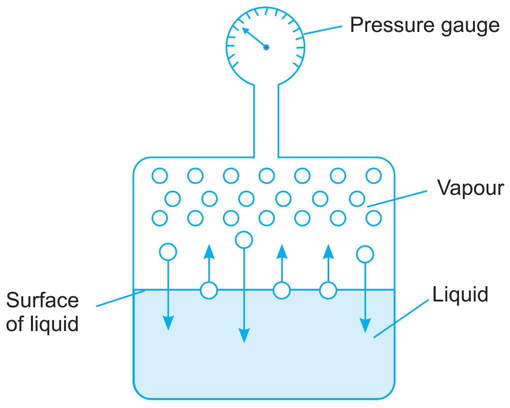


Fig. 9.3: *Illustration of vapour pressure*

9.9.1 Important Factors that affect the Vapour Pressure

Two important factors on which the vapour pressure of a liquid depends are:

(*a*) **Nature of the Liquid:** If the intermolecular forces of attraction in the liquid are weak, the molecules can easily leave the liquid and come into the vapour phase and hence the vapour pressure is higher. For example, the vapour pressures of ether, acetone, benzene, etc. are higher than that of water at the same temperature. This is illustrated in Fig. 9.4. Acetic acid gives lower vapour pressure than water as the former has greater intermolecular forces caused by hydrogen bonding.

(*b*) **Effect of Temperature:** As the temperature of a liquid is increased, the number of molecules with higher kinetic energy increases. Hence the vapour pressure of the liquid increases. This is again evident from each curve in Fig. 9.4.

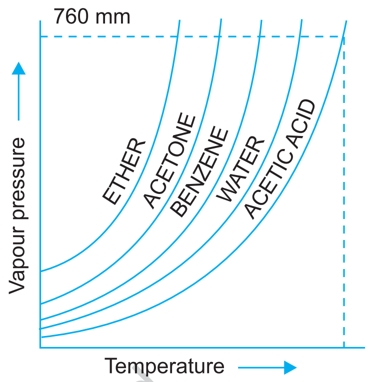


Fig. 9.4: *Vapour pressure-Temperature curves for some liquids*

9.9.2 Boiling Point of a Liquid

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the boiling point of the liquid. For example, boiling point of water is 100°C. The boiling point for any liquid is obtained from the vapour pressure-temperature curves, as shown for acetic acid (Fig. 9.4). If the atmospheric pressure is 760 mm, the boiling point is called normal boiling point.

Obviously, if the external pressure is higher, more heat will be required to make the vapour pressure equal to the external pressure and hence higher will be the boiling point. Similarly, if the external pressure is decreased, the boiling point is lowered. This is the reason that a liquid boils at a lower temperature on the top of a mountain (where pressure is low) than on the seashore.

9.9.3 Heat of Vaporisation (ΔH_v) of a Liquid

After the liquid starts boiling, the extra heat supplied to the liquid is used up not in increasing the temperature of the liquid but to overcome the intermolecular forces of attraction existing in the liquid and thus changing the liquid into vapour. Hence, the temperature remains constant till whole of the liquid changes into vapour.

The amount of heat required to change 1 mole of the liquid into its vapour at the boiling point is called the heat of vaporisation of the liquid.

Obviously, greater the intermolecular force of attraction present in a liquid, greater is the heat of vaporisation. For example, the heat of vaporisation of water is greater than that of ether, acetone or benzene.

9.10 RAOULT'S LAW

Raoult's Law States

Case 1. ***When the solute is volatile.*** *In a solution, the vapour pressure of a component at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state.* Mathematically,

$$P_i = x_i \times P_i^{\circ}$$

where

P_i = Vapour pressure of component i in the mixture
x_i = Mole fraction of component i
P_i° = Vapour pressure of pure component i,

Raoult

Thus, in a *binary solution,*

Vapour pressure of the solvent in the solution = Mole fraction of the solvent in solution × Vapour pressure of the pure solvent ...(*i*)

We can write a similar equation for the solute.

Case 2. *When the solute is non-volatile.* If the solute is non-volatile, it will not contribute to the total vapour pressure of the solution. Thus, the vapour pressure of the solution will be the vapour pressure due to solvent in the solution only.

For such solutions,

Vapour pressure of the solution = Mole fraction of the solvent in solution × Vapour pressure of the pure solvent or in terms of symbols, we can write

$$P_s = x_1 \times P^o \qquad ...(ii)$$

This can be rewritten in the form $\frac{P_s}{P^o} = x_1$ ...(*iii*)

If the solution contains n_2 moles of the solute dissolved in n_1 moles of the solvent, we have

Mole fraction of the solvent in solution $(x_1) = \frac{n_1}{n_1 + n_2}$

Substituting this value in equation (*iii*), we get

$$\frac{P_s}{P^o} = \frac{n_1}{n_1 + n_2}$$

Subtracting each side from 1, we get

$$1 - \frac{P_s}{P^o} = 1 - \frac{n_1}{n_1 + n_2}$$

or

$$\boxed{\frac{P^o - P_s}{P^o} = \frac{n_2}{n_1 + n_2}} \qquad ...(iv)$$

In this expression, $P^o - P_s$, represents the lowering of vapour pressure, $\frac{P^o - P_s}{P^o}$ is called relative lowering of vapour pressure, $\frac{n_2}{n_1 + n_2}$ represents the mole fraction of the solute in the solution.

Hence, the expression (*iv*) may be expressed in words as follows:

The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

This is another definition of Raoult's law.

9.10.1 Numerical Problems on Raoult's Law

Formulae and Units:

(*i*) $X_1 = \frac{n_1}{n_1 + n_2}$; $X_2 = \frac{n_2}{n_1 + n_2}$ and $X_1 + X_2 = 1$

where, X_1 = Mole fraction of solvent

X_2 = Mole fraction of solute

n_1 = No. of moles of solvent

n_2 = No. of moles of solute

(*ii*) $P_A = P^o_A \,.\, X_A$; $P_B = P^o_B \,.\, X_B$ and $P = P_A + P_B$

where;

P_A = Vapour pressure of component A of solution

P_B = Vapour pressure of component B of solution

P = Vapour pressure of solution

P^o_A = Vapour pressure of pure component A

P^o_B = Vapour pressure of pure component B

X_A = Mole fraction of component A in solution

X_B = Mole fraction of component B in solution.

Example 1. *The vapour pressure of two pure liquids A and B are 15000 and 30000 Nm^{-2} at 298 K. Calculate the mole fractions of A and B in the vapour phase when an equimolar solution of the liquids is made.*

Solution. $P^o_A = 15000\ Nm^{-2}$

and $P^o_B = 30000\ Nm^{-2}$

In equimolar solution, mole fractions of A and B, *i.e.*, X_A and X_B are equal.

$X_A = 0.5$

or $X_B = 1 - 0.5 = 0.5$

Applying Raoult's law to ideal solution,

$P_A = P^o_A \,.\, X_A = 15000 \times 0.5 = 7500\ Nm^{-2}$

and $P_B = P^o_B \,.\, X_B = 30000 \times 0.5 = 15000\ Nm^{-2}$

Total pressure $P = P_A + P_B = 7500 + 15000 = 22500\ Nm^{-2}$

In the vapour phase,

$$\text{Mole fraction of A} = \frac{\text{Partial pressure of A}}{\text{Total pressure}} = \frac{7500}{22500} = 0.3333$$

Mole fraction of B = 1 – 0.3333 = 0.6667

Example 2. *Liquid A (molecular mass 46) and liquid B (molecular mass 18) form an ideal solution. At 293 K, the vapour pressures of pure A and B are 44.5 and 17.5 mm of Hg respectively. Calculate (a) the vapour pressure of a solution of A in B containing 0.2 mole fraction of A, and (b) the composition of the vapour phase.*

Solution.

(*a*) $P^o_A = 44.5$ mm of Hg, $X_A = 0.2$

$P^o_B = 17.5$ mm of Hg, $X_B = (1 - 0.2) = 0.8$

According to Raoult's law,

Partial pressure of A = Vapour pressure of pure A × Mole fraction of A

∴ Partial pressure of A, $P_A = P^o_A \,.\, X_A = 44.5 \times 0.2 = 8.9$ mm of Hg

and Partial pressure of B, $P_B = P^o_B \,.\, X_B = 17.5 \times 0.8 = 14.0$ mm of Hg

∴ Total pressure $P = P_A + P_B = 8.9 + 14 = 22.9$ mm of Hg

(*b*) In vapour phase,

$$\text{Mole fraction of A} = \frac{\text{Partial pressure of A}}{\text{Total pressure}}$$

or

$$X_A = \frac{P_A}{P_A + P_B} = \frac{8.9}{8.9 + 14} = \frac{8.9}{22.9} = 0.39$$

$X_B = 1 - 0.39 = 0.61$

Example 3. *The vapour pressures of pure components A and B are 120 mm and 96 mm of Hg respectively. What will be the partial pressures of the components and the total pressure when the solution contains 1 mole of component A and 4 moles of component B and the solution is ideal? What will be the composition in the vapour phase?*

Solution. P_A^o = 120 mm of Hg and P_B^o = 96 mm of Hg

Here, Mole fraction of A,

$$X_A = \frac{\text{No. of moles of A}}{\text{No. of moles of A + No. of moles of B}} = \frac{1}{1+4} = \frac{1}{5} = 0.2$$

Mole fraction of B, $X_B = 1 - 0.2 = 0.8$

Partial pressure of component A,

$$P_A = P_A^o \times X_A = 120 \times 0.2 = 24.0 \text{ mm Hg}$$

Partial pressure of component B, $P_B = P_B^o \times X_B = 96 \times 0.8 = 76.8$ mm

Total pressure = $P_A + P_B$ = (24.0 + 76.8) mm = 100.8 mm

Mole fraction of component A in vapour phase

$$= \frac{P_A}{\text{Total pressure}} = \frac{24}{100.8} = 0.238$$

Mole fraction of component B in vapour phase = 1 – 0.238 = 0.762.

Example 4. *Benzene C_6H_6 (b.p. 353.1 K) and toluene C_7H_8 (b.p. 383.6 K) are two hydrocarbons that form a very nearly ideal solution. At 313 K, the vapour pressures of pure liquids are 160 mm Hg and 60 mm Hg respectively. Assuming an ideal solution behaviour, calculate the partial pressures of benzene and toluene and the total pressure over the following solutions:*

(i) One made by combining equal number of toluene and benzene molecules.
(ii) One made by combining 4 mole of toluene and 1 mole of benzene.
(iii) One made by combining equal masses of toluene and benzene.

Solution. (*i*) When the number of molecules of toluene and benzene are equal, that means the number of moles of the two liquids are also equal.

Thus, mole fraction of benzene, $X_A = \frac{1}{1+1} = 0.5$

and mole fraction of toluene, $X_B = 1 - 0.5 = 0.5$

According to Raoult's law

$$P = P^o \,.\, X$$

Partial pressure of benzene, $P_A = P_A^o \,.\, X_A = 160 \times 0.5 = 80$ mm

Partial pressure of toluene, $P_B = P_B^o \,.\, X_B = 60 \times 0.5 = 30$ mm

Total vapour pressure, $P = P_A + P_B = 80 + 30 = 110$ mm

(*ii*) Mole fraction of benzene, $X_A = \frac{1}{1+4} = \frac{1}{5} = 0.2$

Mole fraction of toluene, $X_B = 1 - 0.2 = 0.8$

Partial pressure of benzene, $P_A = P_A^o \,.\, X_A = 160 \times 0.2 = 32$ mm

Partial pressure of toluene, $P_B = P_B^o \,.\, X_B = 60 \times 0.8 = 48$ mm

Total vapour pressure, $P = P_A + P_B = 32 + 48 = 80$ mm

(*iii*) Here the masses of the two liquids are the same. Let the amount of each be *m* g.

Then mole fraction of benzene, $X_A = \frac{m/78}{m/78 + m/92} = 0.541$

Mole fraction of toluene, $X_B = 1 - 0.541 = 0.459$

Partial pressure of benzene, $P_A = P_A^o . X_A = 160 \times 0.541 = 86.56$ mm of Hg

Partial pressure of toluene, $P_B = P^o_B . X_B = 60 \times 0.459 = 27.54$ mm of Hg

Total vapour pressure = 86.56 + 27.54 = 114.1 mm

9.11 RELATIVE LOWERING OF VAPOUR PRESSURE

Suppose the vapour pressure of the pure solvent, $A = P_A^o$

Let the solute be B.

Let the vapour pressure of the solvent in the solution = P_A

Since $P_A^o > P_A$

$\therefore$ Lowering of vapour pressure = $P_A^o - P_A$

Relative lowering of vapour pressure = $\dfrac{P_A^o - P_A}{P_A^o}$

According to Raoult's law, the relative lowering of vapour pressure is equal to the mole fraction of the solute in the solution.

$$\therefore \qquad \frac{P_A^o - P_A}{P_A^o} = X_B \qquad ...(i)$$

where X_B is the mole fraction of the solute.

Mole fraction of the solute $X_B = \dfrac{n_2}{n_1 + n_2}$

where n_2 = No. of moles of the solute and n_1 = No. of moles of the solvent.

$$\therefore \qquad X_B = \frac{n_2}{n_1 + n_2}$$

Thus, the relation (*i*) becomes

$$\frac{P_A^o - P_A}{P_A^o} = \frac{n_2}{n_1 + n_2} \qquad ...(ii)$$

It is evident from (*ii*) that *the relative lowering of vapour pressure depends only upon the mole fraction or molar concentration of the solute.* Therefore, the relative lowering of vapour pressure is a colligative property.

Molecular Mass of Non-volatile Solute

Now, the number of moles of the solute, $n_2 = \dfrac{w}{m}$

where, w = Mass of the solute and m = Molecular mass of the solute

And the number of moles of the solvent, $n_1 = \dfrac{W}{M}$

where, W = Mass of the solvent and M = Molecular mass of the solvent

The expression (*ii*) becomes

$$\frac{P_A^o - P_A}{P_A^o} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}} \qquad ...(iii)$$

In a dilute solution, n_2 is negligible as compared to n_1. Therefore, neglecting n_2 (or w/m) in the denominator, we get from expression (*iii*)

$$\frac{P_A^o - P_A}{P_A^o} = \frac{\frac{w}{m}}{\frac{W}{M}} = \frac{w}{m} \times \frac{M}{W}$$

or $$\frac{P_A^o - P_A}{P_A^o} = \frac{wM}{mW} \qquad \text{...}(iv)$$

Thus, by measuring the lowering of vapour pressure of a solution, the molecular mass m of a solute in a given solution of a known concentration can be determined, if other quantities are known.

9.11.1 Numerical Problems on Lowering of Vapour Pressure

Formulae and Units:

$$\frac{P^o - P_s}{P^o} = \frac{n_2}{n_1 + n_2} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}} = \frac{w}{m} \times \frac{M}{W} \text{ (for dilute solution)}$$

where, P^o = Vapour pressure of pure liquid.

and P_s = Vapour pressure of solution containing non-volatile solute.

n_2, w and m = No. of moles, amount in gram and molecular mass of solute respectively.

and n_1, W and M = No. of moles, amount in gram and molecular mass of solvent respectively.

Example 1. *At 298 K, the vapour pressure of water is 23.75 mm of Hg. Calculate the vapour pressure at the same temperature over 5% aqueous solution of urea (NH_2CONH_2).*

Solution. The solution may be considered as a dilute solution and the approximate relation given below may be used.

$$\frac{P_A^o - P_A}{P_A^o} = \frac{wM}{mW}$$

In the present case $P_A^o = 23.75$, $w = 5$ g

Therefore, $W = 100 - 5 = 95$ g

$M = 18$, $m = 60$ (mol. mass of urea)

Substituting these values in the equation above, we get

$$\frac{23.75 - P_A}{23.75} = \frac{5 \times 18}{60 \times 95}$$

or $$P_A = 23.375 \text{ mm}$$

Example 2. *The vapour pressure of water at 293 K is 17.51 mm of Hg, lowering of vapour pressure of sugar solution is 0.0614 mm of Hg. Calculate:*

(a) Relative lowering of vapour pressure
(b) Vapour pressure of the solution
(c) Mole fraction of water.

Solution. V.P. of solvent (water) = 17.51

Lets, V.P. of the solution = P (to be calculated)

∴ Lowering of V.P. = $P^o - P = 0.0614$ mm of Hg (*a*) Relative lowering of V.P. = $\frac{P^o - P}{P^o} = \frac{0.0614}{17.51} = 0.00351$

(*b*) Vapour pressure of the solution,

$$P = P^o - (P^o - P) = 17.51 - 0.0614$$
$$= 17.4486 \text{ mm of Hg}$$

Now according to Raoult's law,

$$\frac{P^o - P}{P^o} = \text{mole fraction of the solute}$$

$$\frac{P^o - P}{P^o} = \frac{n_2}{n_1 + n_2} = X_2$$

∴ Mole fraction of the solute = $\frac{P^o - P}{P^o} = \frac{0.0614}{17.51} = 0.00351$

(*c*) Hence, the mole fraction of the solvent = (1 – 0.00351) = 0.99649

∴ Mole fraction of water = 0.99649

Example 3. *The vapour pressure of a 5% aqueous solution of non-volatile organic substance at 373 K is 745 mm of Hg. Calculate the molecular mass of the solute.*

Solution. Mass of non-volatile organic solute, $w = 5$ g

Mass of solvent (water), $W = 95$ g

Molecular mass of solvent (water), $M = 18$

Molecular mass of non-volatile solute, $m = ?$

V.P. of the pure solvent (water) at 373 K, $P^o = 760$ mm of Hg

V.P. of the solution, $P = 745$ mm of Hg

Substituting the value in the relation,

$$\frac{P^o - P}{P^o} = \frac{w}{m} \times \frac{M}{W}$$

or $$\frac{760 - 745}{760} = \frac{5 \times 18}{m \times 95}$$

or $$\frac{15}{760} = \frac{5 \times 18}{m \times 95}$$

or $$m = \frac{5 \times 18 \times 760}{15 \times 95} = 48$$

Example 4. *A solution containing 6.0 grams of benzoic acid in 50 grams of ether ($C_2H_5.O.C_2H_5$) has a vapour pressure equal to 5.466×10^4 Nm^{-2} at 300 K. Given that vapour pressure of ether at the same temperature is 5.893×10^4 Nm^{-2}, calculate the molecular mass of benzoic acid.*

Solution. Vapour pressure of ether (solvent), $P^o = 5.893 \times 10^4 \text{ Nm}^{-2}$

Vapour pressure of solution, $P = 5.466 \times 10^4 \text{ Nm}^{-2}$

Molecular mass of solvent ($C_2H_5.O.C_2H_5$), $M = 74$

Mass of solute (benzoic acid), $w = 6$ g

Mass of solvent (ether), $W = 50$ g

Let the molecular mass of solute (benzoic acid) = m

Substituting the value in the relation,

$$\frac{P^o - P}{P^o} = \frac{w}{m} \times \frac{M}{W}, \text{ we have}$$

$$\frac{5.893 \times 10^4 - 5.466 \times 10^4}{5.893 \times 10^4} = \frac{6 \times 74}{m \times 50}$$

or
$$\frac{0.427 \times 10^4}{5.893 \times 10^4} = \frac{6 \times 74}{m \times 50}$$

or
$$\frac{0.427}{5.893} = \frac{6 \times 74}{m \times 50}$$

or
$$m = \frac{6 \times 74 \times 5.893}{50 \times 0.427}$$

or
$$m = 122.55$$

Hence, the molecular mass of solute (benzoic acid) = 122.55 u.

PROBLEMS FOR PRACTICE

1. The vapour pressure of water at 298 K is 23.75 mm of Hg and that of a solution containing 5 g of a solute in 100 g water is 23.402 mm of Hg. Calculate the molecular wt. of the solute. [**Ans.** 60.4]
2. The vapour pressure of a 5% aqueous solution of a non-volatile organic substance at 373 K is 745 mm of Hg. Calculate the molecular mass of the solute. [**Ans.** 48]

   [**Hint:** Vapour pressure of pure water at 373 K is taken as 760 mm of Hg]
3. Calculate the vapour pressure of a solution at 293 K containing 2 g urea (mol. mass = 60) in 50 g of water assuming the solution as a concentrated solution. Vapour pressure of water at the same temperature is 17 mm of Hg. [**Ans.** 16.799 mm of Hg]

9.12 DALTON'S LAW OF PARTIAL PRESSURE

Dalton's law of partial pressure states that *in a mixture of non-reacting gases, the total pressure exerted is equal to the sum of partial pressures of each individual gas.*

Mathematically, the pressure of a mixture of non-reactive gases can be written as

$$p_{\text{total}} = \sum_{i=1}^{n} p_i \qquad \text{or} \qquad p_{\text{total}} = p_1 + p_2 + p_3 + \ldots\ldots + p_n$$

where, p_1, p_2, p_3 ...., p_n represent the partial pressure of each component.

Also
$$p_i = p_{\text{total}} \times y_i$$

It is possible to calculate the total pressure of a mixture of gases in a container of known volume if we know the number of moles of individual gases. If n_1, n_2, n_3..... represent the number of moles of gases 1, 2, 3, ... etc, then the partial pressures of individual gases in that container can be written as:

$$p_1 = \frac{n_1 RT}{V}$$

$$p_2 = \frac{n_2 RT}{V}$$

$$p_3 = \frac{n_3 RT}{V} \text{ and so on}$$

The total pressure p_{total} can then be summed up as

$$p_{\text{total}} = p_1 + p_2 + p_3 + \ldots\ldots\ldots$$

where y_i is the mole fraction of the ith component in the total mixture of n components.

Daltons' law is not strictly followed by real gases with deviation being considerably large at high pressure.

9.13 IDEAL AND NON-IDEAL SOLUTIONS

Ideal Solutions: A solution of two components is said to be ideal if each component of the solution obeys Raoult's law at all temperatures and concentrations. That is the vapour pressure of each component in the solution at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state at the same temperature. Thus, if two liquids A and B are mixed together, the solution formed by them will be ideal if

$$P_A = x_A \times P_A^{\circ}$$

and $$P_B = x_B \times P_B^{\circ}$$

where,

P_A = vapour pressure of component A in the solution

x_A = mole fraction of the component A in the solution

P_A° = vapour pressure of the liquid A in the pure state

P_B, x_B, P_B° are the corresponding terms for the component B.

It is observed that *the solution formed by two liquids A and B is ideal if the interactions (i.e., the intermolecular forces of attraction) among the molecules of A and B in the solution are just the same as among the molecules of pure A or B.*

Further, it is observed that the solution formed on mixing the two liquids is ideal if

(i) *there is no volume change on mixing i.e.,* $\Delta V_{mix} = 0$

(ii) *there is no enthalpy change on mixing i.e.,* $\Delta H_{mix} = 0$

For example, if 50 mL of *n*-hexane is mixed with 50 mL of *n*-heptane, the total volume of the solution is found to be 100 mL and the temperature of the solution is found to be same as that of pure *n*-hexane and *n*-heptane before mixing showing that no heat is evolved or absorbed on mixing. Such a solution is an ideal solution. Another example of ideal solution is a mixture of benzene and toluene.

Non-ideal Solution: On the other hand, a solution formed by mixing of two liquids is said to be non-ideal if it does not obey Raoult's law or the interactions of A and B molecules in the solution are not similar to those of pure A and pure B or $\Delta V_{\text{mix}} \neq 0$, and $\Delta H_{\text{mix}} \neq 0$.

9.13.1 Vapour Pressure-Composition Diagram for Ideal Solutions

In case of ideal solutions, the partial pressure of each component can be calculated using Raoult's law *i.e.*,

$$p_A = x_A \times p_A^{o}$$

and $$p_B = x_B \times p_B^{o}$$

where, p_A, p_A^o, p_B and p_B^o are all measured at the same temperature.

Thus, $P_{sol} = x_A p_A^o + x_B p_B^o$

At any particular temperature, the values of P_{sol} can be determined experimentally for different mole fractions. The values p_A^o and p_B^o for the pure liquids can be measured at the same temperature and hence p_A and p_B can be calculated for any particular mole fraction. For an ideal solution, the straight line plots are obtained for vapour pressure *vs.* composition as shown in Fig. 9.5 where dotted lines represent the plots of the partial pressures and the solid line that of the solution.

In these plots, for any mole fraction (say x), the total vapour pressure of the solution is the sum of the partial pressures of its components A and B.

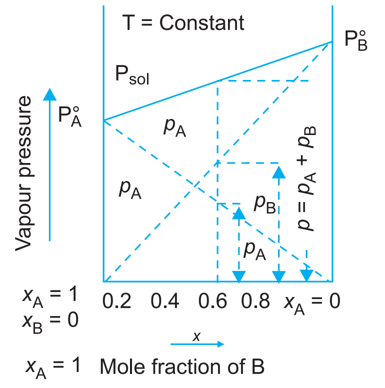


Fig. 9.5: *Vapour pressure-composition diagram for an ideal solution*

9.13.2 Vapour Pressure-Composition Curves for Non-ideal Solutions

In case of non-deal solutions, the plots of vapour pressures *vs.* composition (mole fraction) are curved lines instead of straight lines. Non-ideal solutions are divided into the following three types:

Type I: *Those which show small positive deviation from Raoult's law.* The vapour pressure-composition graphs of these solutions curve slightly upwards as shown in Fig. 9.6. The dotted straight line plots are for ideal solution, calculated by using Raoult's law.

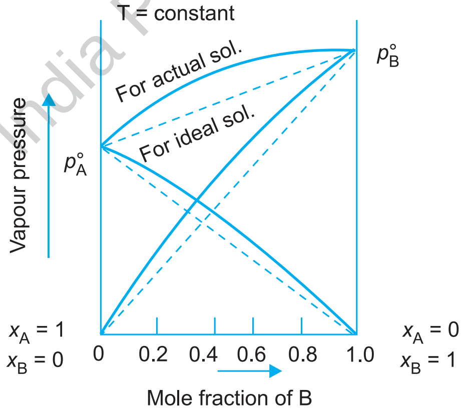


Fig. 9.6: *Vapour pressure-composition plots for non-ideal solution showing small positive deviation*

Some examples of solutions of this type are benzene + toluene, water + methyl alcohol, carbon tetrachloride + cyclohexane, etc.

Type II: *Those which show large positive deviation from Raoult's law.* The vapour pressure-composition plots of these solutions curve upwards considerably as shown in Fig. 9.7. The dotted straight line plots, included in the figure for comparison, are for ideal solution (calculated by means of Raoult's laws).

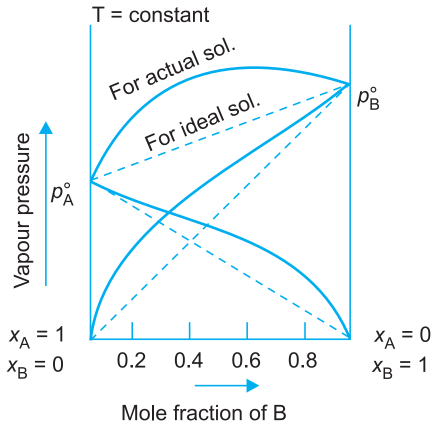


Fig. 9.7: *Vapour pressure-composition plots for non-ideal solution showing large positive deviation*

It is obvious from Figs. 9.6 and 9.7 that for any mole fraction, the total vapour pressure of the solution is more than that for ideal solution. This means that the tendency for the molecules to escape from the solution is more than that from the pure liquids. This indicates that in such solutions, the intermolecular forces of attraction between the molecules of the solution (*A–B* attractions) are weaker than those of either of the pure components (*A–A* attractions or *B–B* attractions). Such a behaviour is associated with an increase in volume and absorption of heat on mixing.

Some examples of liquid pairs showing large positive deviation include water + ethanol, ethanol + chloroform.

Type III: *Those which show negative deviation from Raoult's law.* The vapour pressure-composition plots of these solutions curve downwards as shown in Fig. 9.8. The dotted straight line plots are for the ideal solution, calculated on the basis of Raoult's law and are included in the figure for comparison. It is obvious from the figure that for any mole fraction, the total vapour pressure of the solution is less than that for ideal solution. This means that the tendency for the molecules to escape from the solution is less than that from the pure liquids. This indicates that in such solutions, the intermolecular forces of attraction between the molecules of the solution (*A–B* attractions) are stronger than those of either of the pure components (*A–A* attractions or *B–B* attractions). It is related to the contraction in volume and evolution of heat in making the solution.

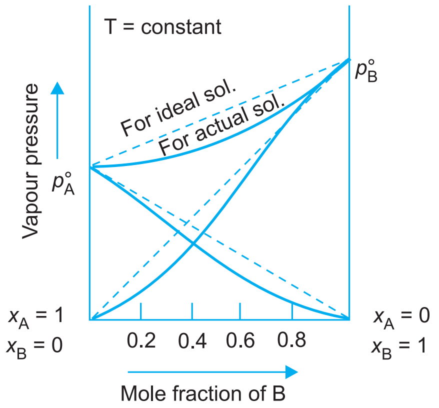


Fig. 9.8: *Vapour pressure-composition plots for non-ideal solution showing negative deviation*

Some examples of the liquid pairs showing negative deviation are water + nitric acid, water + sulphuric acid, acetone + chloroform, etc.

9.13.3 Vapour Pressure-Composition Diagrams

Vapour pressure-composition diagrams discussed earlier were vapour pressure vs. liquid composition. However, it was discovered that at a particular temperature, composition of the liquid and vapour phases were different. Hence, we have different *vapour pressure-vapour composition curves*. These can be obtained by measuring the vapour pressure and the composition of the vapour phase corresponding to each composition of the liquid mixutre.

These are the following three types of vapour pressure-composition diagrams:

Type I: *Those in which total vapour pressure is intermediate between those of the pure components and do not show any maximum or minimum (i.e., ideal solutions or solutions which show small positive deviation).*

Type II: *Those which* **show a maximum** *in the total vapour pressure curve.*

Type III: *Those which* **show a minimum** *in the total vapour pressure curve.*

The vapour pressure-liquid composition curves as well as the vapour pressure-vapour composition curves of all three types are given in Fig. 9.9 in which liquid B is more volatile than liquid A.

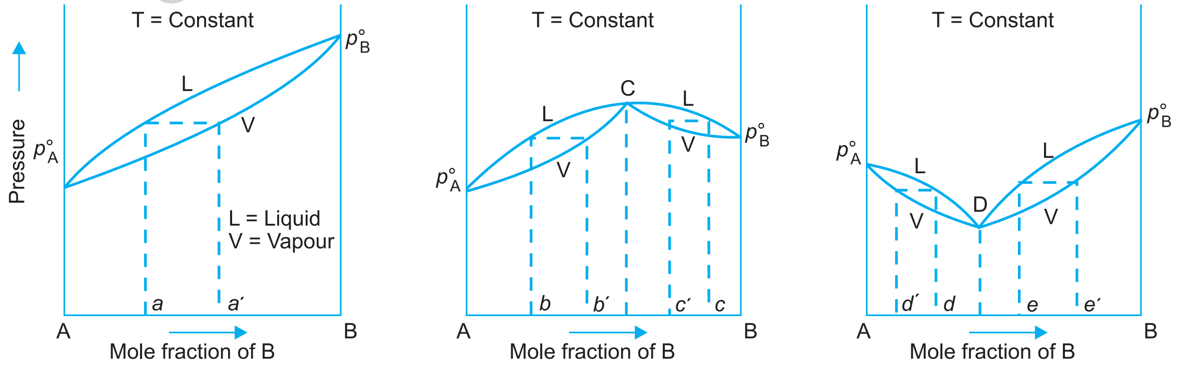


Fig. 9.9: *Vapour pressure-composition diagrams of binary miscible real solutions at constant temperature*

It may be observed that in these three types, the vapour composition curve lies below the liquid composition curve. This may be explained for each type as under:

(*i*) In *Type I*, as *B* is more volatile than *A*, corresponding to composition *a* of the liquid phase, vapour phase will be richer in *B*, *i.e.*, corresponding to composition *a´*.

(*ii*) In *Type II*, up to the point *C*, behaviour is same as in *Type I*, at *C*, the liquid phase and the vapour phase have the same composition and after point *C*, the vapour phase is richer in *A* (or less rich in *B*) as seen from points *c* and *c´*.

(*iii*) *In Type III*, up to the point *D*, the vapour phase is richer in *A* (or less rich in *B*) than the liquid phase, at the point *D* both have the same composition and after point *D*, the behaviour is similar to *Type I*.

The study of vapour pressure-composition curves helps to study the boiling point-composition curves, as discussed below.

9.13.4 Boiling Point-Composition Diagrams

Boiling point is the temperature at which the total vapour pressure becomes equal to the atmospheric pressure. Thus, a liquid or a solution which has low vapour pressure will have a higher boiling point because it has to be heated more to make the vapour pressure equal to the atmospheric pressure. Thus, pure liquid *A* which has less vapour pressure will have a higher boiling point and the pure liquid *B* which has higher vapour pressure will have lower boiling point. In between these two extremes, a solution of any composition having lower vapour pressure will have higher boiling point. These facts help us to construct the boiling point-composition diagrams from the vapour pressure-composition diagrams as shown in Fig. 9.10.

The point *C* in Type II which corresponds to maximum vapour pressure represents the lowest boiling point. Similarly, the point *D* in Type III which represents the lowest vapour pressure corresponds to the highest boiling point. The liquid mixtures having compositions corresponding to points *C* and *D* have constant boiling points and are called *azeotropes* or *azeotropic mixtures*.

9.13.5 How to Construct Vapour Pressure-Composition Curve from the Knowledge of Raoult's Law and Dalton's Law?

Liquid phase

As far as the curve for liquid phase is concerned, we can obtain the values of vapour pressure corresponding to different mole fractions as under:

Let the mole fraction of the component A = x_1

And, mole fraction of component B = x_2

Vapour pressure of pure liquid A = P_A°

(At a particular temperature)

Vapour pressure of pure liquid B = P_B°

According to Raoult's law

Vapour pressure of the mixture = $(x_1 \times P_A^\circ) + (x_2 \times P_B^\circ)$

A plot of graph between the vapour pressure of the mixture corresponding to different values of x_1 or x_2 will give the vapour pressure-composition curve for the liquid.

Vapour phase

We derived earlier the following relation under Dalton's law:

$$p_i = p_{\text{total}} \times y_i$$

where p_i is the partial pressure and y_i is the mole fraction of the component *i*. p_{total} is the total vapour pressure

or
$$y_i = \frac{p_i}{p_{\text{total}}}$$

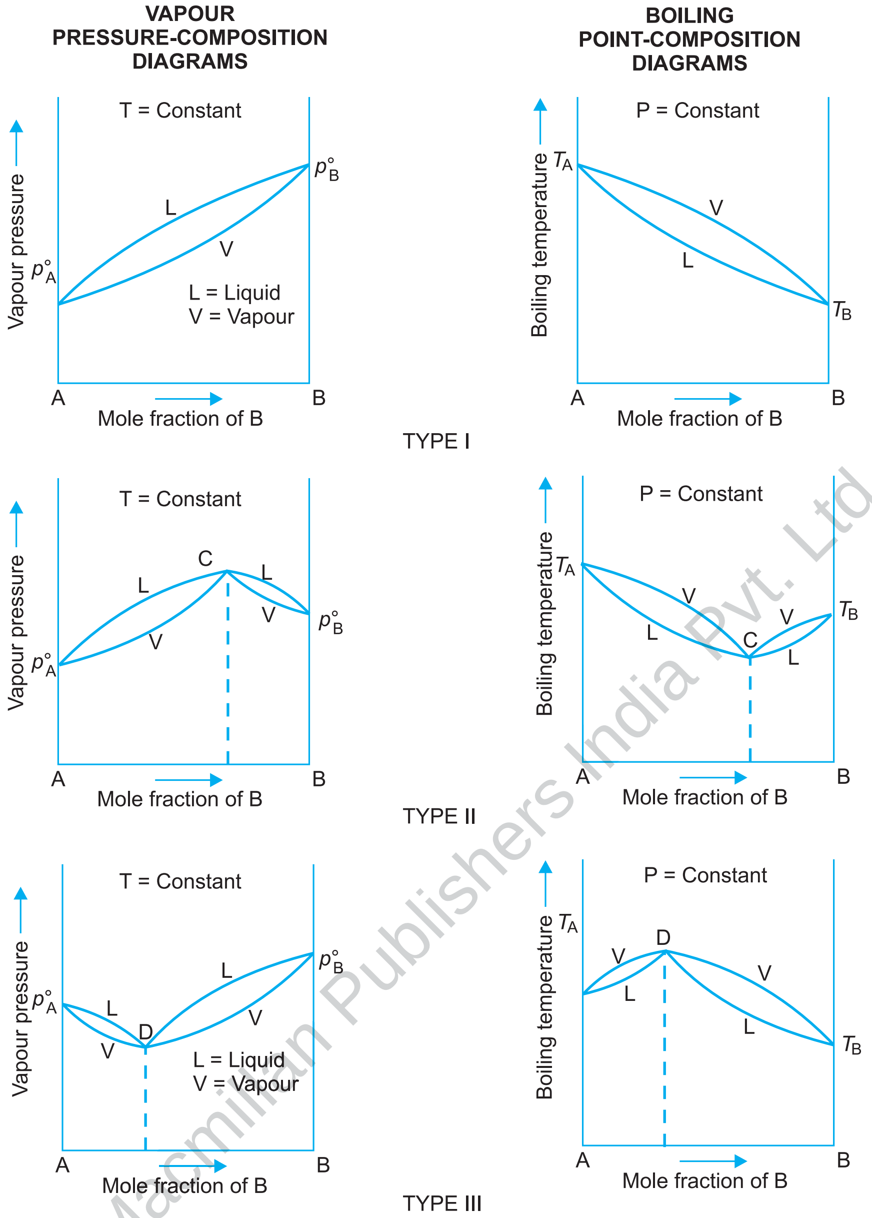


Fig. 9.10: *Boiling point-composition diagrams constructed from the vapour pressure-composition diagrams of binary miscible solutions*

Thus, mole fraction of a component in the vapour phase can be obtained by dividing the vapour pressure of the component by the total vapour pressure. Thus,

$$y_A = \frac{x_1 \times p^{\mathrm{o}}_{\mathrm{A}}}{(x_1 \times p^{\mathrm{o}}_{\mathrm{A}}) + (x_2\, p^{\mathrm{o}}_{\mathrm{B}})}$$

Thus, corresponding to different total pressure values, we can obtain the values of y_A and plot the curve for vapour pressure-composition for the vapour phase.

9.14 AZEOTROPES

Mixtures of liquids which boil at constant temperature like a pure liquid such that the distillate has the same composition as that of the liquid mixture are called **constant boiling mixtures** or **azeotropic mixtures** or

simply azeotropes. Evidently, the components of an azeotrope cannot be separated by fractional distillation. These azeotropes are of two types.

(*i*) **Minimum Boiling (Point) Azeotropes:** These azeotropes are formed by those liquid pairs which show positive deviations from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the highest and hence the boiling point is the lowest. Such azeotropes have boiling points lower than either of the pure components. Ethyl alcohol-water is an example of this type of azeotrope.

(*ii*) **Maximum Boiling (Point) Azeotropes:** These azeotropes are formed by those liquid pairs which show negative deviations from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is minimum and hence the boiling point is maximum. Such azeotropes have boiling points higher than either of the pure components. Water–HCl is an example of this type of azeotrope.

9.15 PRINCIPLE OF FRACTIONAL DISTILLATION OF IDEAL SOLUTION

A complete separation of components is possible by distillation. The less volatile component is left as residue and the more volatile component is obtained as distillate. We obtain better result by **fractional distillation**. This is carried out by using fractionating columns shown in Fig. 9.11.

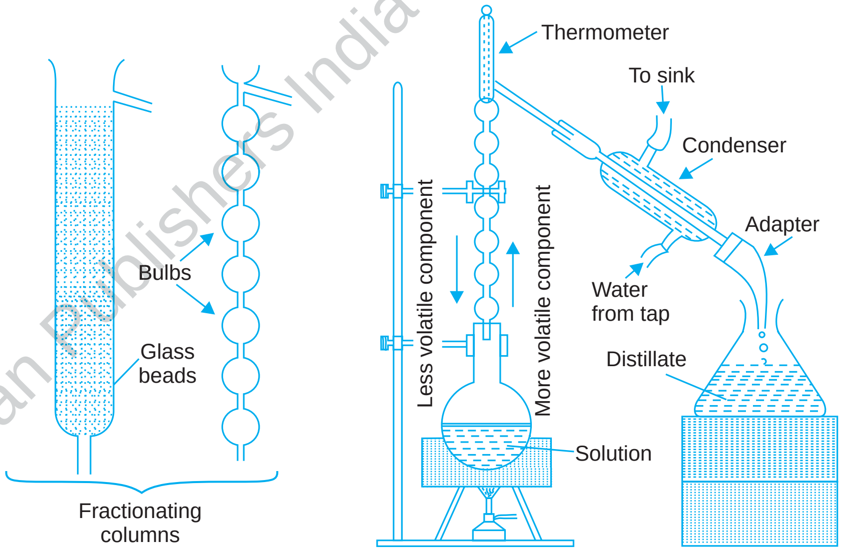


Fig. 9.11: *Method of fractional distillation*

A simple fractionating column consists of a long glass tube packed with glass beads or it has a large number of bulbs with narrow necks. The aim is to have a large surface area. At the top, it has a side tube which can be connected to the condenser. The column is fitted into the distillation flask, heated from below.

As vapours rise up into the column, they first condense in the lower part. However, as more hot vapours ascend the column the condensed liquid flowing down is heated up and most of the volatile component changes into vapours again which now condense at a higher place in the column or the tower. Thus, as the process of heating is continued, every time the condensed liquid flowing down meets the hot vapours going up. The place of condensation of the more volatile component keeps on shifting higher and higher in the column and thus ultimately the more volatile component in the pure form emerges out from the top and can be condensed into receivers. The less volatile component is left behind as residue in the distillation flask.

It is not possible to separate the components of a solution showing gross positive and negative deviations by fractional distillation. Consider Fig. 9.10. The boiling temperature-composition diagram of *Type II* solutions. A solution of composition between *A* and *C* on fractional distillation gives a residue of pure *A* and a final distillate of composition *C*. No pure *B* can be recovered. For a solution of composition between *C* and *B*, a residue of pure B and a final distillate of composition C is obtained. No pure *A* can be recovered.

Now consider Fig. 9.10 again, the boiling temperature-composition diagram of *Type III* solutions. For a mixture having composition between *A* and *D*, distillate of pure *A* is obtained and the residue has composition corresponding to point *D* (*i.e.* constant boiling mixture with maximum boiling point).

And for the mixture having composition between *D* and *B*, a distillate of pure *B* and residue of composition corresponding to *D* is obtained. Thus, it is not possible to separate the components of a solution showing gross positive and negative deviations by fractional distillation.

MISCELLANEOUS SOLVED QUESTIONS

1. *Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.*

Solution. A solution is a homogeneous mixture of two or more substances whose composition can be varied within certain limits.

Depending upon the state of solute or solvent, there may be the following nine types of solutions:

Types of Solutions

S. No.	*Solute*	*Solvent*	*Type*	*Example*
1.	Solid	Solid	Solid in solid	Alloys
2.	Liquid	Solid	Liquid in solid	Hydrated salts
3.	Gas	Solid	Gas in solid	Hydrogen in Pd
4.	Solid	Liquid	Solid in liquid	Salt in water
5.	Liquid	Liquid	Liquid in liquid	Alcohol in water
6.	Gas	Liquid	Gas in liquid	Aerated drinks
7.	Solid	Gas	Solid in gas	Suspended particles in air
8.	Liquid	Gas	Liquid in gas	Humidity in air
9.	Gas	Gas	Gas in gas	Air

2. *Suppose a solid solution is formed between two substances, one whose particles are very large and other whose particles are very small. What kind of solid solution is this likely to be?*

Solution. The solid substance whose particles size is small enter into the cavities or interstices of the solid substance whose particle size is large to form an interstitial solid solution. Tungsten (W) and Carbon (C) form interstitial solid WC. Small solute particles fit into voids/interstices in the host lattice. Tungsten carbide (WC) is extremely hard and is an example of such solid solution.

QUICK SCAN (FOR REVISION)

1. Ideal solution is formed between liquids having similar intermolecular interactions, *e.g.*, benzene + toluene, hexane + heptane, etc.
2. If intermolecular forces of attraction increase on mixing the two liquids, the solution shows negative deviations, *e.g.*, chloroform + acetone.
3. If intermolecular forces of attraction decrease on mixing the two liquids, the solution shows positive deviations, *e.g.*, ethyl alcohol + cyclohexane.
4. The boiling point of azeotrope showing positive deviation is less than the boiling points of the pure liquids. Likewise, the boiling point of azeotrope showing negative deviation is greater than the boiling points of pure liquids.
5. **For volatile solutes,** vapour pressure of any component in the solution = Mole fraction of that component × Vapour pressure of that component in the pure state ($P_A = X_A \times P^o_A$)

For non-volatile solutes, $\dfrac{P^o - P_s}{P^o} = \dfrac{n_2}{n_1 + n_2}$

$\approx \dfrac{n_2}{n_1} = \dfrac{w_2/M_2}{w_1/M_1}$ for dilute solutions.

EXERCISES

Very Short Answer Type Questions

1. Define an ideal solution.
2. How much molecular mass of NaCl is obtained experimentally using colligative properties?
3. How is molecular mass of a solute related to the depression in freezing point of the solution?
4. Define azeotropic mixture.
5. Under what condition do non-ideal solutions show negative deviations?
6. Why is vapour pressure of a solvent lowered when a non-volatile solute is dissolved in it?
7. What is the difference between lowering of vapour pressure and relative lowering of vapour pressure?

Short Answer Type Questions

1. State and derive Raoult's law for a solution containing non-volatile solute.
2. Explain why vapour pressure of solvent is lowered by the addition of a non-volatile solute.
3. State Raoult's law for solution containing (*i*) volatile solutes, (*ii*) non-volatile solutes.
4. Show that the relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute when solvent alone is volatile.
5. How can you justify the observation that the vapour pressure of solution of a non-volatile solute in a given solvent is less than that of the pure solvent?

   Also state the law concerning this observation.
6. Define vapour pressure of a liquid. What happens to the vapour pressure when (*a*) a volatile solute dissolves in the liquid and (*b*) the dissolved solute is non-volatile.
7. What are the characteristics of an ideal solution? Why do solutions behave ideally only at low concentration?
8. Distinguish between ideal and non-ideal solutions.
9. What is the non-ideal solution? Discuss giving two examples.
10. What would be an ideal solution of two volatile liquids? Why is the vapour pressure of a solvent lowered on the addition of a solute in it?
11. What is Raoult's law? State the factors responsible for deviations from this law. Illustrate deviations with suitable examples.
12. How does a non-ideal solution differ from an ideal solution? When does the positive deviation occur from ideality?
13. What type of deviation (positive or negative) from ideal behaviour will be shown by the solution of cyclohexane and ethanol? Give suitable reason.
14. What are ideal and non-ideal solutions? Give reasons for their formation. Give one example in each case.
15. Explain why the non-ideal solutions deviate from Raoult's law.
16. Explain the term azeotrope.
17. Why constant boiling mixtures behave like a single component when subjected to distillation?
18. Do colligative properties have something in common?
19. How Raoult's law can be used for determining molecular weight of a dissolved substance?

Long Answer Type Questions

1. What are ideal and non-ideal solutions? What type of non-idealities are exhibited by cyclohexane-ethanol and acetone-chloroform mixtures? Give reasons for your answer.
2. Explain along with the diagram why some of the non-ideal solutions show positive deviations while some other negative deviations from ideal solution.
3. Show that relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute when solvent alone is volatile.
4. With the help of diagrams, illustrate different types of non-ideal solutions. Explain the reasons for negative and positive deviations.
5. State and explain Raoult's law. Show graphically the variation of total vapour pressure over a mixture of two volatile liquids, with the composition of the mixture.
6. Mention three characteristics of ideal solutions. What causes deviations from ideal behaviour? Discuss positive deviation and negative deviation from ideal behaviour of liquid pairs.
7. Explain the following:
   - (*i*) If vapour pressure of liquid A is greater than the vapour pressure of liquid B at 25ºC, then the boiling point of liquid A is lower than the boiling point of liquid B.
   - (*ii*) A mixture of chlorobenzene and bromobenzene is nearly an ideal solution but a mixture of chloroform and acetone is not.
8. Differentiate between molarity and molality. When and why is molality preferred over molarity in handling solutions in chemistry?
9. With the help of suitable diagrams, illustrate the two types of non-ideal solutions.
10. State Raoult's law. Discuss the factors responsible for the deviation from this law.
11. State Raoult's law for solutions of non-volatile solutes in volatile solvents. Derive a mathematical expression for this law.
12. Show graphically how the vapour pressures of a solvent and a solution in it of a non-volatile solute change with temperature. Show on this graph the boiling points of the solvent and the solution. Which is higher and why?

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. Refer to the text.
2. 58.5/2 = 29.25
3. $M = (1000 \times K_f \times w_2)/(w_1 \times \Delta T_f)$.
4. Refer to the text.
5. When the new forces of interaction between the components are greater than those in the pure components.
6. Some of the molecules of the solvent on the surface are replaced by the molecules of the solute which are non-volatile.
7. Lowering of V.P. = $P^o - P_s$,

   Relative lowering of

$$\text{V.P.} = \frac{P^o - P_s}{P^o}$$

COMPETITION FILE

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. Which one of the following statements is **FALSE**?
   (*a*) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction.
   (*b*) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$, where M is the molarity of the solution.
   (*c*) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is

   $BaCl_2 > KCl > CH_3COOH >$ sucrose

   (*d*) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression.
2. Density of a 2.05 M solution of acetic acid in water is 1.02 g/ml. The molality of the solution is
   (*a*) 1.14 mol kg^{-1} (*b*) 3.28 mol kg^{-1}
   (*c*) 2.28 mol kg^{-1} (*d*) 0.44 mol kg^{-1}
3. 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is
   (*a*) 759.00 torr (*b*) 7.60 torr
   (*c*) 76.00 torr (*d*) 752.40 torr
4. A solution of acetone in ethanol
   (*a*) obeys Raoult's law
   (*b*) shows a negative deviation from Raoult's law
   (*c*) shows a positive deviation from Raoult's law
   (*d*) behaves like a near ideal solution.
5. Concentrated aqueous sulphuric acid is 98% H_2SO_4 by mass and has a density of 1.80 g mL^{-1}. Volume of acid required to make one litre of 0.1 M H_2SO_4 solution is
   (*a*) 16.65 mL (*b*) 22.50 mL
   (*c*) 5.55 mL (*d*) 11.10 mL
6. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be
   (*a*) 1.45 (*b*) 1.64
   (*c*) 1.88 (*d*) 1.22
7. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm of Hg at 300 K. The vapour pressure of propyl alcohol is 200 mm of Hg. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be
   (*a*) 360 (*b*) 350
   (*c*) 300 (*d*) 700
8. Two liquids X and Y form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be, respectively
   (*a*) 200 and 300 (*b*) 300 and 400
   (*c*) 400 and 600 (*d*) 500 and 600
9. A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution?
   (*a*) The solution formed is an ideal solution.
   (*b*) The solution is non-ideal, showing +ve deviation from Raoult's law.
   (*c*) The solution is non-ideal, showing –ve deviation from Raoult's law.
   (*d*) *n*-heptane shows +ve deviation while ethanol shows –ve deviation from Raoult's law.
10. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium

carbonate dissociates completely, molar concentration of sodium ion, Na^+ and carbonate ions, CO_3^{2-} are respectively (Molar mass of Na_2CO_3 = 106 g mol^{-1})

(*a*) 0.955 M and 1.910 M

(*b*) 1.910 M and 0.955 M

(*c*) 1.90 M and 1.910 M

(*d*) 0.477 M and 0.477 M

(B) Fill in the Blanks

Fill in the blank spaces:

1. An ________ solution obeys ________ law.
2. Vapour density of a substance can be determined by ________ method and ________ method.

(C) True/False Statements

Write T for true and F for false statements:

1. There is no difference between molecular mass and formula mass of a substance.
2. An ideal solution obeys Raoult's law.
3. van't Hoff factor is the ratio of normal molecular mass to the observed molecular mass.
4. Vapour pressure of a solution increases when some solute is dissolved in it.
5. Quantity of substance contained in 6.02×10^{23} molecules is equal to one mole.
6. 22400 mL of oxygen gas at S.T.P. contains 6.02×10^{23} molecules.

(D) Assertion-Reason Type Questions

In each question given below, there are two statements, Assertion (A) and Reason (R). Answer the questions as instructed below:

(*a*) If both **A** and **R** are correct, and **R** is the correct reason for **A.**

(*b*) If both **A** and **R** are correct, but **R** is not the correct reason for **A**.

(*c*) If **A** is correct but **R** is wrong.

(*d*) If both **A** and **R** are incorrect.

1. ***Assertion (A)*** : An ideal solution is that in which every component obeys Raoult's law under all conditions of temperature and concentration.

   Reason (R) : Hexane + heptane forms a non-ideal solution.

2. ***Assertion (A)*** : van't Hoff factor is the ratio of observed colligative property to calculated colligative property.

   Reason (R) : Molal depression constant, molality and depression in freezing point of a solution are related as:

   $K_f = \Delta T_f . m$

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. At equilibrium the rate of dissolution of a solid solute in a volatile liquid solvent is

   (*a*) less than the rate of crystallisation

   (*b*) greater than the rate of crystallisation

   (*c*) equal to the rate of crystallisation

   (*d*) zero

2. A beaker contains a solution of substance 'A'. Precipitation of substance 'A' takes place when small amount of'A' is added to the solution. The solution is

   (*a*) saturated (*b*) supersaturated

   (*c*) unsaturated (*d*) concentrated

3. Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does **not** depend upon

   (*a*) Temperature (*b*) Nature of solute

   (*c*) Pressure (*d*) Nature of solvent

4. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to

   (*a*) low temperature

   (*b*) low atmospheric pressure

   (*c*) high atmospheric pressure

   (*d*) both low temperature and high atmospheric pressure

5. Considering the formation, breaking and strength of hydrogen bond, predict which of the following mixtures will show a positive deviation from Raoult's law?

   (*a*) Methanol and acetone

   (*b*) Chloroform and acetone

   (*c*) Nitric acid and water

   (*d*) Phenol and aniline

6. Colligative properties depend on

   (*a*) the nature of the solute particles dissolved in solution.

   (*b*) the number of solute particles in solution.

   (*c*) the physical properties of the solute particles dissolved in solution.

   (*d*) the nature of solvent particles.

7. Value of Henry's constant K_H

   (*a*) increases with increase in temperature.

   (*b*) decreases with increase in temperature.

   (*c*) remains constant.

   (*d*) first increases then decreases.

8. The value of Henry's constant K_H is
   (*a*) greater for gases with higher solubility
   (*b*) greater for gases with lower solubility
   (*c*) constant for all gases
   (*d*) not related to the solubility of gases

9. Relative lowering of vapour pressure is a colligative property because
   (*a*) it depends on the concentration of a non-electrolyte solute in solution and does not depend on the nature of the solute molecules.
   (*b*) it depends on the number of particles of electrolyte solute in solution and does not depend on the nature of the solute particles.
   (*c*) it depends on the concentration of a non-electrolyte solute in solution as well as on the nature of the solute molecules.
   (*d*) it depends on the concentration of an electrolyte or non-electrolyte solute in solution as well as on the nature of solute molecules.

10. Which of the following binary mixtures will have same composition in liquid and vapour phase?
   (*a*) Benzene-Toluene (*b*) Water-Nitric acid
   (*c*) Water-Ethanol (*d*) *n*-Hexane-*n*-Heptane

II. Short Answer Type Questions

1. Components of a binary mixture of two liquids A and B were being separated by distillation. After sometime separation of components stopped and composition of vapour phase became same as that of liquid phase. Both the components started coming in the distillate. Explain why this happened.
2. Explain the solubility rule "like dissolves like" in terms of intermolecular forces that exist in solutions.
3. Concentration terms such as mass percentage, ppm, mole fraction and molality are independent of temperature, however molarity is a function of temperature. Explain.
4. Why is the vapour pressure of an aqueous solution of glucose lower than that of water?

III. Long Answer Type Questions

1. Explain the terms ideal and non-ideal solutions in the light of forces of interactions operating between molecules in liquid solutions.
2. Why is it not possible to obtain pure ethanol by fractional distillation? What general name is given to binary mixtures which show deviation from Raoult's law and whose components cannot be separated by fractional distillation? How many types of such mixtures are there?

ANSWERS

(A) Multiple Choice Questions

1. (*d*) 2. (*c*) 3. (*d*) 4. (*c*) 5. (*c*) 6. (*d*) 7. (*b*) 8. (*c*)
9. (*b*) 10. (*b*)

(B) Fill in the Blanks

1. ideal, Raoult's 2. Duma's, Victor Meyer's

(C) True/False Statements

1. False 2. True 3. True 4. False 5. True 6. False

(D) Assertion-Reason Type Questions

1. (*c*) 2. (*c*)

Some Additional Questions

I. Multiple Choice Questions

1. (*c*) 2. (*b*) 3. (*c*) 4. (*b*) 5. (*a*) 6. (*b*) 7. (*a*) 8. (*b*)
9. (*a*), (*b*) 10. (*b*), (*c*)

10

CHAPTER

Introduction To Organic Chemistry

LEARNING OBJECTIVES

- State the difference among the terms empirical formula, molecular formula, structural formula, homologous series and functional group.
- Represent an organic compound in terms of empirical formula, molecular formula and structural formula.
- Apply the IUPAC rules to the nomenclature of simple organic compounds.

10.1 INTRODUCTION

Organic chemistry is the branch of chemistry that deals with the study of carbon and its compounds, their reaction paths, interactions, and applications. However, some carbon containing compounds such as carbonates and oxides of carbon are considered as inorganic compounds. The simplest organic compounds, i.e. hydrocarbons are made up of carbon and hydrogen atoms.

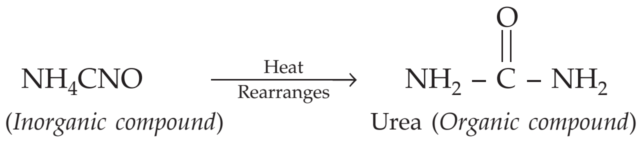
10.2 VITAL FORCE THEORY

Earlier, it was believed that organic compounds cannot be prepared in the laboratory. They can only be isolated from animals and plants. On the basis of this belief, Berzelius, a leading Swedish chemist, in 1815, propounded **Vital Force Theory**. According to this theory, organic compounds are produced only under the influence of some mysterious force existing in the living organisms. This mysterious force was called the **Vital Force**. Since such a mysterious force cannot be created artificially, it is impossible to synthesize organic compounds in the laboratory. This theory ruled for quite some time.

Wohler, a **German chemist**, made an interesting discovery in 1828. He accidentally obtained *urea*, a well-known organic compound by evaporating an aqueous solution of ammonium cyanate, a typical inorganic compound.

Wohler

$$NH_4Cl + KCNO \longrightarrow \underset{\text{Ammonium cyanate}}{NH_4CNO} + KCl$$



$$\underset{(\text{Inorganic compound})}{NH_4CNO} \xrightarrow[\text{Rearranges}]{\text{Heat}} \underset{\text{Urea (Organic compound)}}{NH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2}$$

This synthesis demonstrated that *no mysterious force was required in the formation of organic compounds in the laboratory*. The elegant synthesis of acetic acid by *Kolbe* in 1845, from purely inorganic sources finally disproved Vital Force Theory. Thereafter, innumerable organic compounds have been synthesized in the laboratory.

$$2C + H_2 \xrightarrow[\text{arc}]{\text{Electric}} \underset{\text{Acetylene}}{HC \equiv CH} \xrightarrow[HgSO_4]{\text{Dil. } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{\text{Oxidation}} \underset{\text{Acetic acid}}{CH_3COOH}$$

10.2.1 Modern Definition of Organic Compounds

With the downfall of *Vital Force Theory*, the term organic lost its original significance.

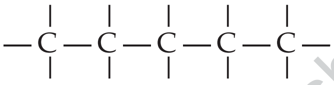
Organic compounds *are now defined as compounds of carbon containing usually hydrogen and one or more additional elements like oxygen, nitrogen, sulphur, halogens, phosphorus, etc., and the branch of chemistry which deals with the study of organic compounds is called* **Organic Chemistry**.

10.3 WHY A HUGE NUMBER OF ORGANIC COMPOUNDS?

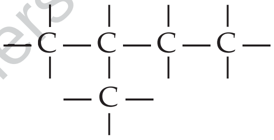
The total number of organic compounds known to date is more than *five millions*. They make up about 90% of all the known compounds. We must know why carbon forms so many compounds. There are four main reasons for this as discussed below:

1. **Catenation.** The foremost reason for the existence of a huge number of carbon compounds is that carbon can combine with other carbon atoms to form long straight or branched chains or rings of different shapes and sizes. This self-linking of carbon atoms is due to high bond energies.

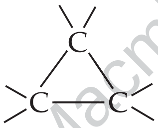
   The property of self-linking of carbon atoms through covalent bonds to form long straight or branched chains and rings of different sizes is called catenation. How the various carbon atoms link with one another to form straight chain, branched chain and cyclic compounds is illustrated as follows:



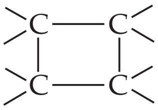
Straight chain



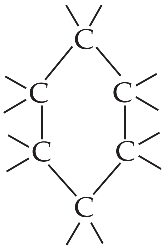
Branched chain



Three membered ring



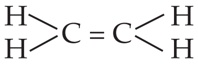
Four membered ring



Six membered ring

   Silicon also belongs to the group of carbon, but carbon shows catenation, whereas silicon does not. It is mainly due to the reason that C—C bonds are much stronger (355 kJ mol^{-1}) than Si—Si (200 kJ mol^{-1}) bonds.

2. **Tendency to form multiple bonds.** Due to the small size, carbon also forms multiple (double and triple) bonds with other carbon atoms, oxygen and nitrogen, as illustrated below:



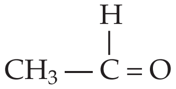
Ethylene

$H - C \equiv C - H$

Acetylene

$CH_3 - C \equiv N$

Acetonitrile



$$CH_3 - \overset{\overset{\displaystyle H}{|}}{C} = O$$

Acetaldehyde

3. **Electronegativity and strength of bonds.** The electronegativity of carbon is 2.5 which is close to a number of elements such as hydrogen (2.1), nitrogen (3.0), phosphorus (2.1), chlorine (3.0), oxygen (3.5), etc. As a result, carbon forms strong covalent bonds with these elements as well adding to the number of carbon compounds.

4. **Isomerism.** Another important reason that contributes to the abundance of carbon compounds is the phenomenon of isomerism.

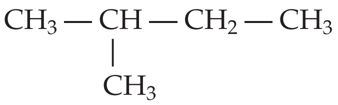
   If two or more compounds have the same molecular formula but different arrangement of atoms, they are called **isomers** and the phenomenon is called **isomerism**. Since each different arrangement of atoms represents a different structure, isomers may also be defined as compounds which have the same molecular formula but different structures.

   Further due to different structures, isomers have different physical and chemical properties. For example,

   (*i*) There are three compounds, I, II and III which have the same molecular formula, C_5H_{12} but have different structures as shown below:

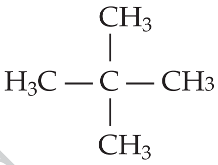
$$CH_3-CH_2-CH_2-CH_2-CH_3$$

(I)



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

(II)



$$H_3C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

(III)

   Compound I is known as *pentane*, compound II as *iso-pentane* and compound III as *neo-pentane*. These are three different compounds having different b.p., etc.

   (*ii*) Molecular formula, C_2H_6O represents two different compounds, as shown below:

$$CH_3-CH_2-OH \qquad\qquad CH_3-O-CH_3$$

(*Ethyl alcohol*) (*Dimethyl ether*)

   Above two compounds are isomers of each other. Because of different structures, these two compounds have different properties. For example, ethanol reacts with sodium to evolve H_2 gas but methoxymethane does not. Similarly, many examples can be cited for isomers.

10.4 REASONS FOR STUDYING ORGANIC COMPOUNDS SEPARATELY FROM INORGANIC COMPOUNDS

Organic compounds have certain distinct features as mentioned below, because of which such compounds are studied separately and organic chemistry is, therefore, a separate and distinct branch of chemistry.

1. **Huge Number.** The total number of organic compounds exceeds five millions as compared to inorganic compounds which total approximately to 50,000. This is mainly due to the reason that carbon shows the phenomenon of catenation, a property of self-linking to other carbon atoms.
2. **Composition.** Organic compounds are essentially made up of carbon and hydrogen atoms. A few other elements which are normally present are O, N, S, P and halogens (F, Cl, Br, I). Inorganic compounds, on the other hand, are formed through the union of two or more of the 105 elements known so far.
3. **Large and Complex Molecules.** Some of the organic compounds such as proteins, vitamins, enzymes, hormones, carbohydrates, etc., have high molecular masses and extremely complex structures.

   Inorganic compounds such as NaCl, $BaCl_2$ etc., on the other hand, have low molecular masses and simple structures.
4. **Nature of Bonds or Linkages.** Most of the organic compounds form covalent bonds by the sharing of electrons. Inorganic compounds, on the other hand, form ionic bonds by the transference of electrons.
5. **Nature of Reactions.** *Reactions of organic compounds are* **molecular in nature** *and are generally slow and reversible.* For example, the reaction of ethanol with ethanoic acid in presence of a trace of conc. H_2SO_4 as catalyst to form ethyl ethanoate is a *slow and reversible reaction*.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Ethanoic acid}}{CH_3COOH} \xrightleftharpoons{\text{Conc. } H_2SO_4} \underset{\text{Ethyl ethanoate}}{CH_3COOCH_2CH_3} + H_2O$$

The reactions of the inorganic compounds, on the other hand, are **ionic in nature** and are *generally fast and irreversible*. For example, NaCl immediately gives a white ppt. of silver chloride when treated with an aqueous solution of $AgNO_3$.

$$NaCl \rightarrow Na^+ + Cl^- ; \quad AgNO_3 \rightarrow Ag^+ + NO_3^- ; Ag^+ + Cl^- \rightarrow \underset{(\textit{White ppt.})}{AgCl}$$

6. **Isomerism.** Organic compounds show the phenomenon of isomerism as discussed. Inorganic compounds, however, do not generally show isomerism. For example, NaCl represents only one compound and nothing else.
7. **Homologous Series.** The number of organic compounds is very large, but their study has been simplified by grouping the organic compounds, which is called *homologous series*. This grouping is based upon the functional group. Thus, methyl alcohol, ethyl alcohol, propyl alcohol, etc., can be grouped in one family or homologous series. Each such family consists of a large number of members called *homologues* and the concept is called **homology**. All the members of a given family can be represented *by the same general molecular formula, can be prepared by the same general methods of preparation and any two successive members of a given homologous series differ by a* CH_2 *group*.
8. **Melting Points and Boiling Points.** In inorganic compounds, there are ions which are held together by strong electrostatic forces to form the lattice. Thus, to melt an inorganic compound, it is necessary to break the lattice. This requires large amount energy and, hence, *the melting points and boiling points of inorganic compounds are usually high*. Molecules in the crystal lattice of an organic compound are held together by weak *van der Waals'* forces of attraction. Since the energy required to overcome these weak forces is small, so the *melting points and boiling points of organic compounds are generally low*.

   Thus, *inorganic compounds are generally hard solids, whereas organic compounds are often gases, liquids or soft solids with low melting points.*
9. **Origin.** Most of the organic compounds are obtained from animals and plants although some of them are being synthesised in the laboratory. The chief sources of inorganic compounds are, however, rocks and minerals.
10. **Stability.** Organic compounds are less stable than inorganic compounds. Some organic compounds decompose even at room temperature while many others decompose when heated. Inorganic compounds, on the other hand, are quite stable even at sufficiently high temperatures.
11. **Colour and Odour.** Certain classes of organic compounds possess characteristic colours and odours. Inorganic compounds are generally colourless and odourless with the exception of salts of transition and inner transition elements.
12. **Electrical Conductivity.** Organic compounds are covalent and, hence, they do not ionize. This accounts for their low conductivity in aqueous solutions. In other words, aqueous solutions of organic compounds possess low electrical conductivity as compared to inorganic compounds which ionize in water to give the ions which conduct electricity.
13. **Solubility.** Inorganic compounds being polar are soluble only in polar solvents like water while they are insoluble in non-polar solvents such as ether, benzene and carbon tetrachloride. Organic compounds, on the other hand, being non-polar are highly soluble in non-polar solvents but are practically insoluble in polar solvents such as water.
14. **Polymerism.** Many organic compounds have the same *empirical formula* but have *different molecular formula*. Such compounds are called **polymers** and the phenomenon is called *polymerism*. For example, acetylene (C_2H_2) and benzene (C_6H_6) have the same empirical formula (CH) but different molecular formulae and hence, are called polymers. Inorganic polymers are also known but to a small extent.
15. **Combustibility.** Since organic compounds contain high carbon content, they are highly combustible. However, inorganic compounds are generally incombustible.

10.5 CLASSIFICATION OF ORGANIC COMPOUNDS

In order to simplify and systematize the study of organic chemistry, all the known organic compounds have been broadly divided into two categories, depending upon the nature of their carbon skeleton. These are:

I. *Acyclic or open chain compounds.*
II. *Cyclic or closed chain or ring compounds.*

10.5.1 Acyclic or Open Chain Compounds

These compounds contain open chains of carbon atoms in their molecules. The carbon chains may be either straight chains or branched chains. For example,

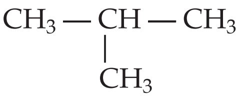
Straight chain compounds

$CH_3-CH_2-CH_2-CH_3$
n-Butane

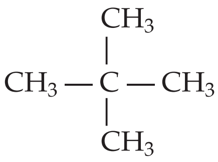
$CH_3-CH=CH-CH_3$
But – 2 – ene
(*formerly* 2 – *butene*)

$CH_3-CH_2-C\equiv CH$
But – 1 – yne
(*formerly* 1 – *butyne*)

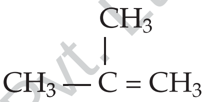
Branched chain compounds


$CH_3-\underset{CH_3}{CH}-CH_3$

Isobutane


$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

Neopentane


$CH_3-\overset{CH_3}{C}=CH_3$

Isobutylene

The above three compounds have been named according to the common system of nomenclature. Open chain compounds are also called as **aliphatic compounds** since the earlier compounds of this class were obtained either from animal or vegetable fats (Greek, *aliphatos* = fat).

10.5.2 Cyclic or Closed Chain or Ring Compounds

These compounds contain one or more closed rings of atoms in their molecules. They are further divided into the following two categories:

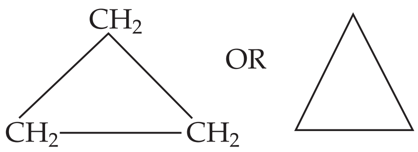
1. *Homocyclic or carbocyclic compounds*
2. *Heterocyclic compounds*

1. Homocyclic or Carbocyclic Compounds. *These compounds contain rings which are made up of only carbon atoms.* These are further sub-divided into the following types:

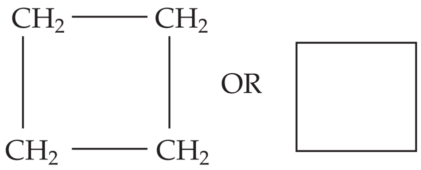
(*i*) Alicyclic compounds

Carbocyclic compounds which resemble aliphatic compounds in most of their properties are called **alicyclic compounds**. *They usually contain C–C single bonds in the molecule.*

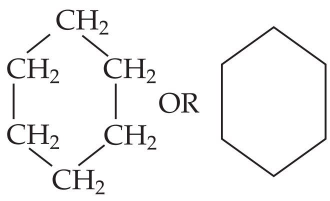
For example,



Cyclopropane



Cyclobutane



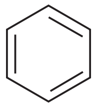
Cyclohexane

(*ii*) Aromatic compounds. Benzene is the parent aromatic compound. It has six carbon atoms arranged in a closed chain with three alternate single and double bonds. Thus, *organic compounds containing one or more fused or isolated benzene rings are called* **aromatic compounds.**

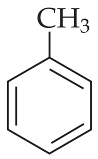
These are also called **benzenoid compounds. Aroma** means fragrant smell. Most of the compounds of this class discovered earlier had pleasant smells. However, the term aromatic has now lost its original significance because many aromatic compounds are now known to possess unpleasant odours. They are further classified as monocyclic, bicyclic, tricyclic, etc., as they contain one, two, three, etc., fused benzene rings respectively in their molecules.

Some important examples of monocyclic, bicyclic and tricyclic aromatic compounds are:

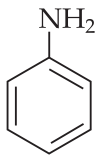
(*i*) *Monocyclic aromatic compounds:*



Benzene

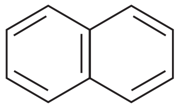


Toluene

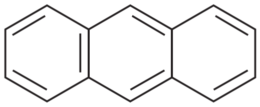


Aniline

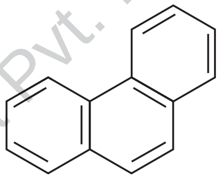
(*ii*) *Bicyclic and tricyclic aromatic compounds:*



Naphthalene
(Bicyclic)



Anthracene
(Tricyclic)

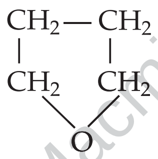


Phenanthrene
(Tricyclic)

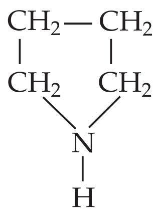
2. **Heterocyclic Compounds:** *Cyclic compounds containing one or more heteroatoms like nitrogen, oxygen and sulphur in their rings are called* **heterocyclic compounds**.

Depending upon the chemical behaviour, they are further classified into the following two categories:

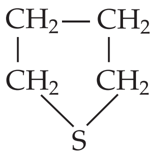
(*i*) **Alicyclic heterocyclic compounds.** *Aliphatic cyclic compounds containing one or more heteroatoms in their rings are called alicyclic heterocyclic compounds*. For example,



Tetrahydrofuran
(THF)

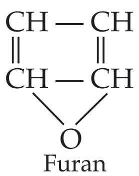


Pyrrolidine

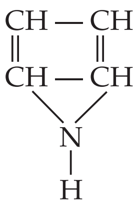


Tetrahydrothiophene

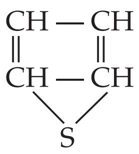
(*ii*) **Aromatic heterocyclic compounds.** *Aromatic cyclic compounds containing one or more heteroatoms in their molecules are called aromatic heterocyclic compounds*. For example,



Furan

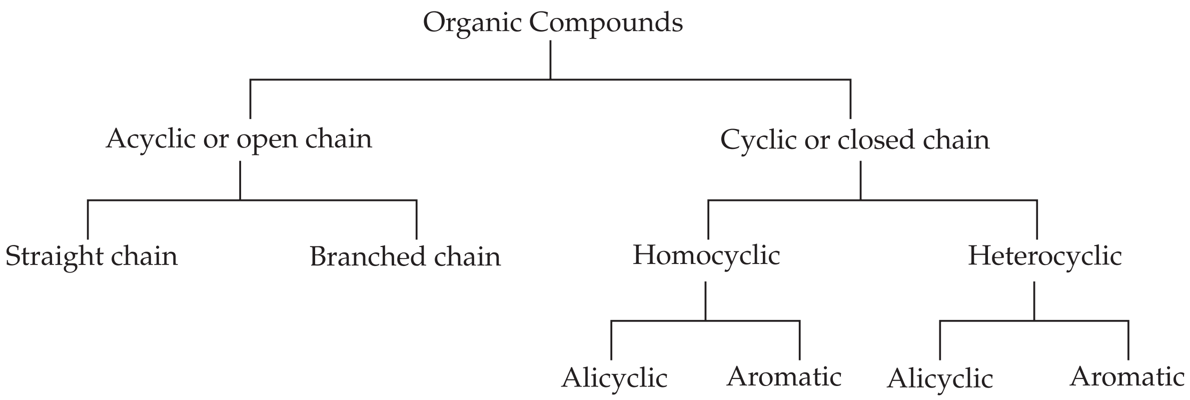


Pyrrole



Thiophene

The above classification may be summarised as follows:



10.6 FUNCTIONAL GROUPS

Hydrocarbons are the parent organic compounds. All other compounds are considered to have been derived from them by replacing one or more of their hydrogen atoms by some other atom or group (G).

$$\underset{\text{Hydrocarbon}}{R-H} \xrightarrow[+G]{-H} \underset{\text{Derivative of hydrocarbon}}{R-G}$$

Thus, each organic molecule consists of two parts R and G. The first part, 'R' denotes the *carbon-hydrogen framework* of the molecule while the second part, 'G' is called the *functional group*.

Thus, a **functional group** *may be defined as an atom or a group of atoms present in a molecule which largely determines the chemical behaviour of the molecule.*

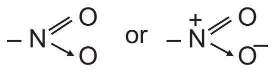
The remaining part of the molecule (*e.g.* R) may affect the physical properties such as melting point, boiling point, density, solubility, refractive index, etc. In alcohols, OH is the functional group as in all the chemical reactions of alcohols it is the OH group that undergoes a change. Similarly, functional group of carboxylic acids is —COOH.

It may be understood that the *chemical properties of any organic compound are the properties of its functional group*. In other words, all the organic compounds containing the same functional group show similar chemical behaviour. For example, methyl alcohol, ethyl alcohol or propyl alcohol, each having –OH as the functional group reacts with sodium metal to liberate hydrogen.

Some of the common functional groups that we come across in organic compounds are listed in Table 10.1.

Table 10.1: Names and Structures of Functional Groups

Class of Organic Compounds	Name of the Functional Group	Structure of the Functional Group
Alkenes	Double bond	$>C=C<$
Alkynes	Triple bond	$-C\equiv C-$
Halogen derivatives	Halogen	–X (F, Cl, Br, I)
Alcohols	Hydroxy	– OH
Ethers	Divalent oxygen	—O—
Aldehydes	Aldehydic (*formyl*)	$-\overset{\overset{O}{\Vert}}{C}-H$
Ketones	Ketonic (*keto*)	$>C=O$
Carboxylic acids	Carboxyl	$-\overset{\overset{O}{\Vert}}{C}-OH$

Class of Organic Compounds	Name of the Functional Group	Structure of the Functional Group
Primary amines	Amino	$-NH_2$
Secondary amines	Imino	$>NH$
Tertiary amines	Tertiary N-atom	$>N^-$
Nitroalkanes	Nitro	 $-N(=O)\rightarrow O$ or $-\overset{+}{N}(=O)\rightarrow O^-$
Alkyl nitrites	Nitrito	$-O-N=O$
Alkyl cyanides or alkanenitriles	Cyano or nitrile	$-C\equiv N$
Alkyl isocyanides or isonitriles	Isonitrile or isocyano	$-N\equiv C$

10.7 HOMOLOGOUS SERIES

All the organic compounds have been grouped into different families or groups depending upon their structure and chemical properties. Each such family or group is called a *homologous series*. This becomes necessary to study the compounds systematically, keeping in view the large number of organic compounds.

A homologous series *is defined as a group of structurally similar organic compounds, all the members of which contain the same functional group, show a gradation in physical properties and similarity in chemical properties and any two adjacent members of which differ by a* $-CH_2$ *group. The individual members of such a series are called homologues and the phenomenon is called* **homology.**

For example, alkanes constitute a homologous series. The first six members of this series are:

CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}
Methane	Ethane	Propane	Butane	Pentane	Hexane

These hydrocarbons can be represented by the same general formula, C_nH_{2n+2}, where n is the number of carbon atoms. Any two adjacent members of this class differ by CH_2.

Similarly, methanol, ethanol and propanol are the first three members of the homologous series of alcohols. The different members of this series can be represented by the general formula $C_nH_{2n+1}OH$.

Formula	*Names*
CH_3OH	Methanol
CH_3CH_2OH	Ethanol
$CH_3CH_2CH_2OH$	Propanol

Adjacent members of this series again differ by $-CH_2$ in their molecules. Some other homologous series are alkenes, alkynes, alkyl halides, ethers, aldehydes, ketones, amines, esters and carboxylic acids, etc.

10.7.1 Characteristics of a Homologous Series

1. Each homologous series can be represented by a general formula. For example, $C_nH_{2n+1}OH$ is the general formula of an alcohol.
2. All the members of a given homologous series possess the same functional group. For example, methanol and ethanol, members of a homologous series possess the same functional group —OH.
3. The individual members of a homologous series can be prepared by the general methods of preparation for that series.
4. The physical properties such as density, melting point, boiling point of the members of a homologous series show a regular gradation with rise in molecular mass.
5. The chemical properties of the members of a homologous series are similar though the first member may vary considerably from rest of the members. Rates of reactions could vary from one member to another.
6. The successive members of a homologous series differ by a CH_2 group or by 12 + 2 × 1 = 14 mass units.

10.8 NOMENCLATURE OF ORGANIC COMPOUNDS

Nomenclature means naming of organic compounds. In case of aliphatic compounds, two systems of nomenclature are generally used which are: (*i*) *Trivial or common system and* (*ii*) *IUPAC system.*

(*i*) **Trivial or Common System.** Earlier, organic compounds were named after the source from which they were first isolated. For example, urea got its name since the compound was first obtained from the urine of mammals. Similarly, methyl alcohol was called *wood spirit* because it was prepared by the destructive distillation of *wood*. Acetic acid got its name from *acetum* (Latin: *acetum* means *vinegar*) since it is present in vinegar. Similarly, the name formic acid was derived from *formica* (Latin: *formica* means *red ants*) as it could be obtained by the destructive distillation of red ants. These are called **trivial names or common names** of the organic compounds. Thus, originally these names were origin-dependent. Later on, certain rules were developed to name the organic compounds by the common system. However, these rules were not rational or scientific and couldn't be used to name all organic compounds.

(*ii*) **IUPAC System.** In order to systematize the nomenclature of organic compounds, IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature was first introduced in 1947. These rules underwent modifications from time to time. The most exhausted rules for nomenclature of organic compounds were published in 1979 and later revised and updated in 1993. The rules discussed in this book are the latest and are based upon 1979 and 1993 IUPAC nomenclature of organic compounds.

10.9 IUPAC SYSTEM FOR NAMING ORGANIC COMPOUNDS

The IUPAC name of any organic compound essentially consists of three parts, viz.,

1. *Word root* 2. *Suffix* and 3. *Prefix*

1. **Word Root.** *It is the basic unit of the name. It denotes the number of carbon atoms present in the* **principal chain** *which is the longest possible continuous chain of carbon atoms including the functional group and the multiple bonds in the molecule.* For one to four carbon atoms, special word roots (based upon the common names of alkanes) are used but for chains of five or more carbon atoms *Greek number* roots are used. These are given below:

Chain Length	*Word Root*	*Chain Length*	*Word Root*
C_1	Meth-	C_7	Hept-
C_2	Eth-	C_8	Oct-
C_3	Prop-	C_9	Non-
C_4	But-	C_{10}	Dec-
C_5	Pent-	C_{11}	Unidec-
C_6	Hex-	C_{12}	Dodec-

In general, the word root for any carbon chain is **alk**.

2. **Suffix.** Suffixes are of two types:

(*i*) **Primary suffix.** *A primary suffix is always added after the word root to indicate whether the carbon chain is saturated or unsaturated.* The three basic primary suffixes are given below:

Type of Carbon Chain	*Primary Suffix*	*General Name*
(*a*) Saturated (containing single bonds only)	-ane	Alkane
(*b*) Unsaturated with *one double bond*	-ene	Alkene
(*c*) Unsaturated with *one triple bond*	-yne	Alkyne

If the parent carbon chain contains two, three, four or more double or triple bonds, numerical prefixes such as **di** (for two), **tri** (for three), **tetra** (for four), etc., are added to the primary suffix. For example,

Type of Carbon Chain	*Primary Suffix*	*General Name*
(*a*) Unsaturated with *two double bonds*	-diene	Alkadiene
(*b*) Unsaturated with *two triple bond*	-diyne	Alkadiyne

Use of word roots and primary suffixes in naming organic compounds has been explained as follows:

Organic Compound	*Word Root*	*Primary Suffix*	*IUPAC Name*
$CH_3CH_2CH_2CH_3$	But	ane	Butane
$CH_3CH = CH_2$	Prop	ene	Propene
$CH \equiv CH$	Eth	yne	Ethyne
$CH_2 = CH - CH = CH_2$	Buta*	diene	Butadiene
$HC \equiv C–C \equiv CH$	Buta*	diyne	Butadiyne

*Extra '*a*' has been added to the word root since the primary suffix, *i.e. diene or diyne begins with a consonant, i.e.* '*d*' instead of a vowel as in the case of first three compounds.

(ii) **Secondary suffix.** *A secondary suffix is added after the primary suffix to indicate the nature of the functional group present in the organic compound*. Secondary suffixes of some important functional groups are given below:

Class of Organic Compounds	*Functional Group*	*Secondary Suffix*
Alcohols	—OH	-ol
Aldehydes	—CHO	-al
Ketones	$> C = O$	-one
Carboxylic acids	—COOH	-oic acid
Acid amides	—$CONH_2$	-amide
Acid chlorides	—COCl	-oyl chloride
Esters	—COOR	alkyl.....oate
Nitriles	—CN	nitrile
Thiol	—SH	thiol
Amines	—NH_2	amine

It may be noted that while adding the secondary suffix to the primary suffix, the terminal 'e' of the primary suffix (i.e. ane, ene, and yne) is dropped if the secondary suffix begins with a vowel but is retained if the secondary suffix begins with a consonant.

The following examples will illustrate the use of word root, primary suffix and secondary suffix in naming organic compounds.

Organic Compound	*Word Root*	*Primary Suffix*	*Secondary Suffix*	*IUPAC Name*
CH_3CH_2OH	Eth	an (*e*)*	ol	Ethanol
$CH_3CH_2CH_2NH_2$	Prop	an (*e*)*	amine	Propanamine
$CH_3CH_2CH_2COOH$	But	an (*e*)*	oic acid	Butanoic acid
CH_3CH_2CN	Prop	ane	nitrile	Propanenitrile
$CH_2 = CHCHO$	Prop	en (*e*)*	al	Prop-2-en-l-al
$HC \equiv CCOOH$	Prop	...yn (*e*)*	oic acid	Prop-2-yn-l-oic acid

*The terminal '*e*' from the primary suffix has been dropped because the secondary suffix begins with a vowel.

It may be noted that according to 1993 recommendations of IUPAC nomenclature of Organic Compounds:

(*i*) *Locants (numericals and/or letters) are placed immediately before the part of the name to which they relate*. For example,

But-2-ene	Propan-2-ol
(*formerly 2-butene*)	(*formerly 2-propanol*)

This is the major difference between 1979 and 1993 versions of IUPAC nomenclature.

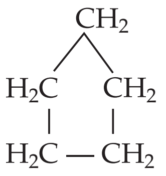
(*ii*) *The locant 1 (unity) is often omitted when there is no ambiguity*. For example,

$CH_3CH_3CH_2NH_2$: Propan-l-amine is often named as Propanamine
$ClCH_2CH_2OH$: 2-Chloroethan-l-ol is often named as 2-Chloroethanol
$CH_3CH_2CH_2CHO$: Butan-l-al is often written as Butanal

Note: *However, in this book, we shall include numerical locant 1 when another numerical locant appears in the same name.*

3. Prefix. Prefixes are of two kinds:

(*i*) **Primary prefix.** A primary prefix is used simply to distinguish cyclic from acyclic compounds. For example, in case of carbocyclic compounds, a primary prefix, **cyclo** is used immediately before the word root. Thus,



Cyclo .... **pent** .... **ane**
Primary prefix Word root Primary suffix

Cyclopentane
IUPAC name

(*ii*) **Secondary prefix.** In IUPAC system of nomenclature, certain groups are not considered as functional groups but instead are treated as *substituents. Parts of their names called* **secondary prefixes** *are added immediately before the word root* (or *the primary prefix in case of carbocyclic compounds*) *in alphabetical order to denote the side chains or substituent groups*. The secondary prefixes for some groups which are always treated as substituent groups are given as:

Substituent Group	*Secondary Prefix*	*Substituent Group*	*Secondary Prefix*
— F	Fluoro	— OCH_3	Methoxy
— Cl	Chloro	— OC_2H_5	Ethoxy
— Br	Bromo		
— I	Iodo	— CH_3	Methyl
— NO_2	Nitro	— C_2H_5	Ethyl
— NO	Nitroso	— $CH_2CH_2CH_3$	*n*-Propyl
— N ≡ N	Diazo	— $CH(CH_3)_2$	Isopropyl
— OR	Alkoxy	— $C(CH_3)_3$	*tert*.-Butyl

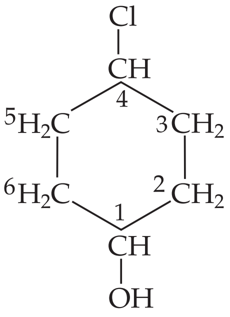
Thus, the complete IUPAC name of an organic compound consists of the following parts:

Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix

The following examples illustrate the use of word root, primary and secondary prefixes and suffixes in naming organic compounds:

Organic Compounds	*Secondary Prefix*	*Word Root*	*Primary Suffix*	*IUPAC Name*
CH_3CH_2I	Iodo	eth	ane	Iodoethane
CH_3NO_2	Nitro	meth	ane	Nitromethane
$C_2H_5OC_2H_5$	Ethoxy	eth	ane	Ethoxyethane

In case of carbocyclic compounds, primary prefixes are also used. For example,



4-Chloro	**cyclo**	**hex**	**an(e)**	**1-ol**
Secondary prefix	Primary prefix	Word root	Primary suffix	Secondary suffix

4-Chlorocyclohexan-1-ol
IUPAC name

10.9.1 Nomenclature of Different Classes of Organic Compounds

1. **Hydrocarbons:** *Compounds of carbon and hydrogen are* ***called hydrocarbons***. These are further divided into two classes: *saturated and unsaturated hydrocarbons.*

   (*a*) **Saturated Hydrocarbons — Alkanes:** *Hydrocarbons in which all the carbon atoms are linked to one another by only single bonds are called* **saturated hydrocarbons.** In the IUPAC system, *saturated acyclic hydrocarbons are called* **alkanes**.

   General formula: C_nH_{2n+2}, where n = 1, 2, 3, 4, ..., etc.

   Primary suffix: **ane.**

   The IUPAC names of alkanes are the same as common names except that *n* (normal) in common name is deleted. The name of an individual alkane is always written as one word. The molecular formulae, IUPAC and common names of the first twelve alkanes are given below:

Formula	*Common Name*	*IUPAC Name*
CH_4	Methane	Methane
CH_3CH_3	Ethane	Ethane
$CH_3CH_2CH_3$	Propane	Propane
$CH_3CH_2CH_2CH_3$	*n*-Butane	Butane
$CH_3CH_2CH_2CH_2CH_3$	*n*-Pentane	Pentane
$CH_3(CH_2)_4CH_3$	*n*-Hexane	Hexane
$CH_3(CH_2)_5CH_3$	*n*-Heptane	Heptane
$CH_3(CH_2)_6CH_3$	*n*-Octane	Octane
$CH_3(CH_2)_7CH_3$	*n*-Nonane	Nonane
$CH_3(CH_2)_8CH_3$	*n*-Decane	Decane
$CH_3(CH_2)_9CH_3$	Monodecane	Monodecane
$CH_3(CH_2)_{10}CH_3$	Dodecane	Dodecane

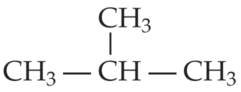
Types of Alkanes. Alkanes can be classified into two types as given below:

(*i*) **Straight chain alkanes.** These alkanes contain straight chains of carbon atoms in their molecules. In other words, *alkanes in which no carbon atom is linked to more than two other carbon atoms, are* **called straight chain alkanes**.

$CH_3–CH_2–CH_2–CH_3$
Butane

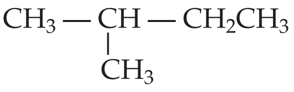
$CH_3–CH_2–CH_2–CH_2–CH_3$
Pentane (*n*-Pentane)

(*ii*) **Branched chain alkanes.** In these alkanes, all the carbon atoms are not present in a straight sequence. In other words, *alkanes in which at least one carbon atom is linked to more than two other carbon atoms are called* **branched chain alkanes**. For example,



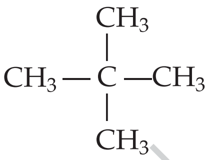
$$CH_3—\overset{\displaystyle CH_3 \atop |}{C}H—CH_3$$

2-Methyl propane
(*Isobutane*)



$$CH_3—\underset{| \atop \displaystyle CH_3}{C}H—CH_2CH_3$$

2-Methyl butane
(*Isopentane*)



$$CH_3—\underset{| \atop \displaystyle CH_3}{\overset{\displaystyle CH_3 \atop |}{C}}—CH_3$$

2, 2-Dimethylpropane
(*Neopentane*)

To distinguish the straight chain alkanes from branched chain alkanes having the same molecular formula, the prefixes *iso* and *neo* are used in the common system. The prefix *iso* is used when the second carbon of the branched chain alkane carries one methyl group while the prefix *neo* is used for those branched chain alkanes which contain *a quaternary carbon*.

Types of Carbon and Hydrogen Atoms in Alkanes

Different carbon atoms in a molecule show different behaviour, depending upon how they attached to other carbon atoms.

The carbon atoms in an alkane molecule may be classified into four types as *primary (1°), secondary (2°), tertiary (3°)* and *quaternary (4°)* as follows:

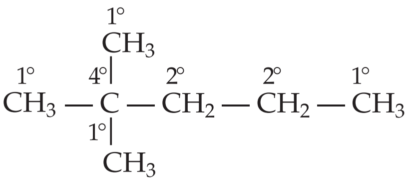
(*i*) *A carbon atom attached to one other* (*or no other*) *carbon atom is called a* **primary carbon atom** and *is designated as* **1° carbon**.

(*ii*) *A carbon atom attached to two other carbon atoms is called a* **secondary carbon atom** *and is designated as* **2° carbon**.

(*iii*) *A carbon atom attached to three other carbon atoms is called a* **tertiary carbon atom** *and is designated as* **3° carbon.**

(*iv*) *A carbon atom attached to four other carbon atoms is called a* **quaternary carbon atom** *and is designated as* **4° carbon**.

The hydrogen atoms attached to 1°, 2° and 3° carbon atoms are called primary (1°), secondary (2°) and tertiary (3°) hydrogen atoms. It may be noted here that there is nothing like quaternary hydrogen atom since a quaternary carbon does not carry any hydrogen. The following example clearly illustrates the various types of carbon and hydrogen atoms.



$$\overset{1°}{CH_3}—\underset{1°| \atop \displaystyle CH_3}{\overset{\displaystyle \overset{1°}{CH_3} \atop 4°|}{C}}—\overset{2°}{CH_2}—\overset{2°}{CH_2}—\overset{1°}{CH_3}$$

Alkyl groups. Alkyl group is obtained by the removal of one hydrogen atom from the molecule of an alkane. Thus, alkyl groups have the general formula, C_nH_{2n+1}. These are often represented by the letter R. Their names are derived by replacing the terminal '*ane*' of the corresponding alkane by the suffix 'yl'.

Alkane – ane + yl = Alkyl

The IUPAC names and structural formulae of some of the alkanes and their alkyl groups are given below:

General formula: C_nH_{2n+1}, where, $n = 1, 2, 3, 4, ...,$ etc.

Name and Structural formula of the Alkane	*Corresponding Alkyl Group*	*IUPAC Name (Common Name)*
Methane, CH_4	CH_3-	Methyl (*Methyl*)
Ethane, $CH_3 - CH_3$	$CH_3 - CH_2 -$	Ethyl (*Ethyl*)
Propane, $CH_3CH_2CH_3$	$\overset{3}{CH_3} - \overset{2}{CH_2} - \overset{1}{CH_2} -$	1-Propyl (*n-Propyl*)
	$\overset{3}{CH_3} - \underset{\vert}{\overset{2}{CH}} - \overset{1}{CH_3}$	2-Propyl (*Isopropyl*)
Butane, $CH_3CH_2CH_2CH_3$	$\overset{4}{CH_3}\overset{3}{CH_3}\overset{2}{CH_2}\overset{1}{CH_2} -$	1-Butyl (*n-Butyl*)
	$\overset{4}{CH_3} - \overset{3}{CH_2} - \underset{\vert}{\overset{2}{CH}} - \overset{1}{CH_3}$	2-Butyl (*sec-Butyl*)

(*b*) **Unsaturated Hydrocarbons.** *Open chain hydrocarbons which contain carbon-carbon double* ($>C = C<$) *or triple* (—$C \equiv C$—) *bonds in their molecules are called* **unsaturated hydrocarbons.** These are further classified into two types: *alkanes and alkynes*.

(*i*) **Alkenes:** *Hydrocarbons containing a carbon-carbon double bond are* called **alkenes**. They are also called **olefins**. Their general formula and suffix are given below:

General formula: $\mathbf{C_nH_{2n}}$, where, $n = 2, 3, 4, ...,$ etc.

Primary suffix: **ene**

Common names: Alkane – ane + ylene = Alkylene

IUPAC names: Alkane – ane + ene = Alkene

The positions of the double bonds are indicated by the Greek letters α, β, γ, etc., in the common system while arabic numerals, *i.e.* 1, 2, 3, 4, etc., are used in the IUPAC system. For example,

Formula	*Common Name*	*IUPAC Name*
$CH_2 = CH_2$	Ethylene	Ethene
$CH_3CH = CH_2$	Propylene	Propene
$CH_3CH_2\underset{2}{\overset{\beta}{CH}} = \underset{1}{\overset{\alpha}{CH_2}}$	α-Butylene	But-1-ene
$CH_3\overset{\beta}{CH} = \overset{\alpha}{CH}CH_3$	β-Butylene	But-2-ene
$CH_3CH_2CH_2\overset{\beta}{CH} = \overset{\alpha}{CH_2}$	α-Pentylene	Pent-1-ene
$CH_3CH_2CH = \overset{\beta}{CH}\overset{\alpha}{CH_3}$	β-Pentylene	Pent-2-ene
$CH_3CH_2CH_2CH_2\overset{\beta}{CH} = \overset{\alpha}{CH_2}$	α-Hexylene	Hex-1-ene

(*ii*) **Alkynes:** *Unsaturated aliphatic hydrocarbons containing a carbon-carbon triple bond are called* **alkynes**. In the common system, they are called **acetylenes** after the name of the first member of this family, *i.e.* acetylene.

General formula: $\mathbf{C_nH_{2n-2}}$ where, $n = 2, 3, 4, ...,$ etc.

Common names: *Acetylene and its alkyl derivatives.*

IUPAC names: alkane – ane + yne = Alkyne

The position of the triple bond on the parent chain is designated by lowest possible arabic numerals.

The common and IUPAC names of a few simple alkynes are given below:

Formula	*Common Name*	*IUPAC Name*
$CH \equiv CH$	Acetylene	Ethyne
$CH_3C \equiv CH$	Methylacetylene or Allylene	Propyne
$CH_3CH_2\overset{2}{C} \equiv \overset{1}{C}H$	Ethylacetylene	But-1-yne
$CH_3C \equiv \overset{2\ 1}{C}CH_3$	Dimethylacetylene	But-2-yne
$CH_3CH_2CH_2C \equiv CH$	*n*-Propylacetylene	Pent-1-yne
$CH_3CH_2C \equiv CCH_3$	Ethylmethylacetylene	Pent-2-yne
$CH_3CH_2CH_2CH_2C \equiv CH$	*n*-Butylacetylene	Hex-l-yne

2. Alkyl Halides or Haloalkanes

General formula: $\mathbf{C_nH_{2n+1}}$ X, where, *n* = 1, 2, 3, ..., etc. and X = F, Cl, Br or I.

or **R–X** where R is any alkyl group.

Functional group: X (halogen)

Secondary prefix: **Halo**

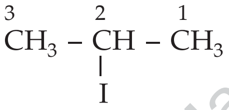
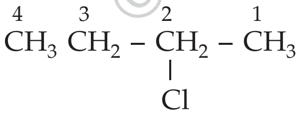
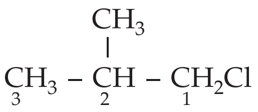
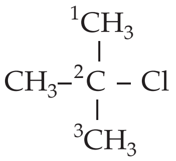
Common names: Add the word halide (fluoride, chloride, bromide, iodide) to the name of the alkyl group,

i.e. **Alkyl + halides = Alkyl halide**

IUPAC names: Add the secondary prefix *halo* to the name of the corresponding alkane,

i.e. **Halo + alkane = Haloalkane**

The IUPAC and common names of some important haloalkanes are given below:

Formula	*Common Name*	*IUPAC Name*
CH_3Cl	Methyl chloride	Chloromethane
CH_3CH_2Br	Ethyl bromide	Bromoethane
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2I$	*n*-Propyl iodide	1-Iodopropane
 $\overset{3}{CH_3} - \underset{\displaystyle I}{\underset{\vert}{\overset{2}{CH}}} - \overset{1}{CH_3}$	*Iso*-Propyl iodide	2-Iodopropane
$\overset{4}{CH_3}\ \overset{3}{CH_2}\ \overset{2}{CH_2}\ \overset{1}{CH_2}Cl$	*n*-Butyl chloride	1-Chlorobutane
 $\overset{4}{CH_3}\ \overset{3}{CH_2} - \underset{\displaystyle Cl}{\underset{\vert}{\overset{2}{CH_2}}} - \overset{1}{CH_3}$	*sec*-Butyl chloride	2-Chlorobutane
 $\underset{3}{CH_3} - \overset{\displaystyle CH_3}{\overset{\vert}{\underset{2}{CH}}} - \underset{1}{CH_2Cl}$	*Iso*-Butyl chloride	1-Chloro-2-methylpropane
 $CH_3 - \overset{\displaystyle {}^1CH_3}{\overset{\vert}{\underset{\underset{\displaystyle {}^3CH_3}{\vert}}{{}^2C}}} - Cl$	*tert*-Butyl chloride	2-Chloro-2-methylpropane

3. Alcohols or Alkanols

General formula: C_nH_{2n+1} OH (where, n = 1, 2, 3, ...) or R–OH (where, R is any alkyl group).

Functional group: –OH (*hydroxyl*)

Secondary suffix: **ol**

Common names: Add the word alcohol to the name of the alkyl group.

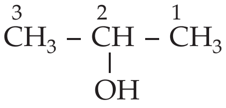
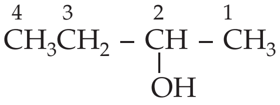
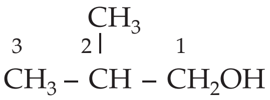
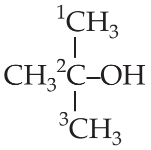
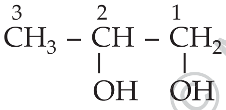
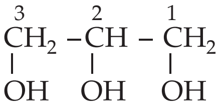
Alkyl + alcohol = Alkyl alcohol

IUPAC names: Replace the terminal '*e*' from the name of corresponding alkane by the suffix *ol*.

Alkane – *e* + ol = Alkanol

Alcohols having two or three hydroxyl groups are called *diols* and *triols* respectively. In these cases, positions of all the hydroxyl groups are indicated by Arabic numerals, *i.e.* 1, 2, 3, ..., etc.

Common and IUPAC names of some alcohols are given below:

Formula	*Common Name*	*IUPAC Name*
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2-OH$	*n*-Propyl alcohol	Propane-1-ol
 $\overset{3}{C}H_3-\underset{\underset{OH}{\vert}}{\overset{2}{C}H}-\overset{1}{C}H_3$	*Iso*-Propyl alcohol	Propan-2-ol
$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2-OH$	*n*-Butyl alcohol	Butan-1-ol
 $\overset{4}{C}H_3\overset{3}{C}H_2-\underset{\underset{OH}{\vert}}{\overset{2}{C}H}-\overset{1}{C}H_3$	*sec*-Butyl alcohol	Butan-2-ol
 $\overset{3}{C}H_3-\overset{CH_3}{\overset{\vert}{\underset{2}{C}H}}-\overset{1}{C}H_2OH$	*Iso*-Butyl alcohol	2-Methylpropane-1-ol
 $CH_3-\overset{^1CH_3}{\overset{\vert}{\underset{\underset{^3CH_3}{\vert}}{^2C}}}-OH$	*tert*-Butyl alcohol	2-Methylpropane-2-ol
 $\overset{3}{C}H_3-\underset{\underset{OH}{\vert}}{\overset{2}{C}H}-\underset{\underset{OH}{\vert}}{\overset{1}{C}H_2}$	Propylene glycol	Propane-1, 2-diol
 $\underset{\underset{OH}{\vert}}{\overset{3}{C}H_2}-\underset{\underset{OH}{\vert}}{\overset{2}{C}H}-\underset{\underset{OH}{\vert}}{\overset{1}{C}H_2}$	Glycerol or Glycerine	Propane-1, 2, 3-triol

4. Ethers or Alkoxyalkanes

General formula: **R–O–R′,** where R and R′ are same or different alkyl groups. If R = R′, ethers are called simple ethers and if R ≠ R′, then ethers are called *mixed ethers.*

Functional group: – O –

Secondary prefix: **Alkoxy**

Common names: In case of mixed ethers, add the word *ether* to the names of the alkyl groups arranged in alphabetical order. In case of simple ethers, the numerical prefix *di* is added to the name of the alkyl group followed by the word ether.

IUPAC names: In the IUPAC system, ethers are called *alkoxyalkanes*. The smaller alkyl group forms a part of the alkoxy group while the bigger alkyl group forms a part of the alkane. The names of the ethers are then derived by adding the suffix *alkoxy* to the name of the *alkane*,

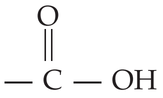
Alkoxy + alkane = Alkoxyalkane

Common and IUPAC names of some ethers are given below:

Formula	*Common Name*	*IUPAC Name*
CH_3OCH_3	Dimethyl ether	Methoxymethane
$CH_3OCH_2CH_3$	Ethyl methyl ether	Methoxyethane
$CH_3CH_2OCH_2CH_3$	Diethyl ether	Ethoxyethane
$CH_3CH_2CH_2OCH_3$	Methyl-*n*-propyl ether	Methoxy propane

5. Monocarboxylic Acids or Alkanoic Acids

General formula: $\mathbf{C_nH_{2n+1}\,COOH}$, where, $n = 0, 1, 2, 3,$ ....., etc. or **R–COOH**, where R = H or any alkyl group.

Functional group: 
$-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ (*carboxyl*)

Secondary suffix: **oic acid**

Common names: These are derived from the name of the plant or animal from which they are isolated.

IUPAC names: Replace terminal '*e*' from the name of the corresponding alkane by the suffix *oic acid*,

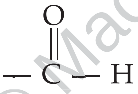
Alkane – *e* + oic acid = Alkanoic acid

Some important examples are:

Formula	*Common Name*	*IUPAC Name*
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	*n*-Butyric acid	Butanoic acid
$CH_3CH_2CH_2CH_2COOH$	Valeric acid	Pentanoic acid

6. Aldehydes or Alkanals

General formula: $\mathbf{C_nH_{2n+1}\,CHO}$ where, $n = 0, 1, 2, 3,$ ...., etc., or **R–CHO** where R = H or any alkyl group.

Functional group: 
$-\overset{\overset{\displaystyle O}{\|}}{C}-H$ (*aldehyde*)

Secondary suffix: **al**

Common names: Replace *ic acid* from the common name of the corresponding acid which they give upon oxidation by the word *aldehyde*. For example,

Acetic acid – ic acid + aldehyde = Acetaldehyde

IUPAC names: Replace the terminal '*e*' from the name of the corresponding alkane by the suffix *al*,

Alkane – *e* + al = Alkanal

Some examples of aldehydes are given below:

Formula	*Common Name*	*IUPAC Name*
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
CH_3CH_2CHO	Propionaldehyde	Propanal
$CH_3CH_2CH_2CHO$	*n*-Butyraldehyde	Butanal

7. Ketones or Alkanones

General formula: $\mathbf{C_nH_{2n+1}COC_nH_{2n+1}}$, where, $n = 1, 2, 3, ...,$ etc. or **R–CO–R´** where R and R´, may be same or different alkyl groups. If R = R´, ketones are called *simple ketones* and if R ≠ R´, ketones are called *mixed ketones*.

Functional groups: > C = O (*Ketonic*)

Secondary suffix: **one**

Common names: In case of mixed ketones, name the alkyl groups in alphabetical order and then add the word ketone. In case of simple ketones, the numerical prefix *di* is used before the name of the alkyl group.

IUPAC names: Replace terminal '*e*' from the name of the corresponding alkane by the suffix *one*, *i.e.*

Alkane – *e* + one = Alkanone

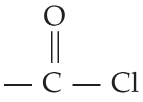
Some examples are:

Formula	*Common Name*	*IUPAC Name*
CH_3COCH_3	Dimethyl ketone or Acetone	Propanone
$CH_3COCH_2CH_3$	Ethyl methyl ketone	Butan-2-one or Butanone
$\overset{1}{CH_3}\overset{2}{CO}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_3}$	Methyl *n*-propyl ketone	Pentan-2-one
$\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CO}\overset{4}{CH_2}\overset{5}{CH_3}$	Diethyl ketone	Pentan-3-one

8. Acid Chlorides or Acyl Chlorides

General formula: **RCOCl**, where, R = H or any alkyl group

Functional group:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$$

Secondary suffix: **oyl chloride**

Common names: Replace *ic acid* from the common name of the corresponding acid by *yl chloride*. For example,

Acetic acid – ic acid + yl chloride = Acetyl chloride

IUPAC names: Replace terminal '*e*' from the name of the corresponding alkane by the suffix *oyl chloride*, *i.e.*, **Alkane – *e* + oyl chloride = Alkanoyl chloride**

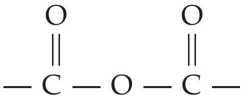
Some important examples are:

Formula	*Common Name*	*IUPAC Name*
HCOCl (*unstable*)	Formyl chloride	Methanoyl chloride
CH_3COCl	Acetyl chloride	Ethanoyl chloride
CH_3CH_2COCl	Propionyl chloride	Propanoyl chloride

9. Acid Anhydrides

General formula: **R — CO — O — CO — R´ or $\mathbf{(RCO)_2O}$**, where, R or R´ may be same or different alkyl groups.

Functional group:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-$$

Secondary suffix: **anhydride**

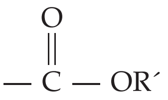
Common or IUPAC names: Replace the word *acid* from the common or IUPAC name of the corresponding acid by the word *anhydride*.

Some important examples are:

Formula	*Common Name*	*IUPAC Name*
$(CH_3CO)_2O$	Acetic anhydride	Ethanoic anhydride
$(CH_3CH_2CO)_2O$	Propionic anhydride	Propanoic anhydride

10. Esters

General formula: **R–COOR´**, where, R = H or any alkyl group while group R´ is always an alkyl group.

Functional group: 
$—\overset{O}{\overset{\|}{C}}—OR'$ (*ester*)

Secondary prefix: ***alkyl***

Secondary suffix: ***oate***

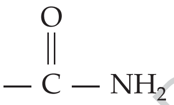
Common or IUPAC names: Write the name of the alkyl group before the common or IUPAC name of the parent acid with its terminal *ic acid* replaced by *oate*.

Some important examples are:

Formula	*Common Name*	*IUPAC Name*
$HCOOC_2H_5$	Ethyl formate	Ethyl methanoate
CH_3COOCH_3	Methyl acetate	Methyl ethanoate
$CH_3COOC_2H_5$	Ethyl acetate	Ethyl ethanoate
$CH_3CH_2COOC_2H_5$	Ethyl propionate	Ethyl propanoate

11. Acid Amides or Alkanamides

General formula: **$RCONH_2$** where, R = H or any alkyl group.

Functional group: 
$—\overset{O}{\overset{\|}{C}}—NH_2$ (*amide*)

Secondary suffix: **amide**

Common names: Replace *ic acid* from the common name of the corresponding acid by the secondary suffix *amide*.

IUPAC names: Replace the terminal '*e*' from the name of the corresponding alkane by the suffix *amide*, *i.e.* **Alkane – *e* + amide = Alkanamide**

Some important examples are:

Formula	*Common Name*	*IUPAC Name*
$HCONH_2$	Formamide	Methanamide
CH_3CONH_2	Acetamide	Ethanamide
$CH_3CH_2CONH_2$	Propionamide	Propanamide
$CH_3CH_2CH_2CONH_2$	Butyramide	Butanamide

12. Primary Amines

General formula: **$R–NH_2$**, where, R is any alkyl group.

Functional group: $–NH_2$ (*amino*)

Secondary suffix: **amine**

Common names: (*i*) Add the word *amine* to the name of the alkyl group.

Alkyl + amine = Alkylamine

(*ii*) Attach the prefix *amino* to the name of the corresponding alkane,

Amino + alkane = Aminoalkane

IUPAC names: Replace the terminal '*e*' from the name of the corresponding alkane by the secondary suffix *amine*, *i.e.* **Alkane – *e* + amine = Alkanamine**

Some important examples are:

Formula	*Common Name*	*IUPAC Name*
CH_3NH_2	Methylamine	Methanamine
$CH_3CH_2NH_2$	Ethylamine	Ethanamine
$\overset{3}{C}H_3\overset{2}{C}H_2\overset{1}{C}H_2NH_2$	*n*-Propylamine	Propanamine
$CH_3CH_2CH_2CH_2NH_2$	*n*-Butylamine	Butanamine

13. Secondary Amines

General formula: **R–NH–R´**, where, R and R´ may be same or different alkyl groups.

Functional group: > NH (*imino*)

Secondary prefix: **N–Alkyl**

Secondary suffix: **amine**

Common names: Name the alkyl groups in alphabetical order and then add the word *amine*. In case the two alkyl groups are the same, the numerical prefix *di* is used before the name of the alkyl group.

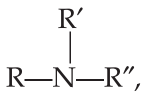
IUPAC names: Add the prefix *N-alkyl* to the name of the alkanamine corresponding to the larger alkyl group,

i.e. **N – Alkyl + alkanamine = N-Alkylalkanamine**

Some important examples are:

Formula	*Common Name*	*IUPAC Name*
CH_3NHCH_3 or $(CH_3)_2NH$	Dimethylamine	N-Methylmethanamine
$CH_3CH_2NHCH_3$	Ethylmethylamine	N-Methylethanamine
$(CH_3CH_2)_2NH$	Diethylamine	N-Ethylethanamine

14. Tertiary Amines

General formula:  $R—\overset{\overset{\textstyle R'}{|}}{N}—R''$, where, R, R´, and R´´ may be same or different alkyl groups or two of them may be same while third may be different.

Secondary prefix: **N-alkyl, N-alkyl**

Functional group:  $—\overset{|}{N}—$ (*tertiary nitrogen atom*)

Secondary suffix: **amine**

Common names: Name the alkyl groups in alphabetical order and add suffix *amine*. If two or all the three alkyl groups are same, the numerical prefixes *di* and *tri* are respectively used.

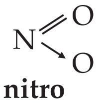
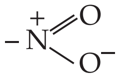
IUPAC names: Add the prefixes *N-alkyl* and *N-alkyl* (smaller alkyl groups) to the name of the *alkanamine* corresponding to the largest alkyl group.

Some important examples are:

Formula	*Common Name*	*IUPAC Name*
$(CH_3)_3N$	Trimethylamine	N, N-Dimethylmethanamine
$CH_3CH_2N(CH_3)_2$	Ethyldimethylamine	N, N-Dimethylethanamine
$(CH_3CH_2)_2NCH_3$	Diethylmethylamine	N-Ethyl-N-methylethanamine
$(CH_3CH_2)_3N$	Triethylamine	N, N-Diethylethanamine

15. Nitroalkanes

General formula: **R–NO$_2$**, where, R is any alkyl group.

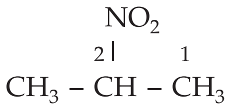
Functional group:  or 

Secondary prefix: **nitro**

Common names: There are no separate common names for nitroalkanes.

IUPAC names: Add the secondary prefix *nitro* to the name of the alkane, *i.e.* **Nitro + alkane = Nitroalkane**

Some important examples are:

Formula	*IUPAC Name*	*Formula*	*IUPAC Name*
CH_3-NO_2	Nitromethane	 $CH_3-\underset{2}{\overset{\overset{NO_2}{\vert}}{CH}}-\overset{1}{CH_3}$	2-Nitropropane
$CH_3CH_2-NO_2$	Nitroethane	$CH_3CH_2CH_2\overset{1}{CH_2}-NO_2$	1-Nitrobutane
$CH_3CH_2\overset{1}{CH_2}-NO_2$	1-Nitropropane		

16. Alkyl Nitrites

General formula: **R–O–N = O**, where, R is any alkyl group.
Functional group: –O – N = O (*nitrite*)
Secondary suffix: **nitrite**

Common names: Add the secondary suffix *nitrite* to the name of the alkyl group, *i.e.* **Alkyl + nitrite = Alkyl nitrite**

IUPAC names: There are no IUPAC names for alkyl nitrites.

Formula	*Common Name*	*Formula*	*Common Name*
$CH_3–O–N = O$	Methyl nitrite	$CH_3CH_2CH_2–O–N = O$	*n*-Propyl nitrite
$CH_3CH_2–O–N = O$	Ethyl nitrite		

17. Alkyl Cyanides or Alkanenitriles

General formula: **R — C ≡ N**, where, R is any alkyl group.
Functional group: —C ≡ N (*cyano or nitrile*)
Secondary suffix: **onitrile**

Common names:

(*i*) Add the suffix *cyanide* to the name of the alkyl group, *i.e.* **Alkyl + cyanide = Alkyl cyanide**
(*ii*) Replace *ic acid* from the common name of the corresponding acid by the suffix *onitrile*, *i.e.* **Acetic acid – ic acid + onitrile = Acetonitrile**

IUPAC names: Add the suffix *nitrile* to the name of the alkane containing the same number of carbon atoms as the alkyl cyanide,
i.e. **Alkane + nitrile = Alkanenitrile**

Some important examples are:

Formula	*Common Name*	*IUPAC Name*
CH_3CN	Methyl cyanide or Acetonitrile	Ethanenitrile
CH_3CH_2CN	Ethyl cyanide	Propanenitrile
$CH_3CH_2CH_2CN$	*n*-Propyl cyanide	Butanenitrile

18. Isocyanides or Isonitriles

General formula: **R–N ≡ C**, where, R is any alkyl group.
Functional group: –N ≡ C (*isocyanide or isonitrile*)
Secondary suffix: **isocyanide or isonitrile**

Common names: Add the suffix *isocyanide or carbylamine* to the name of the alkyl group.

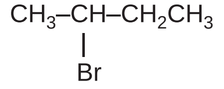
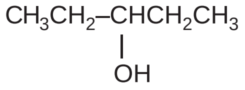
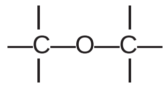
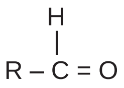
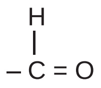
IUPAC names: There are no IUPAC names for isocyanides or isonitriles.

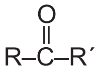
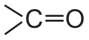
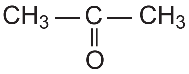
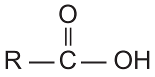
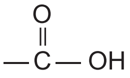
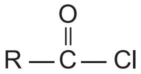
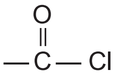
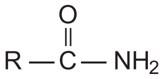
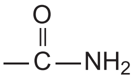
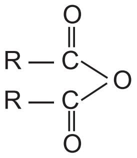
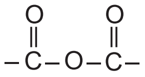
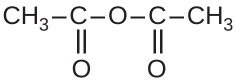
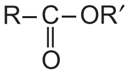
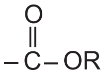
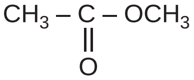
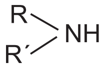
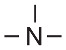
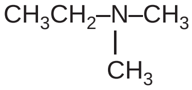
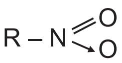
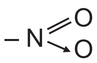
Some important examples are:

Formula	*Common Name*
$CH_3-N \overset{\rightarrow}{\equiv} C$	Methyl isocyanide or Methyl carbylamine
$CH_3CH_2 - N \overset{\rightarrow}{\equiv} C$	Ethyl isocyanide or Ethyl carbylamine

Table 10.2 gives a summary of nomenclature of different classes of organic compounds along with their functional groups, general formulae, suffix or prefix to be attached with examples.

Table 10.2: Summary of Nomenclature of Organic Compounds

Class of Compounds	General Formula	Functional Group	Suffix (s) or Prefix (p) to be Added to Saturated Hydrocarbons	IUPAC Name	Examples
1. Alkanes	C_nH_{2n+2}	–	ane (*s*)	Alkane	$CH_3CH_2CH_3$ Propane
2. Alkenes	C_nH_{2n}	> C = C <	ene (*s*)	Alkane-ane +ene = Alkene	$CH_3CH_2CH=CH_2$ But-1-ene $CH_3CH = CHCH_3$ But-2-ene
3. Alkynes	C_nH_{2n-2}	–C ≡ C–	yne (*s*)	Alkane–ane + yne = Alkyne	$CH_3CH_2C \equiv CH$ But-1-yne
4. Alkyl halides	R – X (X = F, Cl, Br, I and R is an alkyl group)	–X	halo (*p*)	Halo + Alkane = Haloalkane	$CH_3CH_2CH_2CH_2Br$ 1-Bromobutane  $CH_3-\underset{\underset{Br}{\mid}}{CH}-CH_2CH_3$ 2-Bromobutane
5. Alcohols	R – OH	– OH	ol (*s*)	Alkane – e + ol = Alkanol	$CH_3CH_2CH_2CH_2OH$ Butan-1-ol  $CH_3CH_2-\underset{\underset{OH}{\mid}}{CH}CH_2CH_3$ Pentan-3-ol
6. Ethers	R–O–R´ (same or different alkyl groups)	 $-\overset{\mid}{\underset{\mid}{C}}-O-\overset{\mid}{\underset{\mid}{C}}-$	alkoxy (*p*)	Alkoxy + alkane = Alkoxyalkane (smaller alkyl is the substituent and bigger is the alkane)	CH_3OCH_3 Methoxymethane $CH_3OCH_2CH_3$ Methoxyethane
7. Aldehydes	 $R-\overset{\overset{H}{\mid}}{C}=O$	 $-\overset{\overset{H}{\mid}}{C}=O$	al (*s*)	Alkane – e+al = Alkanal	$CH_3CH_2CH_2CHO$ Butanal

Class of Compounds	General Formula	Functional Group	Suffix (*s*) or Prefix (*p*) to be Added to Saturated Hydrocarbons	IUPAC Name	Examples
8. Ketones	 $R-\overset{O}{\overset{\|}{C}}-R'$ (same or different alkyl groups)		one (*s*) = Alkanone	Alkane – e+one	 $CH_3-\underset{O}{\underset{\|}{C}}-CH_3$ Propanone
9. Carboxylic acids	 $R-\overset{O}{\overset{\|}{C}}-OH$ (R = H or alkyl)	 $-\overset{O}{\overset{\|}{C}}-OH$	oic acid (*s*)	Alkane – e + oic acid = Alkanoic acid	CH_3CH_2COOH Propanoic acid
10. Acid chlorides or Acyl chlorides	 $R-\overset{O}{\overset{\|}{C}}-Cl$	 $-\overset{O}{\overset{\|}{C}}-Cl$	oyl halide (*s*)	Alkane – e + oyl chloride = Alkanoyl chloride	$CH_3CH_2CH_2COCl$ Butanoyl chloride
11. Acid amides	 $R-\overset{O}{\overset{\|}{C}}-NH_2$ (R = H or alkyl)	 $-\overset{O}{\overset{\|}{C}}-NH_2$	amide (*s*)	Alkane – e + amide = Alkanamide	$CH_3CH_2CONH_2$ Propanamide
12. Acid anhydrides		 $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$	oic anhydride (s)	Alkane – e + oic anhydride = Alkanoic anhydride	 $CH_3-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3$ Ethanoic anhydride
13. Esters	 $R-\underset{O}{\underset{\|}{C}}-OR'$ (R = H or alkyl R′ = alkyl)	 $-\overset{O}{\overset{\|}{C}}-OR$	alkyl (*p*) and oate (*s*)	Alkyl + alkane – e + oate = Alkyl alkanoate	 $CH_3-\underset{O}{\underset{\|}{C}}-OCH_3$ Methyl ethanate
14. Amines (*i*) Primary (1°)	$R-NH_2$	$-NH_2$	Amine (*s*)	Alkane – e + + amine = Alkanamine	$CH_3CH_2CH_2CH_2NH_2$ Butan–1–amine
(*ii*) Secondary (2°) (same or different alkyl groups)			N–alkyl (*p*) alkanamine (*s*)	N-Alkyl + alkane – e + amine = N -Alkyl – alkanamine (smaller alkyl group is the substituent)	$CH_3CH_2NHCH_3$ N–Methylethanamine
(*iii*) Tertiary (3°) (same or different alkyl groups)	 $R-\overset{R'}{\overset{\mid}{N}}-R''$	 $-\overset{\mid}{N}-$	N-alkyl, N-alkyl (*p*) alkanamine (*s*)	N-Alkyl + N-Alkyl + alkanamine = N-alkyl, alkanamine, N-alkyl – alkanamine two smaller alkyl groups are substituents	 $CH_3CH_2-\underset{CH_3}{\underset{\mid}{N}}-CH_3$ N-Ethyl-N-methyl ethanamine
15. Nitroalkanes			Nitro (*p*)	Nitro + alkane = Nitroalkane	$CH_3CH_2NO_2$ 1-Nitroethane
16. Alkyl nitrites	$R-O-N=O$	$-O-N=O$	nitrite (*s*)	alkyl + nitrite = alkyl nitrite	$CH_3CH_2-O-N=O$ Ethyl nitrite
17. Alkyl cyanides	$R-C\equiv N$	$-C\equiv N$	nitrile (*s*)	Alkane + nitrile = Alkanenitrile	$CH_3CH_2CH_2CN$ Butanenitrile

Class of Compounds	General Formula	Functional Group	Suffix (s) or Prefix (p) to be Added to Saturated Hydrocarbons	IUPAC Name	Examples
18. Alkyl isocyanides or Alkyl carbylamines	$R-N \stackrel{\rightarrow}{=} C$	$-N \stackrel{\rightarrow}{=} C$	isocyanide (*s*) or carbylamine (*s*)	alkyl + isocyanide = alkyl isocyanide = alkyl carbylamine alkyl + carbylamine	$CH_3CH_2-N \stackrel{\rightarrow}{=} C$ Ethyl isocyanide or Ethyl carbylamine

10.10 GENERAL RULES FOR NAMING ORGANIC COMPOUNDS (COMMON SYSTEM)

Some simple branched chain compounds can be named according to the common system. For example, there are three isomeric pentanes. They can be distinguished by prefixes as discussed below:

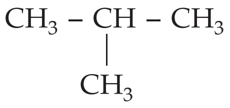
(*i*) **Prefix *n*** (*normal*) is used for those alkanes in which all the carbon atoms are arranged in a straight chain, *i.e.* there is no branching. For example,

$CH_3CH_2CH_2CH_3$ *n*-Butane

$CH_3CH_2CH_2CH_2CH_3$ *n*-Pentane

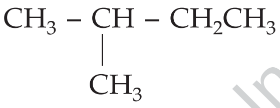
$CH_3CH_2CH_2CH_2CH_2CH_3$ *n*-Hexane

(*ii*) **Prefix iso** is used for those alkanes which contain a methyl group at the second carbon of the continuous chain. For example,



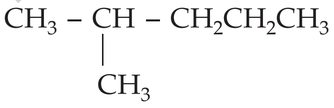
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$

Isobutane



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3$

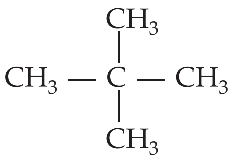
Isopentane



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_2CH_3$

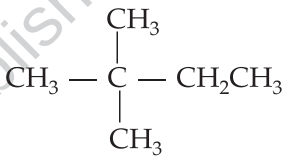
Isohexane

(*iii*) **Prefix neo** is used for those alkanes which have two methyl groups attached to the second carbon atom of the continuous chain. For example,



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

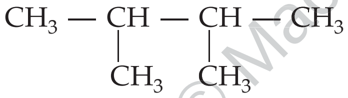
Neopentane



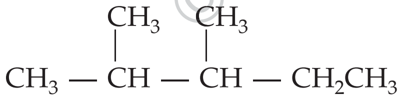
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$

Neohexane

However, if the branching occurs at any carbon atom other than the second carbon atom of the continuous chain, such alkanes cannot be named according to the common system. For example, the following alkanes cannot be named according to the common system.



$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$



$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_3$

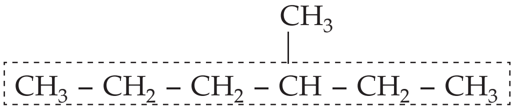
That is why the need arises for IUPAC system.

10.11 RULES OF IUPAC NOMENCLATURE FOR BRANCHED CHAIN ALKANES

The following rules are used for naming branched chain alkanes.

1. **Longest Chain Rule.** *Select the longest continuous chain of carbon atoms.* This is called the **parent chain** while all other carbon atoms which are not included in the parent chain are called **branched chains** or **side chains** or substituents. The compound is then named as a derivative of the parent chain. It may be noted that the longest chain may or may not look straight as written on the paper but it must be

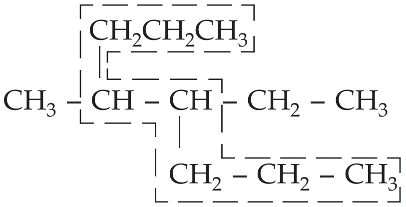
continuous. For example, in compound II, there is the longest chain of eight carbon atoms, shown by dotted lines, although on the paper, these carbon atoms are not written linearly. Thus, compound II is a derivative of **octane.**



$$CH_3-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CH_3$$

I

Longest chain contains six carbon atoms and hence, compound (I) is named as a derivative of **hexane**.

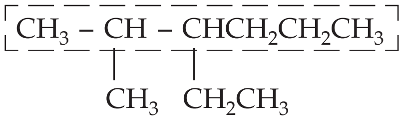


$$CH_3-\overset{\displaystyle CH_2CH_2CH_3}{\overset{|}{CH}}-\underset{\displaystyle CH_2-CH_2-CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

II

Longest chain contains eight carbon atoms and hence, compound (II) is named as a derivative of **octane**.

2. **Rule for Larger Number of Side Chains.** *If two chains of equal lengths are possible, the one with the larger number of side chains is selected.* For example,



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$$

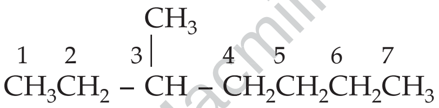
Named as hexane with two alkyl substituents (*Correct*)

≡

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$$

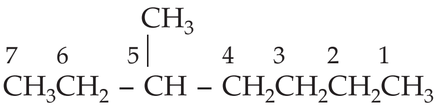
Named as hexane with one alkyl substituent (*Wrong*)

3. **Lowest Number Rule or Lowest Sum Rule.** We have to number the carbon atoms of the parent chain as 1, 2, 3, 4, ..., etc., starting from that end (there are two ends, the left end and the right end) which gives the lowest possible number to the carbon atom carrying the substituent. For example, in structure (III) the numbering can be done in two different ways, *i.e.* III A and III B. The numbering of the carbon chain as given in the structure III A is *correct* since it gives a lower number, *i.e.* 3 to the substituent, *i.e.* methyl group while the numbering as given in structure III B is *wrong* since it gives a higher number, *i.e.* 5 to the substituent.



$$\overset{1}{C}H_3\overset{2}{C}H_2-\overset{\displaystyle CH_3}{\overset{3|}{CH}}-\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_3$$

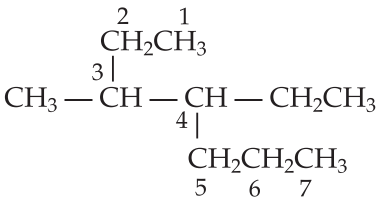
III A (*Correct numbering*)



$$\overset{7}{C}H_3\overset{6}{C}H_2-\overset{\displaystyle CH_3}{\overset{5|}{CH}}-\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_3$$

III B (*Wrong numbering*)

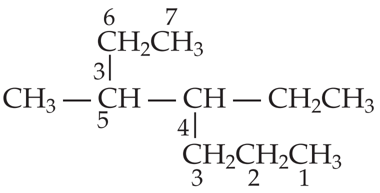
The number that indicates the position of the substituent on the parent chain is called the **locant** *or* **positional number**. *If there are two or more substituents, the numbering of parent chain is done in such a way that the sum of the locants is the lowest.* This is called the **lowest sum rule.** For example, the carbon chains of alkanes given below should be numbered as indicated in structure **A** and not according to structure **B**.



$$CH_3-\overset{\overset{2}{C}H_2\overset{1}{C}H_3}{\overset{3|}{CH}}-\underset{\underset{5}{C}H_2\underset{6}{C}H_2\underset{7}{C}H_3}{\underset{4|}{CH}}-CH_2CH_3$$

A (*Correct*)

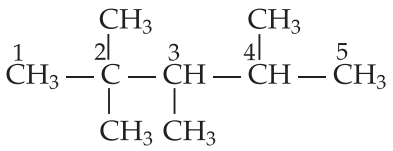
Sum of the locants = 3 + 4 = 7



$$CH_3-\underset{5}{\overset{\overset{6}{C}H_2\overset{7}{C}H_3}{\overset{3|}{CH}}}-\underset{\underset{3}{C}H_2\underset{2}{C}H_2\underset{1}{C}H_3}{\underset{4|}{CH}}-CH_2CH_3$$

B (*Wrong*)

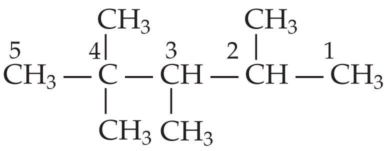
Sum of the locants = 4 + 5 = 9



$$\overset{1}{C}H_3-\overset{2}{C}(CH_3)_2-\overset{3}{C}H(CH_3)-\overset{4}{C}H(CH_3)-\overset{5}{C}H_3$$

A (*Correct*)

Sum of the locants = 2 + 2 + 3 + 4 = 11

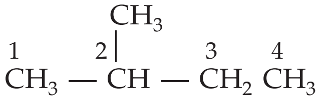


$$\overset{5}{C}H_3-\overset{4}{C}(CH_3)_2-\overset{3}{C}H(CH_3)-\overset{2}{C}H(CH_3)-\overset{1}{C}H_3$$

B (*Wrong*)

Sum of the locants = 2 + 3 + 4 + 4 = 13

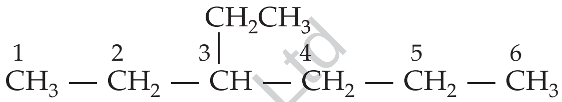
4. **Name of the Branched Chain Alkane.** Prefix the name of the substituent (*i.e.*, the alkyl group) to the name of the parent alkane and indicate its position (on the parent chain) by writing before it the number of the carbon atom carrying the substituent. The name of the substituent is separated from its locant by a hyphen (–). The final name of the alkane is always written as one word. Some examples are given below for illustration.



$$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H_2\,\overset{4}{C}H_3$$

2-Methylbutane

Numerical Prefix : 2
Prefix : *Methyl*
Word Root : *But*
Suffix : *ane*



$$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H(CH_2CH_3)-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_3$$

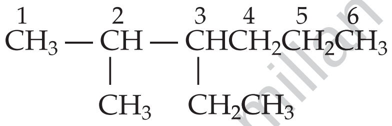
2-Ethylhexane

Numerical Prefix : 3
Prefix : *Ethyl*
Word Root : *Hex*
Suffix : *ane*

The name of the compound for substituted hydrocarbon, as already told in previous section is written by combining the prefixes, word root and suffixes, as given below:

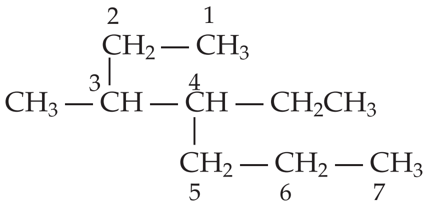
Numerical Prefix....Prefix....Word Root....Suffix

5. **Alphabetical Order of the Side Chains.** When two or more alkyl groups (side chains) are present on the parent chain, each alkyl group prefixed by its positional number is arranged in alphabetical order (irrespective of its positional number) before the name of the parent alkane. For example,



$$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H(CH_2CH_3)\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$$

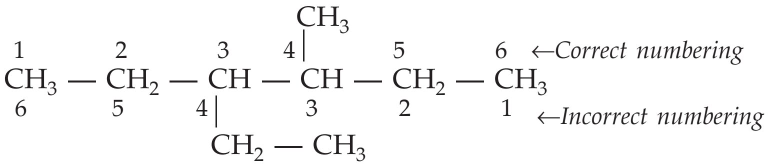
3–Ethyl–2–methylhexane



$$CH_3-\overset{3}{C}H(\overset{2}{C}H_2-\overset{1}{C}H_3)-\overset{4}{C}H(\underset{5}{C}H_2-\underset{6}{C}H_2-\underset{7}{C}H_3)-CH_2CH_3$$

4–Ethyl–3–methylheptane

6. **Numbering of Different Alkyl Groups at Equivalent Positions.** If two different alkyl groups are present at equivalent positions, the numbering of the parent chain is done in such a way that the alkyl group which comes first in the alphabetical order (written first in the name) gets the lower number. For example, in the following example out of methyl, and ethyl group, ethyl starts with **e** and methyl starts with **m**, thus ethyl comes first alphabetically, so it will get lower locant, *i.e.* 3. Thus, numbering should be done from right to left.



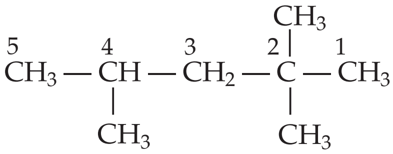
$$\underset{6}{\overset{1}{C}}H_3-\underset{5}{\overset{2}{C}}H_2-\underset{4}{\overset{3}{C}}H(CH_2-CH_3)-\underset{3}{\overset{4}{C}}H(CH_3)-\underset{2}{\overset{5}{C}}H_2-\underset{1}{\overset{6}{C}}H_3$$

←*Correct numbering*

←*Incorrect numbering*

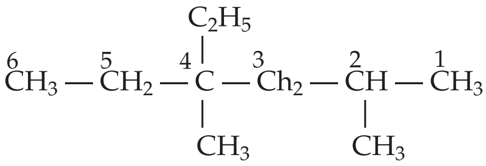
3–Ethyl–4–methylhexane

7. **Naming Same Alkyl Group at Different Positions.** When the same alkyl group occurs more than once on the parent chain at different positions, the positional number or locant of each alkyl group is separated by commas and suitable prefixes such as **di** (for two), **tri** (for three), **tetra** (for four), etc., are attached to the name of the alkyl group. However, the prefixes **di, tri**, etc. are not considered while deciding the alphabetical order of the alkyl groups.



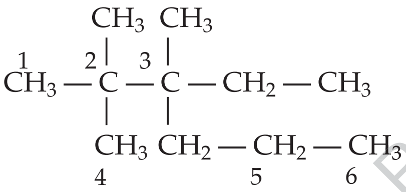
$$\overset{5}{CH_3}-\underset{CH_3}{\overset{4}{CH}}-\overset{3}{CH_2}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{1}{CH_3}$$

2, 2, 4–Trimethylpentane



$$\overset{6}{CH_3}-\overset{5}{CH_2}-\underset{CH_3}{\overset{C_2H_5}{\overset{4}{C}}}-\overset{3}{Ch_2}-\underset{CH_3}{\overset{2}{CH}}-\overset{1}{CH_3}$$

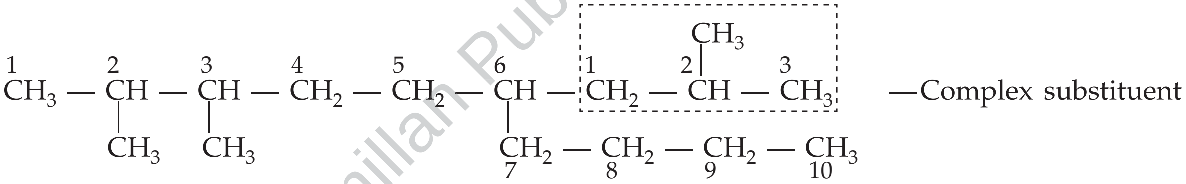
4–Ethyl–2, 4–dimethylhexane



$$\overset{1}{CH_3}-\underset{\underset{4}{CH_3}}{\overset{CH_3}{\overset{2}{C}}}-\underset{\underset{5}{CH_2}-\underset{6}{CH_3}}{\underset{CH_2}{\overset{CH_3}{\overset{3}{C}}}}-CH_2-CH_3$$

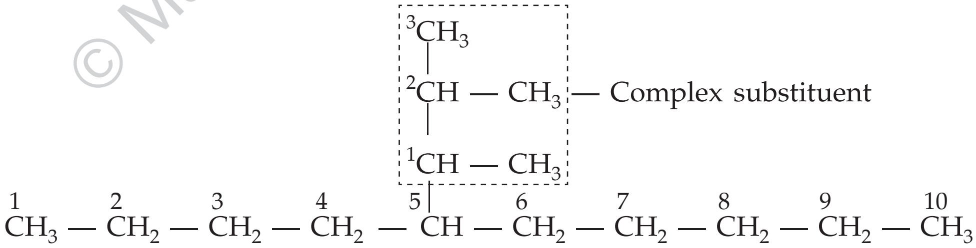
3–Ethyl–2, 2, 3–trimethylhexane

8. **Numbering the Complex Substituent.** In case, the substituent on the parent chain is further branched, it is named as a substituted alkyl group by numbering the carbon atoms of this group attached to the parent chain as 1. The name of such a substituent may be enclosed in brackets to avoid confusion with the numbers of the parent chain. For example,



$$\overset{1}{CH_3}-\underset{CH_3}{\overset{2}{CH}}-\underset{CH_3}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{\underset{7}{CH_2}-\underset{8}{CH_2}-\underset{9}{CH_2}-\underset{10}{CH_3}}{\overset{6}{CH}}-\boxed{\overset{1}{CH_2}-\overset{CH_3}{\overset{2}{CH}}-\overset{3}{CH_3}}\text{—Complex substituent}$$

2, 3-Dimethyl-6-(2-methyl propyl) decane

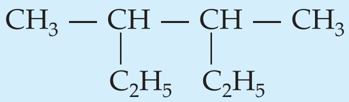


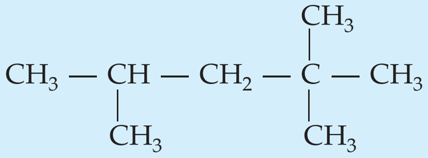
$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{\boxed{\begin{array}{l}{}^{3}CH_3\\ |\\ {}^{2}CH-CH_3\\ |\\ {}^{1}CH-CH_3\end{array}}\text{— Complex substituent}}{\overset{5}{CH}}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_2}-\overset{9}{CH_2}-\overset{10}{CH_3}$$

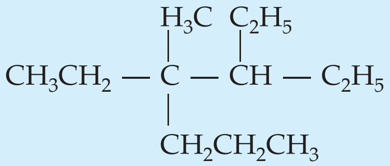
5–(1, 2–Dimethylpropyl) decane

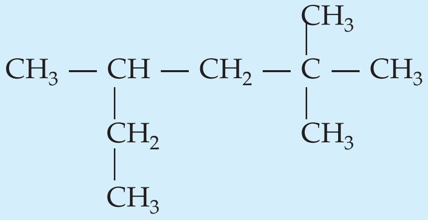
PROBLEMS FOR PRACTICE

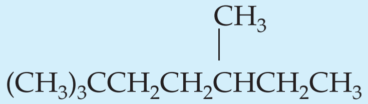
1. Give the IUPAC names of the following alkanes:

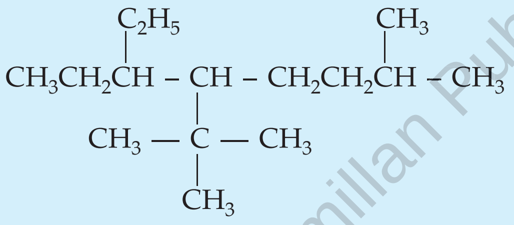
(*i*) 
$CH_3-CH(C_2H_5)-CH(C_2H_5)-CH_3$

(*ii*) 
$CH_3-CH(CH_3)-CH_2-C(CH_3)_2-CH_3$

(*iii*) 
$CH_3CH_2-C(CH_3)(CH_2CH_2CH_3)-CH(C_2H_5)-C_2H_5$

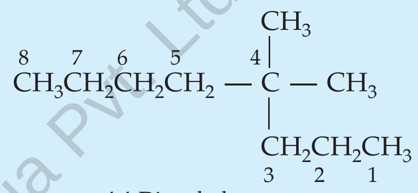
(*iv*) 
$CH_3-CH(CH_2CH_3)-CH_2-C(CH_3)_2-CH_3$

(*v*) 
$(CH_3)_3CCH_2CH_2CH(CH_3)CH_2CH_3$

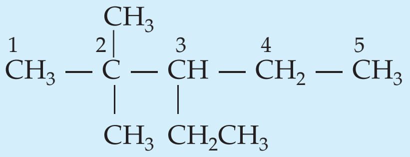
(*vi*) 
$CH_3CH_2CH(C_2H_5)-CH(C(CH_3)_3)-CH_2CH_2CH(CH_3)-CH_3$

[**Ans.**(*i*) 3, 4-Dimethylhexane
(*ii*) 2, 2, 4-Trimethylpentane
(*iii*) 3, 4-Diethyl-4-methylheptane
(*iv*) 2, 2, 4-Trimethylhexane
(*v*) 2, 2, 5-Trimethylheptane
(*vi*) 6-ethyl-5-(1, 1-dimethylethyl)-2-methyloctane]

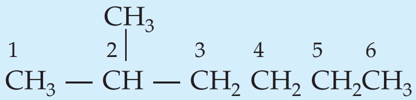
2. What is wrong with the following names? Draw the structures they represent and give their correct names.
   (*i*) 2-Methyl-2-propylhexane
   (*ii*) 4, 4-Dimethyl-3-ethylpentane
   (*iii*) 1, 1-Dimethylpentane
   (*iv*) 4-(2-Methylethyl) heptane

[**Ans.** (*i*) 
$CH_3CH_2CH_2CH_2-C(CH_3)(CH_2CH_2CH_3)-CH_3$

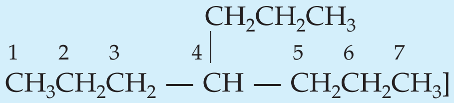
4,4-Dimethyloctane

(*ii*) 
$CH_3-C(CH_3)_2-CH(CH_2CH_3)-CH_2-CH_3$

3-Ethyl-2, 2-dimethylpentane

(*iii*) 
$CH_3-CH(CH_3)-CH_2CH_2CH_2CH_3$

2-Methylhexane

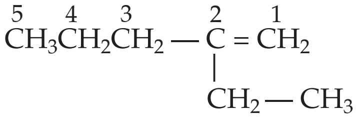
(*iv*) 
$CH_3CH_2CH_2-CH(CH_2CH_2CH_3)-CH_2CH_2CH_3$]

4-Propylheptane

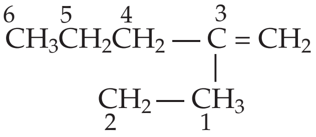
10.12 RULES OF IUPAC NOMENCLATURE FOR UNSATURATED HYDROCARBONS (ALKENES AND ALKYNES)

While naming compounds containing multiple bonds, the following additional rules are applied:

1. *The parent chain must contain the multiple bonds whether it represents the longest continuous chain of carbon atoms or not.* For example, in structure (I) below, the parent chain consists of *five* carbon atoms and not *six* carbon atoms since the latter does not include the double bond.


$CH_3CH_2CH_2-C(=CH_2)-CH_2-CH_3$

IA (*Correct*)


$CH_3CH_2CH_2-C(=CH_2)-CH_2-CH_3$

IB (*Wrong*)

Therefore, the numbering in IA is correct while in IB is wrong.

2. *If both double and triple bonds are present, the numbering of the parent chain should always be done from that end which is nearer to the double or the triple bond, i.e.* the **lowest sum** for the multiple bonds must be followed. Thus, in the following compound, numbering will be done from left to right.

$$\overset{1}{CH_3} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{CH_2} - \overset{5}{C} \equiv \overset{6}{C} - \overset{7}{CH_2} - \overset{8}{CH_3}$$

Sum of locants = 2 + 5 = 7
(*Correct numbering*)

$$\overset{8}{CH_3} - \overset{7}{CH} = \overset{6}{CH} - \overset{5}{CH_2} - \overset{4}{C} \equiv \overset{3}{C} - \overset{2}{CH_2} - \overset{1}{CH_3}$$

Sum of locants = 3 + 6 = 9
(*Wrong numbering*)

3. *If there is a choice in numbering, the double bond is given preference over the triple bond.* For example,

$$\underset{1}{\overset{5}{CH}} \equiv \underset{2}{\overset{4}{C}} - \underset{3}{\overset{3}{CH_2}} - \underset{4}{\overset{2}{CH}} = \underset{5}{\overset{1}{CH_2}}$$

← *Correct numbering*
← *Incorrect numbering*

4. *If the organic compound contains only one double or the triple bond, its locant or the positional number is always placed before its suffix in accordance with 1993 recommendations for IUPAC nomenclature of organic compounds.* For example,

$$\overset{1}{CH_3} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{CH_2}\ \overset{5}{CH_3}$$

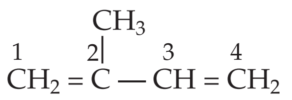
Pent + 2-ene = Pent-2-ene

If both double and triple bonds are present, their locants are written before their respective suffixes, the terminal '*e*' from the suffix '*ene*' is dropped while writing the complete name of the organic compound. Thus, *the organic compound is named as a derivative of an alkyne rather than of an alkene.* For example,

$$\overset{5}{CH_3} - \overset{4}{CH} = \overset{3}{CH} - \overset{2}{C} \equiv \overset{1}{CH}$$

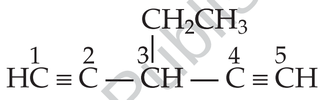
Pent + 3-en (*e*) + 1-yne = Pent-3-en-1-yne

Following examples further illustrate the point:



$$\overset{1}{CH_2} = \overset{CH_3}{\overset{|}{\overset{2}{C}}} - \overset{3}{CH} = \overset{4}{CH_2}$$

2-Methylbuta-1, 3-diene



$$\overset{1}{HC} \equiv \overset{2}{C} - \overset{CH_2CH_3}{\overset{|}{\overset{3}{CH}}} - \overset{4}{C} \equiv \overset{5}{CH}$$

3-Ethylpenta-1, 4-diyne

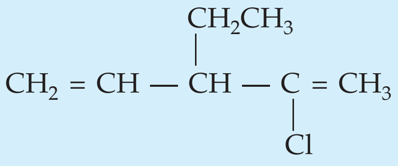
$$\overset{6}{HC} \equiv \overset{5}{C} - \overset{4}{CH} = \overset{3}{CH} - \overset{2}{CH} = \overset{1}{CH_2}$$

Hexa-1, 3-dien-5-yne

PROBLEMS FOR PRACTICE

1. Give the IUPAC names of the following compounds:

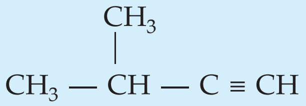
(*i*) $CH_3CH = CH - CH_2Br$

(*ii*)


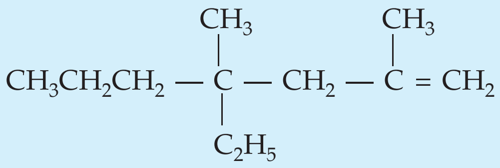
$$CH_2 = CH - \overset{CH_2CH_3}{\overset{|}{CH}} - \underset{\underset{Cl}{|}}{C} = CH_3$$

(*iii*)


$$CH_2 = \overset{Cl}{\overset{|}{C}} - CH = CH_2$$

(*iv*)


$$CH_3 - \overset{CH_3}{\overset{|}{CH}} - C \equiv CH$$

(*v*)


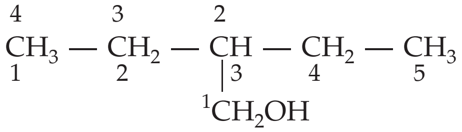
$$CH_3CH_2CH_2 - \underset{\underset{C_2H_5}{|}}{\overset{CH_3}{\overset{|}{C}}} - CH_2 - \overset{CH_3}{\overset{|}{C}} = CH_2$$

[**Ans.** (*i*) 1-Bromobut-2-ene
(*ii*) 2-Chloro-3-ethylpenta-1, 4-diene
(*iii*) 2-Chlorobuta-1, 3-diene
(*iv*) 3-Methylbut-1-yne
(*v*) 4-Ethyl-2, 4-dimethylhept-1-ene]

10.13 RULES FOR IUPAC NOMENCLATURE FOR COMPOUNDS CONTAINING ONE FUNCTIONAL GROUP, MULTIPLE BONDS AND SUBSTITUENTS

The following additional rules are followed while naming organic compounds containing one functional group, multiple bonds, and substituents.

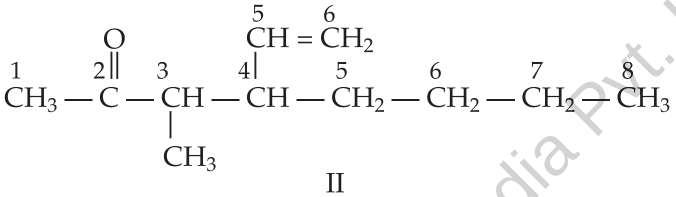
1. **Parent Chain.** Select the longest possible chain of carbon atoms containing the functional group and the maximum number of multiple bonds as the **parent chain**. It may or may not be the longest possible carbon chain. For example, in compound (I), the parent chain containing the functional group has **four** carbon atoms while the longest possible carbon chain has **five** carbon atoms.



$$\overset{4}{\underset{1}{\mathrm{CH_3}}}-\overset{3}{\underset{2}{\mathrm{CH_2}}}-\overset{2}{\underset{\underset{{}^{1}\mathrm{CH_2OH}}{|3}}{\mathrm{CH}}}-\underset{4}{\mathrm{CH_2}}-\underset{5}{\mathrm{CH_3}}$$

I

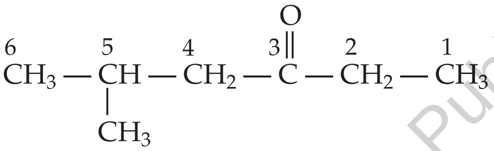
Similarly, in compound (II), the parent chain containing the functional group and the double bond has **six** carbon atoms while the longest possible carbon chain has **eight** carbon atoms.



$$\overset{1}{\mathrm{CH_3}}-\overset{\mathrm{O}}{\overset{2\|}{\mathrm{C}}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{3}{\mathrm{CH}}}-\overset{\overset{5}{\mathrm{CH}}=\overset{6}{\mathrm{CH_2}}}{\overset{4|}{\mathrm{CH}}}-\overset{5}{\mathrm{CH_2}}-\overset{6}{\mathrm{CH_2}}-\overset{7}{\mathrm{CH_2}}-\overset{8}{\mathrm{CH_3}}$$

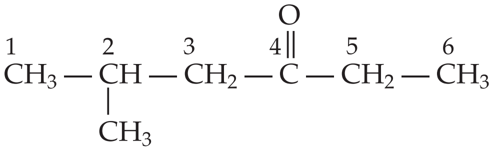
II

2. **Lowest Sum Rule for the Functional Group.** We have to number the parent chain in such a way that the functional group gets the lowest possible number followed by the double and triple bonds even if it violates the lowest **sum rule**. For example, in compound (III), the positional number for the keto group is **3** rather than **4**.



$$\overset{6}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{5}{\mathrm{CH}}}-\overset{4}{\mathrm{CH_2}}-\overset{\mathrm{O}}{\overset{3\|}{\mathrm{C}}}-\overset{2}{\mathrm{CH_2}}-\overset{1}{\mathrm{CH_3}}$$

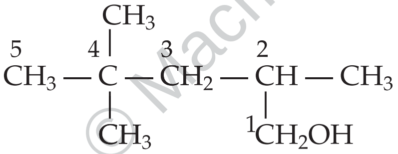
III (*Correct numbering*)



$$\overset{1}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{CH}}}-\overset{3}{\mathrm{CH_2}}-\overset{\mathrm{O}}{\overset{4\|}{\mathrm{C}}}-\overset{5}{\mathrm{CH_2}}-\overset{6}{\mathrm{CH_3}}$$

III (*Wrong numbering*)

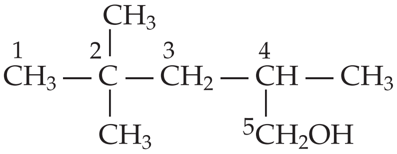
Similarly, for compound (IV), correct numbering gives position **1** to the functional group and not **5** though it violates the lowest sum rule.



$$\overset{5}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{\mathrm{CH_3}}{\overset{4|}{\mathrm{C}}}}-\overset{3}{\mathrm{CH_2}}-\underset{\underset{{}^{1}\mathrm{CH_2OH}}{|}}{\overset{2}{\mathrm{CH}}}-\mathrm{CH_3}$$

IV (*Correct*)

(Sum of the locants = 2 + 4 + 4 = 10)

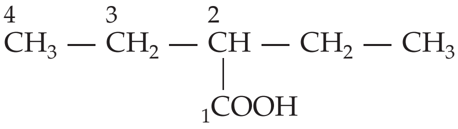


$$\overset{1}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{\mathrm{CH_3}}{\overset{2|}{\mathrm{C}}}}-\overset{3}{\mathrm{CH_2}}-\underset{\underset{{}^{5}\mathrm{CH_2OH}}{|}}{\overset{4}{\mathrm{CH}}}-\mathrm{CH_3}$$

IV (*Wrong*)

(Sum of the locants = 2 + 4 + 4 = 10)

3. **Numbering the Chain Terminating Functional Group.** When a chain terminating functional group such as —CHO, —COOH, —COOR, —$\mathrm{CONH_2}$, —COCl, —C ≡ N, etc., is present, it is always given **number 1** and **number 1** may be omitted from the final name of the compound when there is no ambiguity.



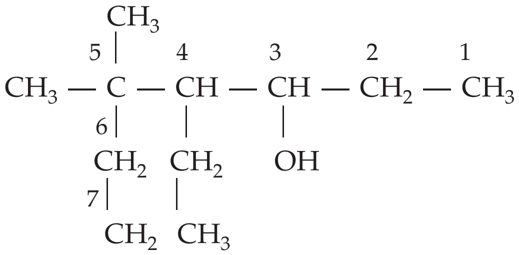
$$\overset{4}{\mathrm{CH_3}}-\overset{3}{\mathrm{CH_2}}-\underset{\underset{{}_{1}\mathrm{COOH}}{|}}{\overset{2}{\mathrm{CH}}}-\mathrm{CH_2}-\mathrm{CH_3}$$

2-Ethylbutan-1-oic acid or simply 2-Ethylbutanoic acid

2-Ethyl.....but.....an......oic acid

Prefix	*Word root*	*Primary suffix*	*Secondary suffix*

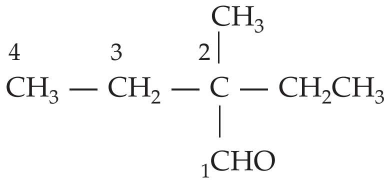
The following examples illustrate the above rules.

(*i*) 

$$CH_3-\underset{\underset{\underset{\underset{CH_2}{|7}}{CH_2}}{|6}}{\overset{\overset{CH_3}{|}}{\overset{5}{C}}}-\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{\overset{4}{C}H}-\underset{\underset{OH}{|}}{\overset{3}{C}H}-\overset{2}{C}H_2-\overset{1}{C}H_3$$

4-Ethyl-5, 5-dimethylheptane-3-ol

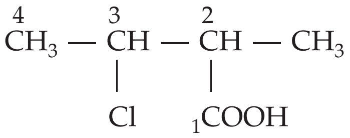
Prefix : *4-Ethyl-5, 5 dimethyl*
Word root : *hept*
Primary suffix : *an*
Secondary suffix : *ol*

(*ii*) 

$$\overset{4}{C}H_3-\overset{3}{C}H_2-\underset{\underset{{}_1CHO}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-CH_2CH_3$$

2-Ethyl-2-methylbutan-1-al

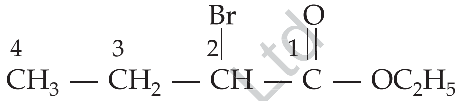
Prefix : *2-Ethyl-2-methyl*
Word root : *but*
Primary suffix : *an*
Secondary suffix : *al*

(*iii*) 

$$\overset{4}{C}H_3-\underset{\underset{Cl}{|}}{\overset{3}{C}H}-\underset{\underset{{}_1COOH}{|}}{\overset{2}{C}H}-CH_3$$

3-Chloro-2-methylbutan-1-oic acid

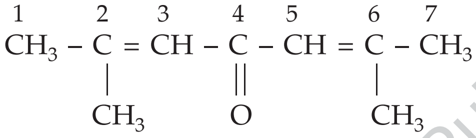
Prefix : *3-chloro-2-methyl*
Word root : *but*
Primary suffix : *an*
Secondary suffix : *oic acid*

(*iv*) 

$$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{\overset{Br}{|}}{\overset{2}{C}H}-\overset{\overset{O}{\|}}{\overset{1}{C}}-OC_2H_5$$

Ethyl 2-bromobutan-1-oate

Prefix : *Ethyl-2-bromo*
Word root : *but*
Primary suffix : *an*
Secondary suffix : *oate*

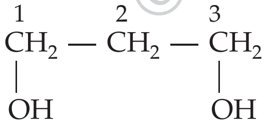
(*v*) 

$$\overset{1}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}}=\overset{3}{C}H-\underset{\underset{O}{\|}}{\overset{4}{C}}-\overset{5}{C}H=\underset{\underset{CH_3}{|}}{\overset{6}{C}}-\overset{7}{C}H_3$$

2, 6-Dimethylhepta-2, 5-dien-4-one

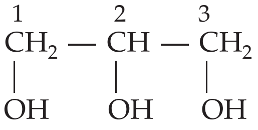
Prefix : *2, 6-Dimethyl*
Word root : *hept*
Primary suffix : *dien*
Secondary suffix : *one*

If a compound contains two or more like groups, the numerical prefixes *di*, *tri*, *tetra*, etc. are used and the terminal '*e*' from the primary suffix is retained (not dropped) while writing the IUPAC name. Following examples illustrate:

(*i*) 

$$\underset{\underset{OH}{|}}{\overset{1}{C}H_2}-\overset{2}{C}H_2-\underset{\underset{OH}{|}}{\overset{3}{C}H_2}$$

Propane-1, 3-diol

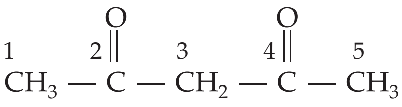
(*ii*) 

$$\underset{\underset{OH}{|}}{\overset{1}{C}H_2}-\underset{\underset{OH}{|}}{\overset{2}{C}H}-\underset{\underset{OH}{|}}{\overset{3}{C}H_2}$$

Propane-1, 2, 3-triol

(*iii*) $HO\overset{1}{O}C-\overset{2}{C}OOH$

Ethane-1, 2-dioic acid

(*iv*) 

$$\overset{1}{C}H_3-\overset{\overset{O}{\|}}{\overset{2}{C}}-\overset{3}{C}H_2-\overset{\overset{O}{\|}}{\overset{4}{C}}-\overset{5}{C}H_3$$

Pentane-2, 4-dione

(*v*) $HOOC-CH=CH-COOH$

But-2-ene-1, 4-dioic acid

(*vi*) $NC-CH=CH-CN$

But-2-ene-1, 4-dinitrile

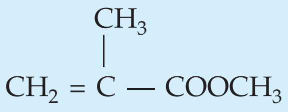
(*vii*) $H_5C_2O\overset{1}{O}C-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}OOC_2H_5$

Diethyl butane-1, 4-dioate

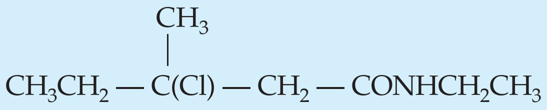
PROBLEMS FOR PRACTICE

1. Give the IUPAC names of the following compounds:

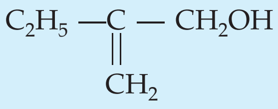
(*i*) $CH_3 — CH = CH — COOH$

(*ii*) 

$CH_2 = \overset{\overset{CH_3}{|}}{C} — COOCH_3$

(*iii*) 

$CH_3CH_2 — \overset{\overset{CH_3}{|}}{C}(Cl) — CH_2 — CONHCH_2CH_3$

(*iv*) 

$C_2H_5 — \underset{\underset{CH_2}{||}}{C} — CH_2OH$

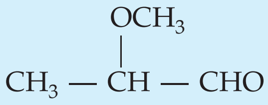
(*v*) $CH_2 = CH — CN$

(*vi*) $NH_2 — CH_2 — CH_2 — CH_2 — NH_2$

(*vii*) $HOOC — C \equiv C — COOH$

(*viii*) $CH_3 — CH = CH — CHO$

(*ix*) $OCH — CHO$

(*x*) 

$CH_3 — \overset{\overset{OCH_3}{|}}{CH} — CHO$

(*xi*) $[(CH_3)_2CH]_3COH$

(*xii*) $(CH_3)_2C = CHCOCH_3$

(*xiii*) $CH_3–CH = CH – CH_2OH$

(*xiv*) $CH_3 – C \equiv C – CH_2 – CHO$

[**Ans.** (*i*) But-2-en-1-oic acid

(*ii*) Methyl 2-methylprop-2-en-1-oate

(*iii*) 3-chloro-N-ethyl-3-methylpentane-1-amide

(*iv*) 2-Ethylprop-1-en-2-ol

(*v*) Prop-2-en-1-nitrile

(*vi*) Propane-1, 3-diamine

(*vii*) But-2-yne-1, 4-dioic acid

(*viii*) But-2-en-1-al

(*ix*) Ethane-1, 2-dial

(*x*) 2-Methoxypropane-1-al

(*xi*) 2, 4-Dimethyl-3-(1-methylethyl) pentane-3-ol

(*xii*) 4-Methylpent-3-en-2-one

(*xiii*) But-2-ene-1-ol

(*xiv*) Pent-3-yn-1-al]

10.14 RULES OF IUPAC NOMENCLATURE FOR POLYFUNCTIONAL COMPOUNDS

Organic compounds which contain two or more functional groups are called **polyfunctional compounds**. Their IUPAC nomenclature is discussed as under:

1. **Principal functional group.** When an organic compound contains two or more different functional groups, one of the functional groups is selected as the **principal functional group** while all other groups (also called the secondary functional groups) are treated as **substituents**. The principal functional group is selected on the basis of the following order of priority:

   Sulphonic acids > carboxylic acids > anhydrides > esters > acid chlorides > acid amides > nitriles > aldehydes > ketones > alcohols > amines > ethers > alkenes > alkynes.

   Groups such as *halo* (fluoro, chloro, bromo, iodo), *nitroso* (–NO), *nitro* ($–NO_2$) and *alkoxy* (–OR) are always treated as substituent groups.

   It may be noted that while writing the names of the polyfunctional compounds, the principal functional group is indicated by the *secondary suffix* to the word root while the other functional groups are indicated by adding suitable *prefixes* to the word root. The prefixes for various functional groups are listed in Table 10.3.

Table 10.3: Prefixes for Various Functional Groups

Functional Group	Prefix	Functional Group	Prefix
–X (F, Cl, Br, I)	Halo	–CHO	Formyl or alkanoyl
–OH	Hydroxy	>C = O	Keto or oxo
–SH	Mercapto	–COOH	Carboxy
–OR	Alkoxy	–COOR	Alkoxycarbonyl or carbalkoxy
$–NH_2$	Amino	–COCl	Halocarbonyl or haloalkanoyl
–NHR	Alkylamino	–CN	Cyano
$–NR_2$	Dialkylamino	$–CONH_2$	Carbamoyl or Carboxamido

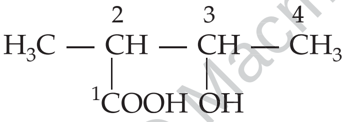
2. **Selecting the principal chain.** While selecting the principal chain present in a polyfunctional compound care should be taken that it must contain the principal functional group and the **maximum** number of other functional groups and multiple bonds, if any.
3. **Numbering the principal chain.** The principal chain present in a polyfunctional compound must be numbered in such a way that the principal functional group gets the lowest possible number followed by double bond, triple bond and the substituents. Thus, the priority will be:

   Principal functional group > other functional group > double bond > triple bond > substituents
4. **Alphabetical order.** The prefixes for the secondary functional groups and other substituents are to be placed in an alphabetical order before the word root. If, however, two groups of the same preference occupy identical positions from either end of the parent chain, the lower number must be given to the group whose prefix comes first in the alphabetical order. For example,

$\overset{3}{Cl}CH_2\overset{2}{C}H_2\overset{1}{C}H_2Br$
1-Bromo-3-chlorobutane
(*Correct*)

$\overset{1}{Cl}CH_2\overset{2}{C}H_2\overset{3}{C}H_2Br$
3-Bromo-1-chlorobutane
(*Wrong*)

Following examples illustrate the nomenclature of polyfunctional compounds:

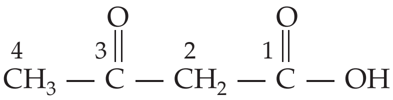
(*i*) 

$$H_3C - \underset{{}^1COOH}{\overset{2}{C}H} - \underset{OH}{\overset{3}{C}H} - \overset{4}{C}H_3$$

3-Hydroxy-2-methylbutanoic acid

– COOH is the principal functional group while

– OH is the substituent group

(*ii*) 

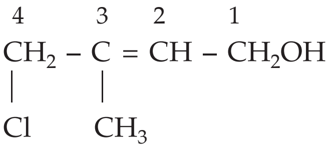
$$\overset{4}{C}H_3 - \overset{O}{\overset{\|}{\underset{3}{C}}} - \overset{2}{C}H_2 - \overset{O}{\overset{\|}{\underset{1}{C}}} - OH$$

3–Ketobutan-1-oic acid

or 3-Oxobutan-1-oic acid

– COOH is the principal functional group while

> C = O is the substituent group

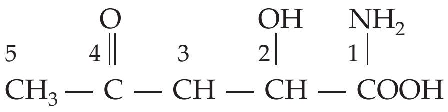
(*iii*) 

$$\underset{Cl}{\overset{4}{C}H_2} - \underset{CH_3}{\overset{3}{C}} = \overset{2}{C}H - \overset{1}{C}H_2OH$$

4-Chloro-3-methylbut-2-en-1-ol

–OH is the principal group while

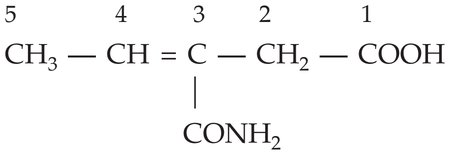
–Cl and $–CH_3$ are the substituent groups

(iv) 

$$\overset{5}{CH_3}-\overset{\overset{\displaystyle O}{4\|}}{C}-\overset{3}{CH}-\overset{\overset{\displaystyle OH}{2|}}{CH}-\overset{\overset{\displaystyle NH_2}{1|}}{COOH}$$

2-Amino-3-hydroxy-4-oxopentan-1-oic acid

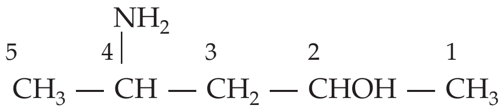
– COOH is the principal functional group while $-NH_2$, – OH and $>C=O$ are the substituent groups

(v) 

$$\overset{5}{CH_3}-\overset{4}{CH}=\underset{\displaystyle CONH_2}{\underset{|}{\overset{3}{C}}}-\overset{2}{CH_2}-\overset{1}{COOH}$$

3-Carbamoylpen-3-en-1-oic acid or
3-Carboxamidopent-3-en-1-oic acid

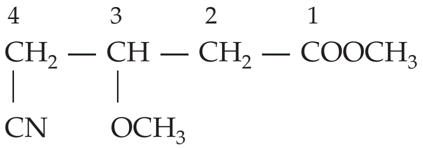
– COOH is the principal functional group while – $CONH_2$ is the substituent group

(vi) 

$$\overset{5}{CH_3}-\overset{\overset{\displaystyle NH_2}{4|}}{CH}-\overset{3}{CH_2}-\overset{2}{CHOH}-\overset{1}{CH_3}$$

4-Aminopentan-2-ol

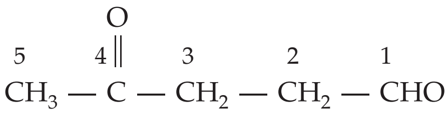
– OH is the principal functional group while $-NH_2$ is the substituent group

(vii) 

$$\underset{\displaystyle CN}{\underset{|}{\overset{4}{CH_2}}}-\underset{\displaystyle OCH_3}{\underset{|}{\overset{3}{CH}}}-\overset{2}{CH_2}-\overset{1}{COOCH_3}$$

Methyl-4-cyano-3-methoxybutan-1-oate

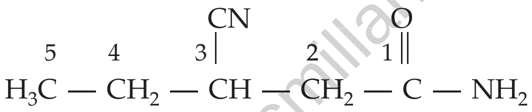
– $COOCH_3$ is the principal functional group while – OCH_3 and –CN are the substituent groups

(viii) 

$$\overset{5}{CH_3}-\overset{\overset{\displaystyle O}{4\|}}{C}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CHO}$$

4-Ketopentane-1-al
or 4-Oxopentan-1-al

– CHO is the principal functional group while $>C=O$ is the substituent group

(ix) 

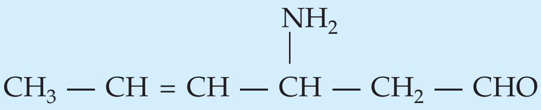
$$\overset{5}{H_3C}-\overset{4}{CH_2}-\overset{\overset{\displaystyle CN}{3|}}{CH}-\overset{2}{CH_2}-\overset{\overset{\displaystyle O}{1\|}}{C}-NH_2$$

3-Cyanopentanamide

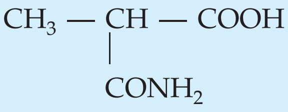
– $CONH_2$ is the principal functional group while – CN is the substituent group

PROBLEMS FOR PRACTICE

1. Give the IUPAC names for the following polyfunctional compounds.

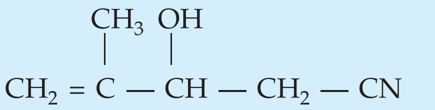
(i) 

$$CH_3-CH=CH-\overset{\overset{\displaystyle NH_2}{|}}{CH}-CH_2-CHO$$

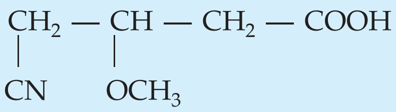
(ii) 

$$CH_3-\underset{\displaystyle CONH_2}{\underset{|}{CH}}-COOH$$

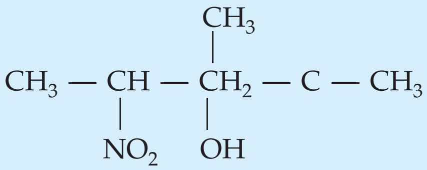
(iii) $CH_3CH_2O-CH_2-CHOH{-}CH_3$

(iv) 

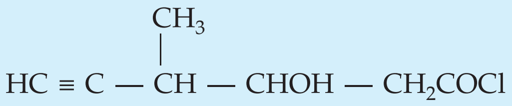
$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-CN$$

(v) 

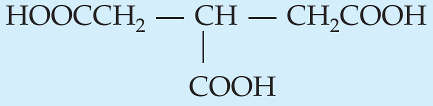
$$\underset{\displaystyle CN}{\underset{|}{CH_2}}-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-CH_2-COOH$$

(vi) 

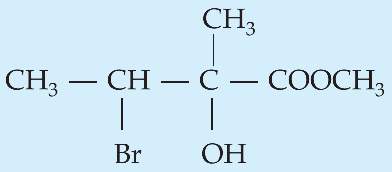
$$CH_3-\underset{\displaystyle NO_2}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{\overset{\overset{\displaystyle CH_3}{|}}{CH_2}}}-C-CH_3$$

(*vii*) 

$$HC \equiv C - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CHOH - CH_2COCl$$

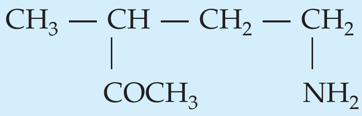
(*viii*) 

$$HOOCCH_2 - \underset{\underset{\displaystyle COOH}{|}}{CH} - CH_2COOH$$

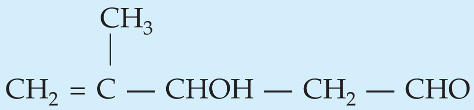
(*ix*) 

$$CH_3 - \underset{\underset{\displaystyle Br}{|}}{CH} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - COOCH_3$$

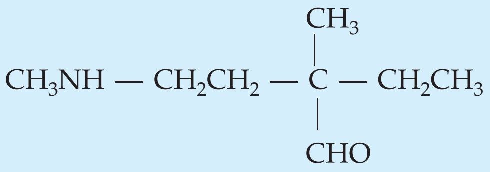
(*x*) $CH_3 - NH - CH_2 - CH_2 - CH_2OH$

(*xi*) 

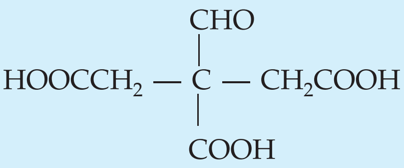
$$CH_3 - \underset{\underset{\displaystyle COCH_3}{|}}{CH} - CH_2 - \underset{\underset{\displaystyle NH_2}{|}}{CH_2}$$

(*xii*) 

$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - CHOH - CH_2 - CHO$$

(*xiii*) 

$$CH_3NH - CH_2CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CHO}{|}}{C}} - CH_2CH_3$$

(*xiv*) 

$$HOOCCH_2 - \overset{\overset{\displaystyle CHO}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}} - CH_2COOH$$

[**Ans.** (*i*) 3-Aminohex-4-en-1-al
(*ii*) 2-Carbamoylpropanoic acid
(*iii*) 1-Ethoxypropan-2-ol
(*iv*) 3-Hydroxy-4-methylpent-4-ene-1-nitrile
(*v*) 4-Cyano-3-methoxybutanoic acid
(*vi*) 4-Nitro-2-methylpentan-2-ol
(*vii*) 3-Hydroxy-4-methylhex-5-yn-1-oyl chloride
(*viii*) 3-Carboxypentane-1-, 5-dioic acid
(*ix*) Methyl3-bromo-2-hydroxy-2-methylbutan-1- oate
(*x*) 3-(N-Methylamino) propan-1-ol
(*xi*) 5-Amino-3-methylpentan-2-one
(*xii*) 3-Hydroxy-4-methylpent-4-en-1-al
(*xiii*) 4-Aminomethyl-2-ethyl-2-methylbutanal
(*xiv*) 3-Formyl-3-carboxypentane-1, 5-dioic acid]

10.15 WRITING STRUCTURAL FORMULAE FROM THE IUPAC NAME OF THE COMPOUND

The following steps are involved in the above process:

1. The parent chain is identified from the name of the compound and accordingly a straight chain of as many carbon atoms is written.
2. Carbon chain is numbered from either direction.
3. Primary suffix, *i.e. ane, ene* or *yne* from the name of the compound is identified. If the compound contains a double bond or a triple bond, identify its position from the name of the organic compound and put the double or the triple bond at its right position along the carbon chain.
4. Name and position of the main functional group (secondary suffix) are identified from the IUPAC name of the compound and it is attached at the right position on the carbon chain.
5. Names and positions of the other substituents are identified from the IUPAC name of the compound and attached at the right positions along the carbon chain.
6. The required numbers of hydrogen atoms are attached to satisfy the tetra covalency of each carbon. Following examples will illustrate the above points.

Example 1. *Give the structural formula of the compound having the IUPAC name as 4-methoxypent-1-yne.*

Solution.

Step 1. The word root '*pent*' indicates that the parent chain contains five carbon atoms.

$$C - C - C - C - C$$

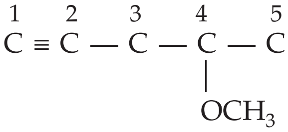
Step 2. Number the parent chain as indicated.

$$\overset{1}{C} - \overset{2}{C} - \overset{3}{C} - \overset{4}{C} - \overset{5}{C}$$

Step 3. The primary suffix *'yne'* suggests that the organic compound contains a triple bond, and the number 1 preceding it indicates that it is present at the terminal position. Therefore, put a triple bond between positions 1 and 2. We have:

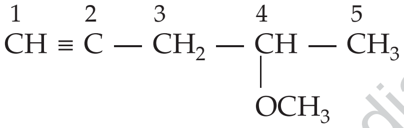
$$\overset{1}{C} \equiv \overset{2}{C} - \overset{3}{C} - \overset{4}{C} - \overset{5}{C}$$

Step 4. The secondary prefix methoxy and the number 4 preceding it suggests that a methoxy group is present at position 4. Therefore, put a methoxy group at position 4. We have:



$$\overset{1}{C} \equiv \overset{2}{C} - \overset{3}{C} - \underset{\underset{OCH_3}{|}}{\overset{4}{C}} - \overset{5}{C}$$

Step 5. Satisfy the tetra covalency of each carbon by attaching the required number of hydrogen atoms. Therefore, the required structural formula of 4-methoxypent-1-yne is



$$\overset{1}{CH} \equiv \overset{2}{C} - \overset{3}{CH_2} - \underset{\underset{OCH_3}{|}}{\overset{4}{CH}} - \overset{5}{CH_3}$$

Example 2. *What is the structural formula for the compound 3-Ethylbut-3-en-1-ol?*

Solution.

Step 1. The word root *'but'* suggests that the principal chain contains four carbon atoms. Connect them in a straight line as shown:

$$C - C - C - C$$

Step 2. Number the carbon chain as indicated.

$$\overset{4}{C} - \overset{3}{C} - \overset{2}{C} - \overset{1}{C}$$

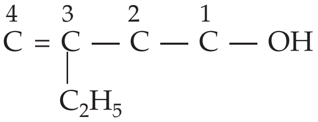
Step 3. The primary suffix *'en'* and the numerical prefix 3 before it suggests that there is a double bond at position 3. Therefore, put a double bond between positions 3 and 4 as shown:

$$\overset{4}{C} = \overset{3}{C} - \overset{2}{C} - \overset{1}{C}$$

Step 4. The secondary suffix *–ol* and the numerical prefix 1 before it suggests that there is a hydroxyl group at position 1. Therefore, attach a hydroxyl group at position 1 as shown:

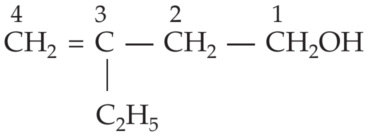
$$\overset{4}{C} = \overset{3}{C} - \overset{2}{C} - \overset{1}{C} - OH$$

Step 5. The secondary prefix ethyl and the numerical prefix 3 before it suggests that an ethyl group is attached at position 3 as shown:



$$\overset{4}{C} = \underset{\underset{C_2H_5}{|}}{\overset{3}{C}} - \overset{2}{C} - \overset{1}{C} - OH$$

Step 6. Attach the required number of hydrogen atoms on each carbon. Thus, the required structural formula for 3-ethylbut-3-en-1-ol is:



$$\overset{4}{CH_2} = \underset{\underset{C_2H_5}{|}}{\overset{3}{C}} - \overset{2}{CH_2} - \overset{1}{CH_2OH}$$

Example 3. *Give the structure for the compound having the following IUPAC name: 4-Chloropentan-2-one.*

Solution.

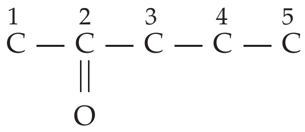
Step 1. The word root *'pent'* indicates that the longest carbon chain contains five carbon atoms.

$$\mathrm{C-C-C-C-C}$$

Step 2. Number the carbon chain as indicated.

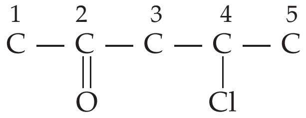
$$\overset{1}{\mathrm{C}}-\overset{2}{\mathrm{C}}-\overset{3}{\mathrm{C}}-\overset{4}{\mathrm{C}}-\overset{5}{\mathrm{C}}$$

Step 3. The secondary suffix *'one'* suggests that the functional group is a ketone. The numerical prefix 2 before it suggests that it is present at position 2. Therefore, put a keto group at position 2.



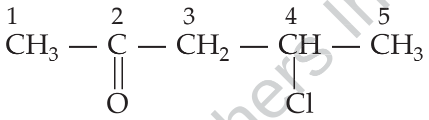
$$\overset{1}{\mathrm{C}}-\underset{\overset{\|}{\mathrm{O}}}{\overset{2}{\mathrm{C}}}-\overset{3}{\mathrm{C}}-\overset{4}{\mathrm{C}}-\overset{5}{\mathrm{C}}$$

Step 4. The secondary prefix *'chloro'* and the number 4 before it suggests that there is a chlorine atom at position 4. Therefore, attach a chlorine atom at position 4.



$$\overset{1}{\mathrm{C}}-\underset{\overset{\|}{\mathrm{O}}}{\overset{2}{\mathrm{C}}}-\overset{3}{\mathrm{C}}-\underset{\overset{|}{\mathrm{Cl}}}{\overset{4}{\mathrm{C}}}-\overset{5}{\mathrm{C}}$$

Step 5. Satisfy the tetra covalency of each carbon with the required number of H-atoms. Thus, the structure for 4 chloropentan-2-one is

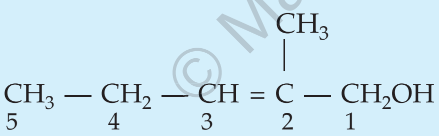


$$\overset{1}{\mathrm{CH_3}}-\underset{\overset{\|}{\mathrm{O}}}{\overset{2}{\mathrm{C}}}-\overset{3}{\mathrm{CH_2}}-\underset{\overset{|}{\mathrm{Cl}}}{\overset{4}{\mathrm{CH}}}-\overset{5}{\mathrm{CH_3}}$$

PROBLEMS FOR PRACTICE

1. Write structural formulae for the following:
   - (*i*) 2-Methylpent-2-en-1-ol
   - (*ii*) Hex-1-en-4-yne
   - (*iii*) 4-Amino-2-ethylpent-2-en-1-al
   - (*iv*) 3, 5-Octadiene.

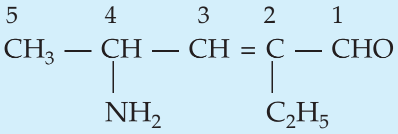
[**Ans.** (*i*)



$$\underset{5}{\mathrm{CH_3}}-\underset{4}{\mathrm{CH_2}}-\underset{3}{\mathrm{CH}}=\underset{2}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}-\underset{1}{\mathrm{CH_2OH}}$$

(*ii*) $\overset{6}{\mathrm{CH_3}}-\overset{5}{\mathrm{C}}\equiv\overset{4}{\mathrm{C}}-\overset{3}{\mathrm{CH_2}}-\overset{2}{\mathrm{CH}}=\overset{1}{\mathrm{CH_2}}$

(*iii*)



$$\overset{5}{\mathrm{CH_3}}-\underset{\overset{|}{\mathrm{NH_2}}}{\overset{4}{\mathrm{CH}}}-\overset{3}{\mathrm{CH}}=\underset{\overset{|}{\mathrm{C_2H_5}}}{\overset{2}{\mathrm{C}}}-\overset{1}{\mathrm{CHO}}$$

(*iv*) $\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH_2}}-\overset{3}{\mathrm{CH}}=\overset{4}{\mathrm{CH}}-\overset{5}{\mathrm{CH}}=\overset{6}{\mathrm{CH}}-\overset{7}{\mathrm{CH_2}}-\overset{8}{\mathrm{CH_3}}$]

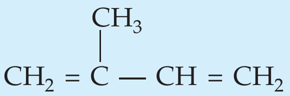
2. Write the condensed formulae for each of the following compounds:
   - (*i*) Isopropyl alcohol
   - (*ii*) Methyl *t*-butyl ether
   - (*iii*) 2-Chloro-1, 1, 1-trifluoroethane
   - (*iv*) 2-Methylbuta-1, 3-diene
   - (*v*) But-2-en-1-ol.

[**Ans.** (*i*) $\mathrm{(CH_3)_2CHOH}$

(*ii*) $\mathrm{CH_3-O-C(CH_3)_3}$

(*iii*) $\mathrm{F_3C-CH_2Cl}$

(*iv*)



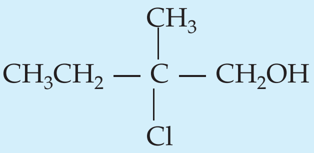
$$\mathrm{CH_2}=\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}-\mathrm{CH}=\mathrm{CH_2}$$

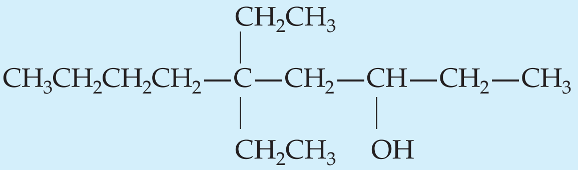
(*v*) $\mathrm{CH_3CH=CHCHO}$]

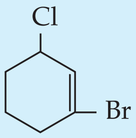
3. Draw the structures of the following compounds:
   - (*i*) Hex-3-en-1-oic acid
   - (*ii*) 2-Chloro-2-methylbutan-1-ol

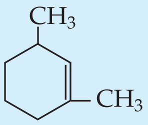
(*iii*) 5, 5-Diethylnonan-3-ol
(*iv*) 1-Bromo-3-chlorocyclohex-1-ene3
(*v*) 1, 3-Dimethylcyclohex-1-ene.

[**Ans.** (*i*) $CH_3CH_2CH = CHCH_2COOH$

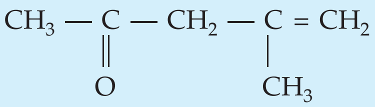
(*ii*) 
$$CH_3CH_2-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large Cl}{|}}{C}}-CH_2OH$$

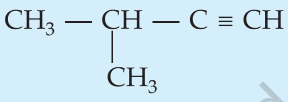
(*iii*) 
$$CH_3CH_2CH_2CH_2-\overset{\overset{\Large CH_2CH_3}{|}}{\underset{\underset{\Large CH_2CH_3}{|}}{C}}-CH_2-\underset{\underset{\Large OH}{|}}{CH}-CH_2-CH_3$$

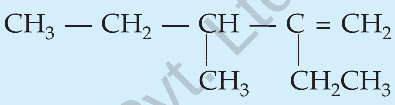
(*iv*) 

(*v*) 

4. Write down the structural formulae of the following:
   (*i*) 4-Methylpent-4-en-2-one
   (*ii*) 3-Methylbut-1-yne
   (*iii*) 2-Ethyl-3-methylpent-1-ene.

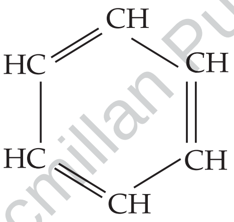
[**Ans.** (*i*) 
$$CH_3-\underset{\underset{\Large O}{||}}{C}-CH_2-\underset{\underset{\Large CH_3}{|}}{C}=CH_2$$

(*ii*) 
$$CH_3-\underset{\underset{\Large CH_3}{|}}{CH}-C\equiv CH$$

(*iii*) ]
$$CH_3-CH_2-\underset{\underset{\Large CH_3}{|}}{CH}-\underset{\underset{\Large CH_2CH_3}{|}}{C}=CH_2$$

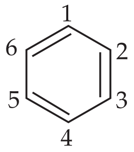
10.16 NOMENCLATURE OF AROMATIC COMPOUNDS

Aromatic compounds are cyclic compounds which contain one or more benzene type rings. Benzene is a simplest hydrocarbon of aromatic series which has a planar cyclic ring of six carbon atoms having three double bonds in alternate positions as shown below:

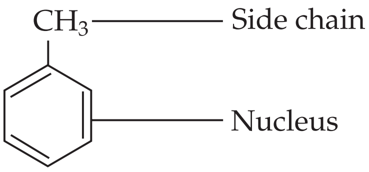


Benzene

or



The carbon atoms of benzene are numbered from 1 to 6 as shown above. The benzene ring is called the **nucleus** and alkyl groups attached to the ring are called **side chains**.

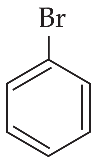


Benzene forms only one mono substituted derivative. However, it can form three disubstituted derivatives; namely 1, 2; 1, 3 and 1, 4 derivatives. These are respectively called *ortho* (or *o*-), *meta* (or *m*-) and *para* (or *p*-) derivatives.

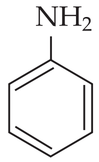
Tri and poly substituted derivatives are named by numbering the chain in such a way that the parent group gets the lowest number and sum of the positions of substituents is the smallest.

Rule 1. The word root for benzene derivatives is benzene.

Rule 2. The name of the substituent group is added as a prefix to the word root in case of mono-substituted benzenes. For example,

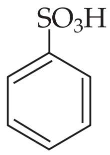


Bromobenzene



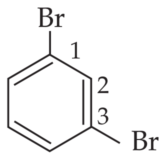
Aminobenzene

In some cases, the name of the group is written as suffix. For example,

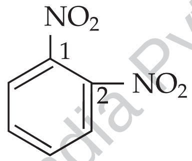


Benzene sulphuric acid

Rule 3. When two similar groups are attached to the benzene ring, numerical prefix *di* is placed before the name of the group, relative portion of the groups are indicated by suitable numbers or by the symbols *o, m* or *p*. For example,

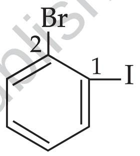


1, 3–Dibromobenzene
or *m*–Dibromobenzene



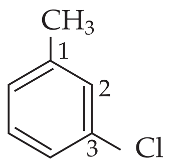
1, 2–Dinitrobenzene
or *o*–Dinitrobenzene

Rule 4. When two different groups are attached to the ring, the names of both groups are added as prefixes, in **alphabetical order**, to the word root and their relative positions are indicated. For example,

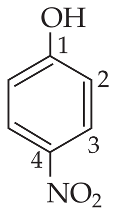


2–Bromo-1-iodobenzene
or *o*–Bromoiodobenzene

If one of the groups gives a special name to the compound, then the name of the other group only is written as prefix. For example,

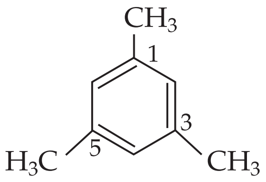


3–Chlorotoluene

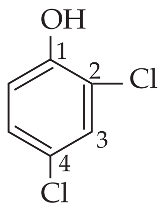


4–Nitrophenol

Rule 5. In case of tri-substituted or higher-substituted derivatives, the positions of groups are indicated by numbers.



1, 3, 5–Trimethylbenzene

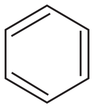


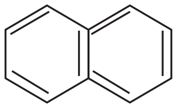
2, 4–Dichlorophenol

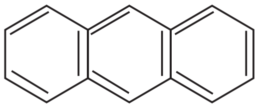
10.16.1 Names of Some Aromatic Compounds

1. Hydrocarbons (Arenes)

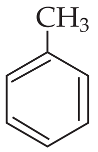
(*a*) *Hydrocarbons containing condensed rings.*


Benzene

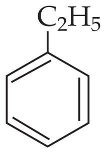

Naphthalene


Anthracene

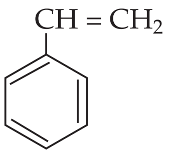
(*b*) *Hydrocarbons containing one ring only.*



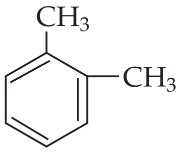
Methylbenzene (Toluene)



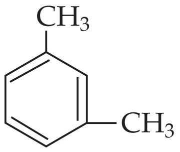
Ethylbenzene



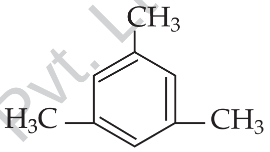
Phenylethene (Styrene)



1, 2–Dimethylbenzene
(*o*-Xylene)

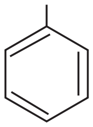


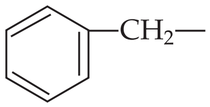
1, 3–Dimethylbenzene
(*m*-Xylene)



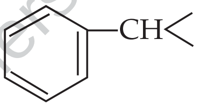
1, 3, 5–Trimethylbenzene
(Mesitylene)

2. Aromatic or Aryl Radicals

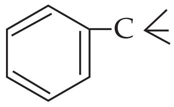

Phenyl radical



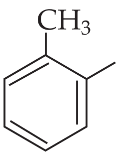
Benzyl (*monovalent*)



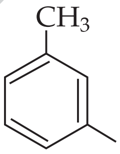
Benzal (*divalent*)



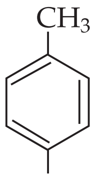
Benzo (*trivalent*)



o-Tolyl

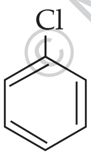


m-Tolyl

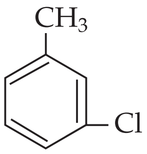


p-Tolyl

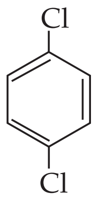
3. Halogen Derivatives



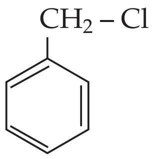
Chlorobenzene



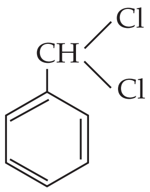
3-Chlorotoluene



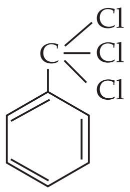
1, 4–Dichlorobenzene



Chlorophenylmethane
(benzyl chloride)

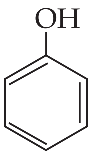


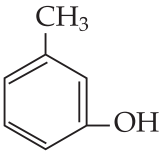
Dichlorophenylmethane
(benzal chloride)

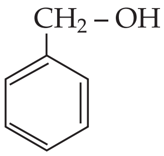


Trichlorophenylmethane
(benzo trichloride)

4. Phenols

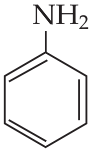

Hydroxybenzene (Phenol)

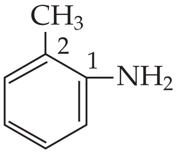

3–Hydroxytoluene (*m*-Cresol)

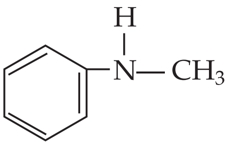

Phenylmethanol (Benzyl alcohol)

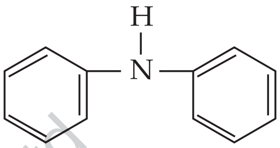
Here benzyl alcohol is not phenol but an aromatic alcohol.

5. Amino Derivatives

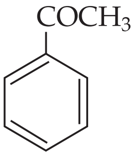

Benzenamine
(Aniline)

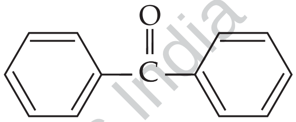

2-Methyl benzenamine
(2–Aminotoluene)


N–Methyl benzenamine
(N-Methylaniline)

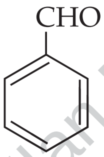

Diphenylamine
(N-Phenylaniline)

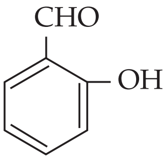
6. Ketones


Methyl phenylketone
or Acetophenone

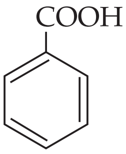

Diphenylketone
or Benzophenone

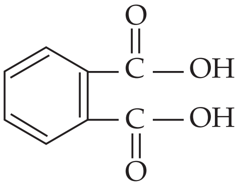
7. Aldehydes


Benzaldehyde

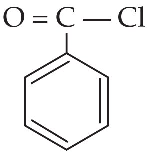

2–Hydroxy benzaldehyde
(Salicylaldehyde)

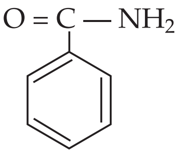
8. Carboxylic Acids

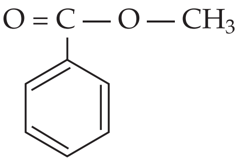

Benzoic acid

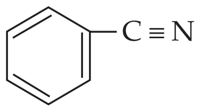

Phthalic acid
(1, 2–Benzene dicarboxylic acid)

9. Acid Derivatives

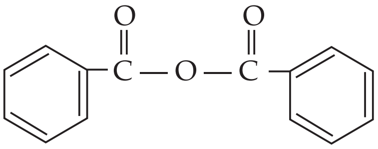

Benzoyl chloride


Benzamide


Methyl benzoate

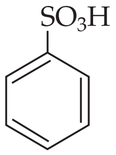


Benzonitrile
(Phenyl cyanide)

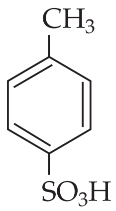


Benzoic anhydride

10. Sulphonic Acid

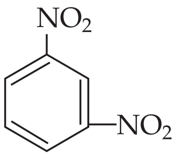


Benzenesulphonic acid

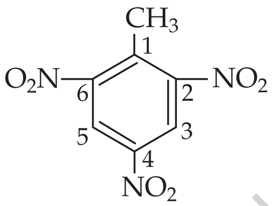


p–Toluene sulphonic acid (PTSA)

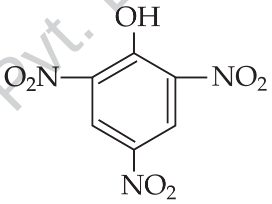
11. Nitro Derivatives



1, 3–Dinitrobenzene
(*m*-Dinitrobenzene)

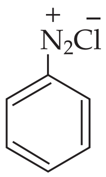


2, 4, 6–Trinitrotoluene
(TNT)

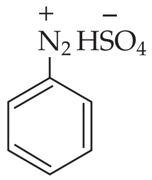


2, 4, 6–Trinitrophenol
(Picric acid)

12. Diazonium Salts

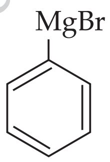


Benzene diazonium chloride

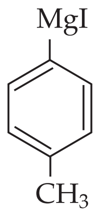


Benzene diazonium hydrogen sulphate

13. Grignard Reagents

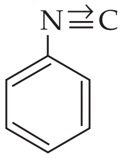


Phenyl magnesium bromide

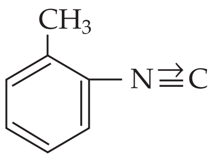


p-Tolyl magnesium iodide

14. Isocyanides



Benzenecarbylamine
(Phenyl isocyanide)



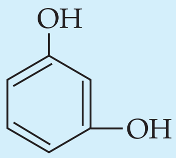
o-Toluenecarbylamine
(2–Methyl phenyl isocyanide)

PROBLEM FOR PRACTICE

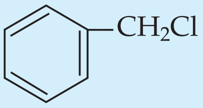
1. Give the IUPAC names and structures of the following compounds:

(*i*) Resorcinol
(*ii*) Benzyl chloride
(*iii*) Benzochloride
(*iv*) Diphenyl ketone
(*v*) *m*-Dinitrobenzene
(*vi*) *m*-Toluidine
(*vii*) Salicylaldehyde
(*viii*) *p*-Tolyl chloride
(*ix*) *m*-Cresol
(*x*) N-Methylaniline
(*xi*) *sym*-Trichlorotoluene

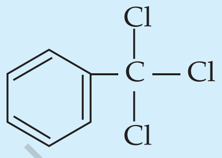
[**Ans.**



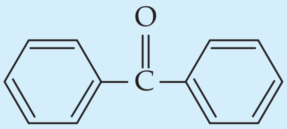
(*i*) 1, 3–Dihydroxybenzene



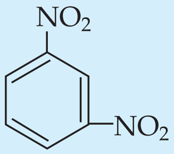
(*ii*) Chloro phenyl methane



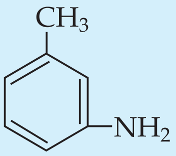
(*iii*) Trichlorophenylmethane



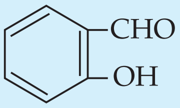
(*iv*) Diphenylketone or Benzophenone



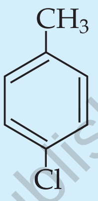
(*v*) 1, 3–Dinitrobenzene



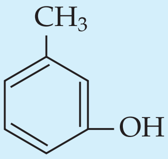
(*vi*) 3–Methylaminobenzene



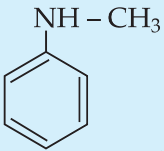
(*vii*) 2–Hydroxybenzaldehyde



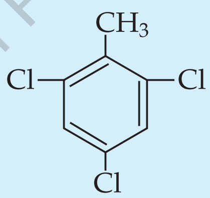
(*viii*) 4–Chlorotoluene



(*ix*) 3–Hydroxytoluene



(*x*) *N*–Methylbenzenamine



(*xi*) 2, 4, 6–Trichlorotoluene

10.17 SOME COMMON ORGANIC COMPOUNDS

The source and utility of important members belonging to each class (functional group) of organic compounds are given below:

1. **Alkanes.** Petroleum and natural gas are the chief sources of different alkanes. A number of fractions such as liquefied petroleum gas (LPG), petrol, kerosene, diesel, furnace oil, wax, etc. are obtained by refining of petroleum. Many of them like hexane, heptane are used as solvents. LPG is mostly as mixture of propane and butane and is used as a fuel for cooking.

   Natural gas mainly consists of methane along with small amounts of ethane, propane, butane and low boiling pentanes and hexanes. It is used as a fuel for industrial and domestic purposes.

2. **Alkenes.** Lower alkenes are obtained during petroleum refining. Alkenes find use in the preparation of different polymers. Polyethylene is obtained from ethene; polypropylene from propene, and synthetic rubber (neoprene) from 2-chlorobuta-1, 3-diene (chloroprene). Alkenes are also used to synthesise other compounds such as alcohols, aldehydes, ketones and carboxy acids.
3. **Alkynes.** Ethyne (acetylene) is an important member of this class and is prepared by the action of water on calcium carbide. It is used to prepare vinyl chloride needed for the manufacture of polyvinyl chloride (P.V.C.). It is also used in oxyacetylene flame for welding purposes. Ethyne is a substance of great synthetic value.
4. **Arenes.** Arenes are aromatic compounds. Arenes are mostly obtained from petroleum and coal. Benzene, toluene, xylenes are used to manufacture synthetic detergents, synthetic fibres and explosives such as 2, 4, 6-trinitrotoluene (TNT), etc. Naphthalene is antiseptic and is the chief constituent of mothballs. Naphthalene and anthracene derivatives are widely used to prepare synthetic dyes for textiles.
5. **Halogen Derivatives of Hydrocarbons.** Dichloromethane CH_2Cl_2, chloroform $CHCl_3$, carbon tetrachloride CCl_4, ethylene dichloride ($ClCH_2 - CH_2Cl$), tetrachloroethane or *westron* ($Cl_2CH - CHCl_2$), trichloroethene or *westrosol* ($CHCl = CCl_2$) and tetrachloroethene ($Cl_2C = CCl_2$) are some of the important compounds of this class which find use as solvents in the laboratory as well as in industry, ethylene dibromide ($BrCH_2 - CH_2Br$) is used as a fumigant against insects. DDT (*p*-dichlorodiphenyltrichloroethane) which is a well known mosquito and insects killer is obtained from chlorobenzene. Freon (dichlorodifluoromethane CCl_2F_2) is a well known refrigerant.
6. **Alcohols.** The first two members, *i.e.* methanol and ethanol are most important alcohols. Methanol is obtained by the catalytic oxidation of methane, ethanol is obtained by fermentation of molasses. Both these alcohols are widely used in industry. Alcohol (under the name power alcohol) has been suggested as a substitute fuel for automobiles. Power alcohol is a 4 : 1 mixture of petrol and alcohol along with small amounts of benzene as cosolvent. Methanol and ethanol are used as solvents as well as starting materials to prepare other important compounds, such as aldehydes and acids. Ethane-1, 2-diol (ethylene glycol) is used as a raw material in the manufacture of dacron–a synthetic fibre. Propane 1, 2, 3-triol (glycerol) is used in cosmetics.
7. **Aldehydes and Ketones.** Formaldehyde and acetaldehyde are well known substances and are widely used in plastic industry as raw materials. A 40% aqueous solution of formalin is used as a disinfectant and preservative for biological specimens. Propanone (acetone) and butan-2-one (methyl ethyl ketone, MEK) are widely used as solvents both in the laboratory and in industry. Cyclohexanone is used in the manufacture of nylon-6.

Balsamic vinegar

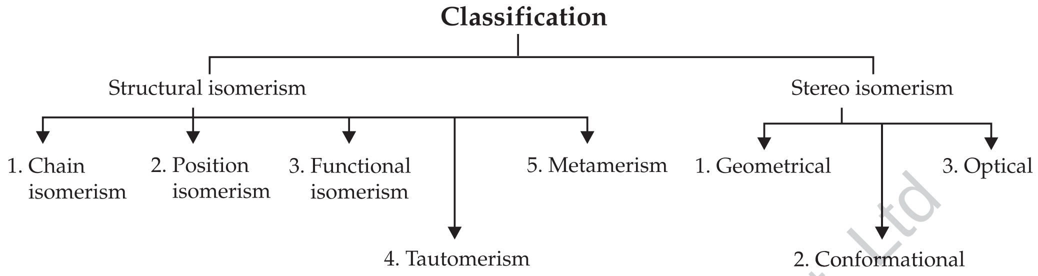
8. **Acids.** Formic acid is present in ants and in the bites of bees and wasps. A 8-10% solution of acetic acid is called *vinegar*. Ethanoic acid is used to prepare rayon, plastics and paints. Sodium and potassium salts of higher fatty acids such as Lauric acid $C_{10}H_{23}COOH$, palmitic acid $C_{15}H_{31}COOH$ and stearic acid $C_{17}H_{35}COOH$ are used as soaps. Cooking oils are triglycerides of these higher fatty acids. They are also used to synthesize esters.
9. **Nitro Compounds.** Nitromethane, nitroethane, nitrobenzene are used as solvents both in the laboratory as well as in industry. A mixture of *di* and *tri* nitroglycerols absorbed over kieselguhr is used as powerful blast material. Nitrocellulose (gun cotton) and 2, 4, 6-trinitrotoluene (TNT) are used as explosives.

   Aromatic nitro compounds on reduction give aromatic amines which are used to prepare dyes.

10. **Amines.** Organic compounds containing both an amino and a carboxylic acid as functional groups are called amino acids. These are the essential constituents of proteins which form the building blocks of all living things. 1, 6-Diaminohexane (hexamethylenediamine) is used in the manufacture of nylon 66. Aniline is used in the manufacture of azo dyes used in dye industry.

10.18 ISOMERISM

Compounds having same molecular formulae but differing from each other at least in some physical properties or chemical properties or both are known as isomers and this phenomenon is called as **isomerism.**



10.18.1 Chain Isomerism

Isomerism which arises due to the difference in the arrangement of carbon chain is called chain isomerism. It is also known as nuclear or skeletal isomerism, *e.g.* C_5H_{12} or pentane exists in the isomeric forms as shown below:

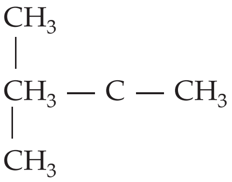
(*i*) $CH_3CH_2CH_2CH_2CH_3$ *n*-Pentane

(*ii*)

$\underset{\underset{\displaystyle CH_3}{|}}{CH_3} — CH — CH_2 — CH_3$

Isopentane (or 2, methyl butane)

(*iii*)

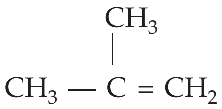


$\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH_3}} — C — CH_3$

Neopentane (or 2, 2-Dimethyl propane)

Chain isomerism is possible in compounds containing functional groups also.

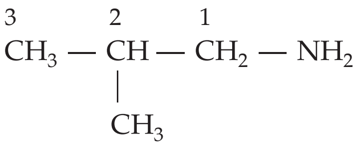
$CH_3CH_2CH = CH_2$
1-Butene



$CH_3 — \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$

2-Methyl propene

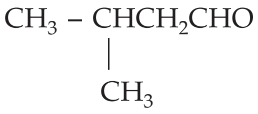
$CH_3CH_2CH_2CH_2NH_2$
1-Amino butane



$\overset{3}{CH_3} — \underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{CH}} — \overset{1}{CH_2} — NH_2$

2-Methyl propanamine

$CH_3CH_2CH_2CH_2CHO$
Pentanal



$CH_3 – \underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2CHO$

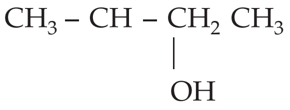
3-Methyl butanal

10.18.2 Position Isomerism

Isomerism that arises due to different positions of the same functional group or substituent is known as position isomerism.

(*i*) $CH_3CH_2CH_2CH_2OH$ and

1-Butanol

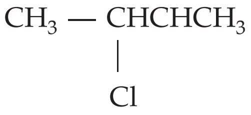


$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2\,CH_3$

2-Butanol

(*ii*) $CH_3CH_2CH_2CH_2Cl$ and

1-Chloro butane

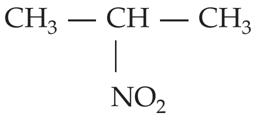


$CH_3-\underset{\underset{Cl}{|}}{CH}CHCH_3$

2-Chloro butane

(*iii*) $CH_3CH_2CH_2NO_2$ and

1-Nitro propane

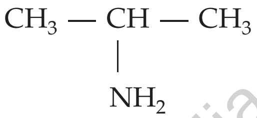


$CH_3-\underset{\underset{NO_2}{|}}{CH}-CH_3$

2-Nitro propane

(*iv*) $CH_3CH_2CH_2NH_2$ and

1-Propanamine



$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3$

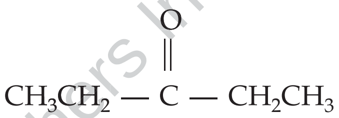
2-Propanamine

(*v*)

$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$

2-Pentanone

and



$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

3-Pentanone

10.18.3 Functional Isomerism

Compounds having same molecular formula but different functional groups are called functional isomers and the phenomenon is called functional isomerism, *e.g.*

(*i*) Alcohol and ethers

CH_3CH_2OH and CH_3-O-CH_3

Ethanol — Methoxy methane

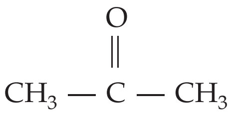
$CH_3CH_2CH_2CH_2OH$ and $CH_3CH_2OCH_2CH_3$

1-Butanol — Ethoxy ethane

(*ii*) Aldehydes and ketones

CH_3CH_2CHO and

Propanal



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Propanone

(*iii*) Alkadienes and alkynes

$H_2C=CH-CH=CH_2$ and $CH_3-CH_2-C\equiv CH$

1, 3-Butadine — 1-Butyne

$H_2C=C=CH-CH_3$ and $CH_3-C\equiv C-CH_3$

1, 2-Butadiene — 2-Butyne

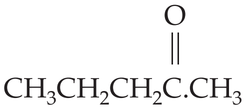
10.18.4 Metamerism

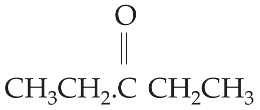
Isomerism that arises due to difference in the arrangement of alkyl groups on either sides of the same functional group is known as metamerism.

(*i*) $CH_3CH_2CH_2OCH_3$ and $CH_3CH_2OCH_2CH_3$
Methoxy propane — Ethoxy ethane

(*ii*) $CH_3CH_2CH_2NH.CH_3$ and $CH_3CH_2NHCH_2CH_3$
Methyl propyl amine — Diethylamine

(*iii*) $(CH_3)_2 — N.CH_2CH_2CH_3$ — $(CH_3CH_2)_2NCH_3$
Dimethyl propyl amine — Diethyl methyl amine

(*iv*)

$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}.CH_3$
2-Pentanone


$CH_3CH_2.\overset{\overset{\displaystyle O}{\|}}{C}\ CH_2CH_3$
3-Pentanone

10.18.5 Tautomerism

The phenomenon by virtue of which a compound can exist in two or more interconvertible structures those differ in the relative position of at least one atomic nuclei (generally hydrogen) is known as tautomerism. It is caused by the wandering of hydrogen atom between two polyvalent atoms. It is also known as Desmotropism. It is of three types:

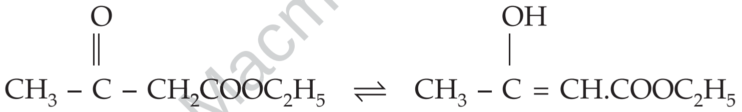
(*i*) Cationotropism: Due to migration of cation
(*ii*) Anionotropsim: Due to migration of anion
(*iii*) Ring chain tautomerism.

(*i*) Diad System: If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is diad, *e.g.*

$H - C \equiv N \rightleftharpoons H - N \equiv C$
Hydrogen cyanide — Hydrogen isocyanide

(*ii*) Triad System: If hydrogen oscillates between first and third in a chain, the system is triad.

(*a*) Keto-enol tautomerism: Acetoacetic ester


$$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2COOC_2H_5 \rightleftharpoons CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = CH.COOC_2H_5$$
Keto form — Enol form

(*b*) Nitroform and Aciform

The less stable form is known as labile form.

(*iii*) Ring Chain Tautomerism: This type of isomerism is due to different modes of linking of carbon atoms, *i.e.* the isomers possess either open chain or closed chain structures.

10.19 CALCULATION OF EMPIRICAL AND MOLECULAR FORMULA

After the detection and estimation of elements have been carried out and the molecular weight has been determined, we can proceed to deduce the empirical and molecular formulae of the compound.

Empirical Formula. *It is the simplest whole number ratio between the atoms of various elements present in one molecule of the compound.* Empirical formula is not the actual formula of the substance, it only tells the relative number of atoms present in the substance. For example, empirical formula of glucose is CH_2O. It means that the relative ratio of carbon, hydrogen and oxygen in glucose is 1 : 2 : 1, whereas a molecule of glucose actually contains six carbon, twelve hydrogen and six oxygen atoms.

Determination of empirical formula. Following steps are employed to calculate the empirical formula:

(*i*) The percentage of each element is divided by the atomic mass of the element to obtain the relative number of elements.

(*ii*) The figures obtained above are divided by the lowest figure to get the simplest ratio of elements.

(*iii*) If whole numbers are not obtained and fractions are obtained then multiply the figures by a suitable number to obtain the whole number simplest ratio.

(*iv*) The empirical formula is expressed by writing the symbol of elements along with the number of elements in the subscript.

Molecular Formula. *It is the actual number of atoms of various elements present in one molecule of the substance.* Molecular formula is either the same as empirical formula or its integral multiple.

$$n = \frac{\text{Molecular wt.}}{\text{Empirical formula wt.}}$$

where n is an integer 1, 2, 3, etc.

Take for example the case of glucose. It has empirical formula CH_2O and molecular formula $C_6H_{12}O_6$.

$$\text{Empirical formula mass} = 12 + (2 \times 1) + 16 = 30$$

$$\text{Molecular mass} = (6 \times 12) + (12 \times 1) + (6 \times 16) = 180$$

$$\text{In this case } n = \frac{180}{30} = 6.$$

Determination of molecular formula. The following steps are employed to calculate the molecular formula:

(*i*) First calculate the empirical formula with the help of percentage values of the elements as explained above.

(*ii*) Add up to get the empirical formula mass.

(*iii*) Divide the molecular mass by the empirical formula mass to obtain the value of n.

(*iv*) Get the molecular formula by the relation

$$\text{Molecular formula} = (\text{Empirical formula}) \times n$$

Multiply the relative number of atoms of elements in the empirical formula by n.

Example 1. *An organic compound was found to contain C, H and N. The percentage of C, H and N are 78.64%, 8.40% and 12.96% respectively. The molecular weight was found to be 107. Determine the molecular formula.*

Solution. Calculation of empirical formula

Elements	*Percentage*	*Atomic mass*	*Relative no. of atoms*	*Simplest ratio*	*Simplest whole number ratio*
C	78.64	12	$\frac{78.64}{12} = 6.55$	$\frac{6.55}{0.93} = 7$	7
H	8.40	1	$\frac{8.40}{1} = 8.40$	$\frac{8.40}{0.93} = 9$	9
N	12.96	14	$\frac{12.96}{14} = 0.93$	$\frac{0.93}{0.93} = 1$	1

Hence, the empirical formula is C_7H_9N

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

$$\begin{aligned}\text{Empirical formula mass} &= C_7H_9N\\ &= 7 \times 12 + 9 \times 1 + 14\\ &= 107\\ \text{Molecular mass} &= 107 \text{ (given)}\end{aligned}$$

$$n = \frac{107}{107} = 1$$

$$\begin{aligned}\text{Hence, the molecular formula} &= (\text{Empirical formula})_n\\ &= C_7H_9N.\end{aligned}$$

Example 2. *A student was required to find out the simplest formula of 0.1 g of an organic compound. He collected the following data:*

(a) (i) Weight of porcelain boat = 6.860 g
(ii) Weight of boat + compound = 6.960 g
(iii) Weight of $CaCl_2$ *tube before combustion = 42.874 g*
(iv) Weight of Potash bulbs before combustion = 105.680 g
(v) Weight of $CaCl_2$ *tube after combustion = 42.9496 g*
(vi) Weight of Potash bulbs after combustion = 105.9682 g
(b) 0.200 g of the compound in Duma's method gave 21.8 mL of nitrogen at 15°C and 760 mm pressure.

[H = 1, C = 12, N = 14]

Solution.

Weight of organic compound = (6.960 – 6.860) = 0.10 g

Weight of CO_2 collected = (105.9682 – 105.680) = 0.2882

Weight of H_2O collected = (42.9496 – 42.874) = 0.0756

Volume of N_2 collected = 21.8 mL at 15ºC and 760 mm pressure

(*a*) Calculation of percentage composition

(*i*) Percentage of carbon $= \dfrac{12 \times \text{Wt. of } CO_2 \times 100}{44 \times \text{Wt. of organic compound}}$

$$= \frac{12 \times 0.2882 \times 100}{44 \times 0.1} = 78.6\%$$

(*ii*) Percentage of hydrogen $= \dfrac{2 \times \text{Wt. of } H_2O \times 100}{18 \times \text{Wt. of organic compound}}$

$$= \frac{2 \times 0.0756 \times 100}{18 \times 0.1} = 8.4\%$$

(*iii*) Vol. of N_2 at S.T.P.

(Given conditions)	(At S.T.P.)
P_1 = 760 mm	P_2 = 760 mm
V_1 = 21.8 mL	V_2 = ?
T_1 = 288 K	T_2 = 273 K

Applying the gas equation, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

We have $$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} = \frac{760 \times 21.8}{288} \times \frac{273}{760}$$

$= 20.66$ mL

(*iv*) Percentage of nitrogen 22400 mL of N_2 at S.T.P. weigh = 28 g

∴ 20.66 N_2 at S.T.P. weigh $= \frac{28}{22400} \times 20.66$

Hence, % of N in the compound $= \frac{28}{22400} \times 20.66 \times \frac{100}{0.2} = 12.91$

Total percentage of elements = 78.60 + 8.40 + 12.91 = 99.91%

(*b*) Calculation of empirical formula

Element	*Percentage*	*Atomic weight*	*Relative no. of atoms*	*Simplest ratio*	*Simplest whole number ratio*
C	78.6	12	$\frac{78.6}{12} = 6.55$	$\frac{6.55}{0.922} = 7.1$	7
H	8.4	1	$\frac{8.4}{1} = 8.4$	$\frac{8.4}{0.922} = 9.1$	9
N	12.91	14	$\frac{12.91}{14} = 0.922$	$\frac{0.992}{0.922} = 1$	1

Hence, the empirical or simplest formula is C_7H_9N.

Example 3. *On analysis, 0.2 g of a monobasic acid gave 0.505 g of CO_2 and 0.0864 g of H_2O. 0.305 g of this acid required 25 cm^3 of N/10 NaOH for complete neutralization. Find the molecular formula of the acid.*

Solution.

(*a*) Calculation of percentage composition

(*i*) Percentage of carbon $= \frac{12}{44} \times \frac{\text{Mass of CO}_2\text{ produced}}{\text{Mass of substance taken}} \times 100$

$= \frac{12}{44} \times \frac{0.505}{0.2} \times 100 = 68.86\%$

(*ii*) Percentage of hydrogen $= \frac{2}{18} \times \frac{\text{Mass of H}_2\text{O formed}}{\text{Mass of substance taken}} \times 100$

$= \frac{2}{18} \times \frac{0.0864}{0.2} \times 100 = 4.8\%$

(*iii*) Percentage of oxygen = 100 – (68.86 + 4.8) = 26.34%

(*b*) Calculation of empirical formula

Element	*Percentage*	*Atomic weight*	*Relative no. of atoms*	*Simplest ratio*	*Simplest whole no. atomic ratio*
Carbon	68.86	12	$\frac{68.86}{12} = 5.74$	$\frac{5.74}{1.65} = 3.47$	7
Hydrogen	4.80	1	$\frac{4.80}{1} = 4.80$	$\frac{4.80}{1.65} = 2.91$	6
Oxygen	26.34	16	$\frac{26.34}{16} = 1.65$	$\frac{1.65}{1.65} = 1.00$	2

Hence, the empirical formula of the compound is $C_7H_6O_2$.

(*c*) Calculation of molecular mass

0.305 g of acid requires 25 cm^3 of N/10 NaOH for neutralization

$\therefore$ 25 cm^3 of N/10 NaOH neutralize = 0.305 g of acid

or 25 cm^3 of 1 N NaOH neutralize = 10 × 0.305 g of acid

or 1000 cm^3 of 1 N NaOH will neutralize $= \dfrac{10 \times 0.305}{25} \times 1000 = 122$ g of acid

But, 1000 cm^3 of 1 N NaOH contain 1 g eq. of NaOH and must neutralize 1 g eq. of the acid

Thus, equivalent mass of the acid = 122

Since, the acid is monobasic, therefore, basicity is one.

$\therefore$ Molecular mass of the acid = Basicity × Equivalent mass = 1 × 122 = 122

(*d*) Calculation of molecular formula

Empirical formula mass of the compound = (7 × 12 + 6 × 1 + 16 × 2) = 122

$$\therefore \qquad n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{122}{122} = 1$$

Thus, molecular formula of the compound = $(\text{Empirical formula})_n$

$= (C_7H_6O_2)_1 = C_7H_6O_2$.

Example 4. *0.246 g of an organic compound gave 0.198 g of carbon dioxide and 0.1014g of water on complete combustion. 0.37 g of the compound gave 0.638 g of silver bromide. What is the molecular formula of the compound if its vapour density is 54.4?*

Solution.

(*a*) Calculation of percentage composition

(*i*) % of Carbon

$$= \frac{12}{44} \times \frac{\text{Molecular } CO_2 \text{ produced}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{12}{44} \times \frac{0.198}{0.246} \times 100 = 21.95\%$$

(*ii*) % of Hydrogen

$$= \frac{2}{18} \times \frac{\text{Molecular } H_2O \text{ produced}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{2}{18} \times \frac{0.1014}{0.246} \times 100 = 4.58\%$$

(*iii*) % of Bromine

$$= \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{80}{188} \times \frac{0.638}{0.37} \times 100 = 73.37\%$$

(*iv*) The given compound does not contain oxygen since the sum of the percentage of carbon, hydrogen and bromine is approx. 100, *i.e.* 21.95 + 4.58 + 73.37 = 99.90%

(*b*) Calculation of empirical formula

Empirical formula of the compound is obtained as under:

Element	*Percentage*	*Atomic weight*	*Relative no. of atoms*	*Simplest atomic ratio*	*Simplest whole no. atomic ratio*
Carbon	21.95	12	$\frac{21.95}{12} = 1.83$	$\frac{1.83}{0.917} = 2$	2
Hydrogen	4.58	1	$\frac{4.58}{1} = 4.58$	$\frac{4.58}{0.917} = 5$	5
Bromine	73.37	80	$\frac{73.37}{80} = 0.917$	$\frac{0.917}{0.917} = 1$	1

Thus, the empirical formula of the compound is C_2H_5Br.

(*c*) Determination of the molecular formula

Vapour density of the compound = 54.4

∴ Molecular mass of the compound = 2 × Vapour density = 2 × 54.4 = 108.8

But, the empirical formula mass of the compound, $C_2H_5Br = 2 \times 12 + 5 \times 1 + 1 \times 80 = 109$

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{108.8}{109} = 1 \text{ (approx.)}$$

Thus, the molecular formula of the compound = $(\text{Empirical formula})_n = (C_2H_5Br)_1 = C_2H_5Br$.

Example 5. *An acid of molecular mass 104 contains 34.6% carbon, and 3.85% hydrogen. 3.812 mg of acid required 7.33 cm^3 of 0.01 N NaOH for neutralization. Suggest a structure for the acid.*

Solution.

(*a*) Percentage composition of elements

(*i*) Percentage of carbon = 34.6%

(*ii*) Percentage of hydrogen = 3.85%

(*iii*) Percentage of oxygen = 100 – (34.6 + 3.85) = 61.55%

(*b*) Calculation of empirical formula

Empirical formula of the compound is obtained as under:

Element	*Percentage*	*Atomic weight*	*Relative no. of atoms*	*Simplest atomic ratio*	*Simplest whole no. atomic ratio*
Carbon	34.6	12	$\frac{34.6}{12} = 2.89$	$\frac{2.89}{2.89} = 1$	3
Hydrogen	3.85	1	$\frac{3.85}{1} = 3.85$	$\frac{3.85}{2.89} = 1.33$	4
Oxygen	61.55	16	$\frac{61.55}{16} = 3.85$	$\frac{3.85}{2.89} = 1.33$	4

Thus, the empirical formula of the compound is $C_3H_4O_4$.

(*c*) Calculation of molecular formula of the acid

Empirical formula mass of the acid = 3 × 12 + 4 × 1 + 4 × 16 = 104

But, molecular mass of the acid = 104

$$\therefore \quad n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{104}{104} = 1$$

∴ Molecular formula of the acid = $(\text{Empirical formula})_n = (C_3H_4O_4)_1 = C_3H_4O_4$.

(*d*) Calculation of the basicity of the acid

3.812 mg of the acid requires 7.33 cm^3 of 0.01 N NaOH for complete neutralization.

Thus, 7.33 cm^3 of 0.01N NaOH require = 3.812 mg of the acid

or 7.33 cm^3 of 1N NaOH require = $\frac{3.812}{0.01}$ mg = 0.3812 g of the acid

or 1000 cm^3 of 1N NaOH will require = $\frac{3.812}{7.33} \times 1000 = 52$ g of the acid

∴ Equivalent mass of the acid = 52

But, the molecular mass of the acid = 104

$$\therefore \quad \text{Basicity } (n) = \frac{\text{Molecular mass}}{\text{Equivalent mass}} = \frac{104}{52} = 2$$

(*e*) Structure of the acid. The acidic character of an organic acid is due to the presence of a carboxylic group (–COOH) as the functional group.

Since, the basicity of the acid is 2, therefore, the given acid contains two –COOH groups. Out of the molecular formula ($C_3H_4O_4$), 2 × COOH = $C_2H_2O_4$ is accounted for by the two carboxylic groups.

∴ Rest of the molecule of the acid = ($C_3H_4O_4$ – $C_2H_2O_4$) = CH_2

The acid is, therefore, $CH_2(COOH)_2$, *i.e.* Malonic acid.

Example 6. *A chloro compound (A) showed the following properties:*

(*i*) *Decolourized bromine in* CCl_4.

(*ii*) *Absorbed hydrogen catalytically.*

(*iii*) *Gave a white precipitate with ammoniacal cuprous chloride.*

(*iv*) *When vaporized, 1.49 g of (A) gave 448 mL of vapours of S.T.P. Identify (A) and write down the equation for reaction of step (iii).*

Solution.

(*a*) To determine the molecular mass of compound (A)

448 mL of vapours at S.T.P. weigh = 1.49 g

∴ 22400 of vapours at S.T.P. will weigh = $\frac{1.49 \times 22400}{448}$ = 74.5 g

Thus, the molecular mass of compound (A) = 74.5 a.m.u.

(*b*) To identify the functional groups

(*i*) Since (A) decolourizes Br_2/CCl_4, (A) must be an unsaturated compound. This is further supported by the fact that (A) also absorbs hydrogen catalytically.

(*ii*) Since (A) gave a precipitate with ammoniacal CuCl, it must be terminal acetylene, *i.e.* it must contain the group – C ≡ CH

(*c*) To determine the molecular formula of the compound (A)

Molecular mass of –C ≡ CH group = 12 + 12 + 1 = 25 u

Atomic mass of chlorine = 35.5 u

Molecular mass of the compound = 74.5 u

∴ Molecular mass of the remaining portion of compound (A) = 74.5 – 25 – 35.5 = 14

Since, the molecular mass of a CH_2 group is 14, therefore, the compound (A) contains a CH_2 group.

Now, compound (A) contains a chlorine atom, one CH_2 group and one terminal acetylenic group, *i.e.* $-C \equiv CH$, therefore, the structure of the organic compound is $ClCH_2C \equiv CH$, (3-Chloroprop-1-yne). The equation for the above reaction can be written as

$$\underset{\text{3-Chloroprop-1-yne}}{ClCH_2 - C \equiv CH} + CuCl + NH_4OH \rightarrow \underset{\text{Copper 3-chloroprop-1-ynide (Red ppt.)}}{ClCH_2C \equiv CCu} + NH_4Cl + H_2O$$

PROBLEMS FOR PRACTICE

1. Determine the molecular formula of a compound from the following data:
   (*a*) It contained C = 16.27%, H = 0.68% and Cl = 72.20%.
   (*b*) 0.2953 g of it displaced (in Victor Meyer's apparatus) 50.64 mL of moist air at 24ºC and 753.7 mm pressure (Aq. tension at 24ºC is 22 mm). [**Ans.** C_2HCl_3O]
2. A monoacid base gave the following results on analysis:
   0.2 g of the base gave 0.5764 g of carbon dioxide and 0.1512 g water.
   0.3 g of the base gave 32.7 mL nitrogen at 15ºC and 760 mm pressure.
   0.535 g of the base required 12.5 mL of $\frac{N}{2.5}$ hydrochloric acid for complete neutralization.
   What is the molecular formula of the base? [**Ans.** C_3H_9N]
3. An organic compound gave the following results on analysis:
   (*i*) 0.118 g of the compound on combustion gave 0.264 g of CO_2 and 0.162 g of water.
   (*ii*) 0.354 g of the compound on treatment by Kjeldahl's method gave ammonia which was absorbed in 70 mL of $\frac{N}{5}$ H_2SO_4. The excess of the acid required 40 mL of $\frac{N}{5}$ NaOH for complete neutralization.
   (*iii*) 0.067 g of the compound displaced 25.4 mL of air at N.T.P. by Victor Meyer's method.
   Calculate the molecular formula of the compound. [**Ans.** C_3H_9N]
4. An organic monobasic acid gave the following results on analysis:
   (*a*) 0.1935 g gave 0.1820 g CO_2 and 0.0270 g H_2O.
   (*b*) 0.101 g of the compound gave 0.222 g AgCl in a Carius determination.
   (*c*) 0.2709 g of the acid dissolved in water neutralized 25.2 mL of $\frac{N}{12}$ sodium hydroxide.
   Calculate the molecular formula of the acid. [**Ans.** $C_2H_2Cl_2O_2$]
5. A dibasic organic acid gave the following results on analysis:
   (*a*) 0.236 g of the acid gave 0.352 g of CO_2 and 0.108 g of H_2O.
   (*b*) 0.177 g of acid required 30 mL of 0.1 N NaOH solution for complete neutralization.
   Calculate the molecular formula of the acid. [**Ans.** $C_4H_9O_4$]
6. A substance gave the following analytical results:
   (*a*) C = 54.5%, H = 0.09% and Oxygen by difference.
   (*b*) A vapour density determination of Victor Meyer's method gave the following results: 0.1 g of the substance displaced 27 cc. of air at 15ºC and 745 mm. pressure. (Vapour tension at 15ºC is 12.7 mm). Determine the molecular formula. [**Ans.** $C_4H_8O_2$]
7. 250 mg of an organic compound yielded on combustion 561 mg of CO_2 and 342 mg of H_2O. The same amount of the substance when decomposed and distilled with caustic soda gave 72 mg of NH_3.
   If the molecular weight is 59, calculate the molecular formula of the substance. Write down the various structural formulae possible for it with their names.
   [**Ans.** $C_3H_9N.C_3H_7NH_2$, Propylamine; $CH_3NHC_2H_5$, Methyl ethylamine; $(CH_3)_3N$, Trimethylamine]

10.20 MODERN ANALYTICAL TECHNIQUES

A number of scientific instruments have been developed in recent times, which make determination of structure of a compound convenient and without hassle. Functional groups in a compound can be identified with the help of visible or I.R. spectroscopy. Nuclear magnetic resonance (NMR) spectroscopy makes it possible to distinguish between various hydrogens in a compound. Three dimensional structure of a compound can be visualised by means of X-ray diffraction and electron-microscopy. For the estimation of carbon and hydrogen, there are automatic instruments, which give percentages of carbon and hydrogen instantly.

The merit of these methods is that a very small amount of the sample is required for the analysis and error-free results are obtained.

10.21 TYPES OF ORGANIC REACTIONS

Organic reactions may be classified into four main types:

(*a*) Substitution reactions
(*b*) Addition reactions
(*c*) Elimination reactions
(*d*) Rearrangements

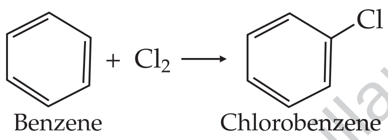
These are separately described as under:

(*a*) Substitution Reaction. A substitution reaction is one in which a part of one molecule is replaced by another atom or group without causing a change in the rest of the molecule. Following are the some examples of substitution reactions:

(*i*) $$\underset{\text{Methane}}{CH_4} + Cl_2 \longrightarrow \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

(*ii*) $$\underset{\text{Bromoethane}}{C_2H_5Br} + KOH \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + KBr$$

(*iii*)



The substitution reactions may be brought about by free-radicals, nucleophilic or electrophilic reagents.

(*b*) Addition Reaction. When two molecules of same or different substances combine together giving rise to a new product, it is an addition reaction. Examples of addition reactions are:

$$\underset{\text{Ethene}}{CH_2 = CH_2} + Br_2 \longrightarrow \underset{\text{Ethylene dibromide}}{CH_2BrCH_2Br}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + HCN \longrightarrow \underset{\text{Acetaldehyde cyanohydrin}}{CH_3CH(OH)CN}$$

Addition reactions could also be brought about by free-radicals, electrophilic or nucleophilic reagents.

(*c*) Elimination Reaction. This reaction involves the removal of atoms or groups from a molecule to form a new compound containing multiple bonds. Dehydrohalogenation of alkyl halides is a common example of this type of reaction.

$$\underset{n\text{-Propyl chloride}}{CH_3 - CH_2CH_2Cl} + KOH \xrightarrow{\text{Alc.}} \underset{\text{Propene}}{CH_3CH = CH_2} + KCl + H_2O$$

(*d*) Rearrangement Reaction. Rearrangement reaction involves the migration of an atom or a group from one atom to the other within the same molecule.

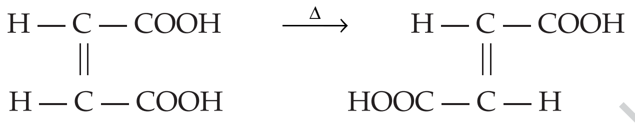
It is interesting to note that the first organic compound, *i.e.* urea synthesized in the laboratory by Wohler actually involved a rearrangement reaction.

$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\Delta} \underset{\text{Urea}}{NH_2-CO-NH_2}$$

Another important example of such reactions is *Hofmann bromamide reaction*. This reaction involves the migration of an alkyl group from the carbon to the nitrogen atom of an amide with the simultaneous elimination of CO as carbonate ion under the influence of Br_2/KOH.

$$\underset{\text{Acetamide}}{CH_3-CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Methylamine}}{CH_3-NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

Similarly, maleic acid, when heated in a sealed tube, is converted into fumaric acid.



$$\begin{array}{c}\text{H}-\text{C}-\text{COOH}\\ \| \\ \text{H}-\text{C}-\text{COOH}\end{array} \xrightarrow{\Delta} \begin{array}{c}\text{H}-\text{C}-\text{COOH}\\ \| \\ \text{HOOC}-\text{C}-\text{H}\end{array}$$

Maleic acid Fumaric acid

10.22 NUCLEOPHILES AND ELECTROPHILES

10.22.1 Nucleophilic Reagents or Nucleophiles

A nucleophilic reagent is a reagent with an atom having an unshared or lone pair of electrons. Such a reagent is in search of a point where it can share these electrons to form a bond. Nucleophiles are of two types:

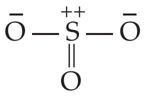
(*i*) **Neutral Nucleophiles.** These are the nucleophiles which are neutral in charge. But they carry some unshared electrons which they like to share with some positive centre or electron deficient centre. Ammonia $\ddot{N}H_3$, water $H_2\overset{..}{\underset{..}{O}}$ and alcohols $R-\overset{..}{\underset{..}{O}}-H$ are the examples of neutral nucleophiles.

(*ii*) **Negative Nucleophiles.** These are the nucleophiles which carry negative charge. Examples of this type of nucleophiles are hydroxyl ion (OH^-), halide ion (X^-), alkoxide ion (RO^-) and cyanide ion (CN^-). Carbanions also come in the category of negative nucleophiles.

10.22.2 Electrophilic Reagents or Electrophiles

An electrophile is a reagent containing electron deficient atoms. Such species have a tendency to attach themselves to the centres of high electron density. There are two types of electrophiles:

(*i*) **Neutral Electrophiles.** These electrophiles don't carry any net charge. Lewis acids such as $AlCl_3$, $FeCl_3$ and BF_3 belong to this category of electrophiles. Sulphonium ion (SO_3) although carries no net charge, but it acts as an electrophile for sulphonation in benzene rings. This is because of its structure.



$$\begin{array}{c}\bar{\text{O}}-\overset{++}{\text{S}}-\bar{\text{O}}\\ \| \\ \text{O}\end{array}$$

As the positive charge is concentrated and the negative charge is scattered, it acts as an electrophile. Substances like $SnCl_4$ which have vacant *d*-orbitals would like to accommodate electrons in them. Thus, such substances also act as electrophiles.

(*ii*) **Positive Electrophiles.** The electrophiles carry a net positive charge. Examples of this category of electrophiles are hydrogen ion (H^+), hydronium ion (H_3O^+), nitronium ion (NO_2^+) and chloronium ion (Cl^+). In the halogenation and nitration of aromatic systems, these electrophiles are involved.

Example. *Classify the following as nucleophiles and electrophiles: H_3O^+, NH_3, $AlCl_3$, ROH, BF_3, CN^-, and SO_3.*

Solution.

Nucleophiles	**Electrophiles**	
NH_3	H_3O^+	
ROH	$AlCl_3$	
CN^-	BF_3	
	SO_3	(Sulphonium ion)

10.23 MECHANISM OF A REACTION

Organic reactions take place by two different mechanisms:

(*i*) **Free-radical Mechanisms.** The reacting species in such reactions are free radicals such as $\dot{Cl}$. Such species are very reactive. For example, chlorination of alkanes takes place by this mechanism.

(*ii*) **Polar Mechanisms.** The reacting species in such reactions are charged particles, either positive or negative. For example, Cl^- (chloride ion) or Cl^+ (chloronium ion). Hydrolysis of an alkyl halide with an alkali takes place by polar mechanism.

10.23.1 Mechanism of a Free-Radical Reaction

The halogenation of alkanes occurs by a free-radical mechanism. It involves three steps: (*a*) Chain initiation, (*b*) Chain propagation and (*c*) Chain termination.

Mechanism of halogenation is explained by considering the chlorination of methane.

(*a*) **Chain Initiation.** When a mixture of CH_4 and Cl_2 is heated or subjected to diffused sunlight, Cl_2 absorbs energy and undergoes homolytic fission producing chlorine free radicals. One molecule gives rise to two radicals.

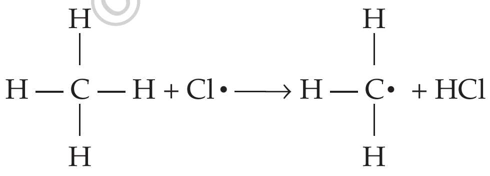
Step 1.

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \xrightarrow[\text{or }\Delta]{h\nu} :\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

Chlorine free radical

(*b*) **Chain Propagation.** The chlorine free radical produced above collides with a molecule of methane forming hydrogen chloride and a methyl free-radical. The methyl free-radical in turn reacts with a molecule of chlorine forming methyl chloride and chlorine free-radical. The newly formed chlorine radical can react with another molecule of methane as in step (2) generating methyl free radical and hydrogen chloride. The methyl free-radical can again repeat as in step (3) and so on. Thus, the sequence of reactions in steps (2) and (3) is repeated over and over again and, thus, the chain is propagated. In other words, a single photon of light initially absorbed by chlorine can bring about the conversion of a large number of molecules of methane into methyl chloride.

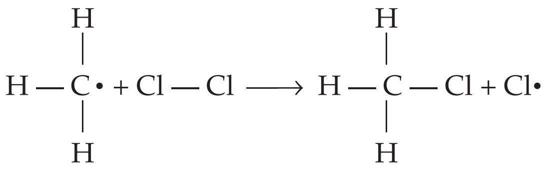
Step 2.



$$H-\overset{H}{\underset{H}{C}}-H + Cl\bullet \longrightarrow H-\overset{H}{\underset{H}{C}}\bullet + HCl$$

Methyl free radical

Step 3.

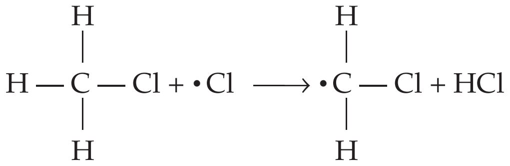


$$H-\overset{H}{\underset{H}{C}}\bullet + Cl-Cl \longrightarrow H-\overset{H}{\underset{H}{C}}-Cl + Cl\bullet$$

Methyl chloride

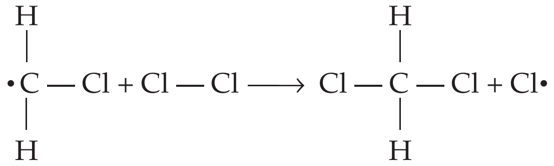
However, the above reaction does not stop at methyl chloride stage but proceeds further till all the H-atoms of methane are replaced by chlorine atoms giving a mixture of mono-, di-, tri- and tetra-chloro methane.

Step 4.



$$\mathrm{H-\overset{H}{\underset{H}{C}}-Cl + {}^{\bullet}Cl \longrightarrow {}^{\bullet}\overset{H}{\underset{H}{C}}-Cl + HCl}$$

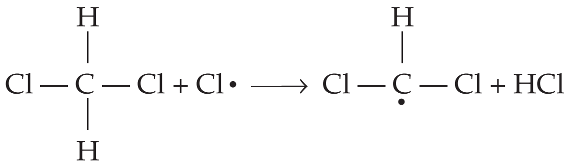
Step 5.



$$\mathrm{{}^{\bullet}\overset{H}{\underset{H}{C}}-Cl + Cl-Cl \longrightarrow Cl-\overset{H}{\underset{H}{C}}-Cl + Cl^{\bullet}}$$

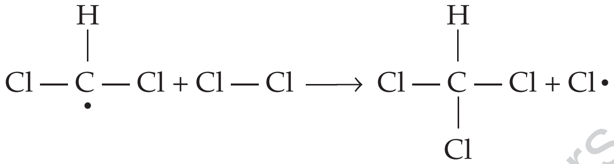
Methylene chloride

Step 6.



$$\mathrm{Cl-\overset{H}{\underset{H}{C}}-Cl + Cl^{\bullet} \longrightarrow Cl-\overset{H}{\underset{\bullet}{C}}-Cl + HCl}$$

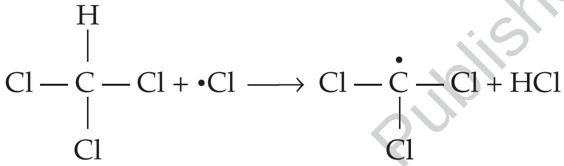
Step 7.



$$\mathrm{Cl-\overset{H}{\underset{\bullet}{C}}-Cl + Cl-Cl \longrightarrow Cl-\overset{H}{\underset{Cl}{C}}-Cl + Cl^{\bullet}}$$

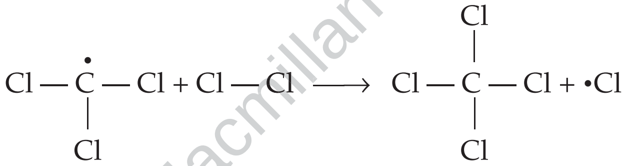
Chloroform

Step 8.



$$\mathrm{Cl-\overset{H}{\underset{Cl}{C}}-Cl + {}^{\bullet}Cl \longrightarrow Cl-\overset{\bullet}{\underset{Cl}{C}}-Cl + HCl}$$

Step 9.



$$\mathrm{Cl-\overset{\bullet}{\underset{Cl}{C}}-Cl + Cl-Cl \longrightarrow Cl-\overset{Cl}{\underset{Cl}{C}}-Cl + {}^{\bullet}Cl}$$

Carbon tetrachloride

(c) **Chain Termination.** The chain reactions mentioned above, however, come to an end if the free radicals combine amongst themselves to form neutral molecules. Some of the chain terminating steps are:

$$\mathrm{{}^{\bullet}Cl + {}^{\bullet}Cl \longrightarrow Cl-Cl}$$
$$\mathrm{{}^{\bullet}CH_3 + {}^{\bullet}Cl \longrightarrow CH_3-Cl}$$
$$\mathrm{{}^{\bullet}CH_3 + {}^{\bullet}CH_3 \longrightarrow CH_3-CH_3}$$

10.23.2 Mechanism of a Polar Reaction

In a reaction, proceeding by polar mechanism, the reacting species are polar in nature, *i.e.* they carry either positive or a negative charge. A polar mechanism can be illustrated by the hydrolysis of methyl bromide with aqueous potassium hydroxide. This is called SN^2 (substitution nucleophilic reaction of second order).

SN^2 Reaction Mechanism of Substitution in Alkyl Halides

Hydrolysis of methyl bromide proceeds by SN^2, (meaning substitution nucleophilic reaction of the second order), mechanism. SN^2 reaction may also be termed as bimolecular substitution reaction. The term bimolecular implies that there are two reacting species in the rate determining step of the reaction.

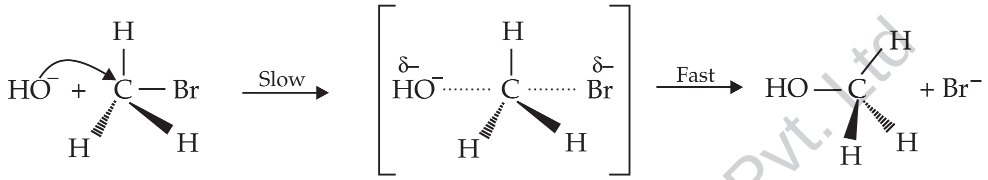
A simple and typical example of SN^2 substitution is the hydrolysis of methyl bromide with aqueous sodium hydroxide.

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

The kinetic data reveal that the rate of the reaction is dependent upon the concentration of both these reactants.

$$\text{Rate} = k[CH_3Br]\,[OH^-]$$

The reaction is of the second order and, thus, it proceeds by a direct displacement mechanism in which both the reactants are present in the rate determining step. It is assumed that the nucleophile attacks the side of the carbon atom opposite to that of bromine. This is referred to as **backside attack.** As a result of this attack, a transition state is formed in which carbon atom is partially bonded to both —OH and —Br groups. In the transition state, the central carbon is sp^2 hybridised and the three hydrogens attached to it lie in the same plane with mutual bond angles of 120°. The reaction may be depicted as:



It may be noted that in the transition state, the hydroxide ion has diminished negative charge since it has started sharing its electrons with carbon. Similarly, bromine develops a partial negative charge as it is tending to depart with the bonding electrons. When carbon-oxygen bond is completely formed, the carbon-bromine bond is altogether broken. The energy required for breaking a bond is compensated by the formation of a new bond. The overall reaction is, thus, a concerted process occurring in one step through the intervention of a single transition state. In a single step, C—Br bond is broken and C—OH bond is formed resulting in the formation of alcohol molecule.

SN^1 Reaction (Hydrolysis of Tertiary Butyl Bromide)

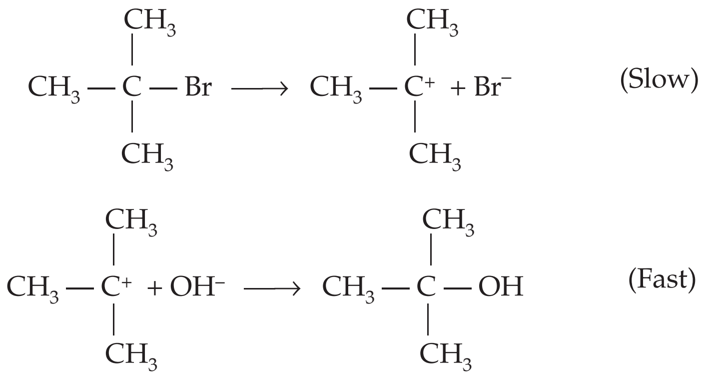
An example of unimolecular substitution reaction (SN^1) is the hydrolysis of tert butyl bromide.

$$(CH_3)_3C — Br + OH^- \longrightarrow (CH_3)_3C — OH + Br^-$$

Chemical kinetics studies reveal that the rate of this reaction depends only on the concentration of tert-butyl bromide. Thus,

$$\text{Rate} = k\,[(CH_3)_3\,C - Br]$$

The reaction is of the first order and, thus, it is believed to occur in two steps:



$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - Br \longrightarrow CH_3 - \underset{CH_3}{\overset{CH_3}{C^+}} + Br^- \qquad \text{(Slow)}$$

$$CH_3 - \underset{CH_3}{\overset{CH_3}{C^+}} + OH^- \longrightarrow CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - OH \qquad \text{(Fast)}$$

It is, thus, clear that the rate determining step of the reaction is the slow ionisation of tert-butyl bromide to form tert-butyl carbocation. The energy required for ionisation is supplied by the formation of many ion-dipole bonds between the ions produced and the polar solvent molecules. The second step involving the combination of carbocation with hydroxide ion to form alcohol is fast.

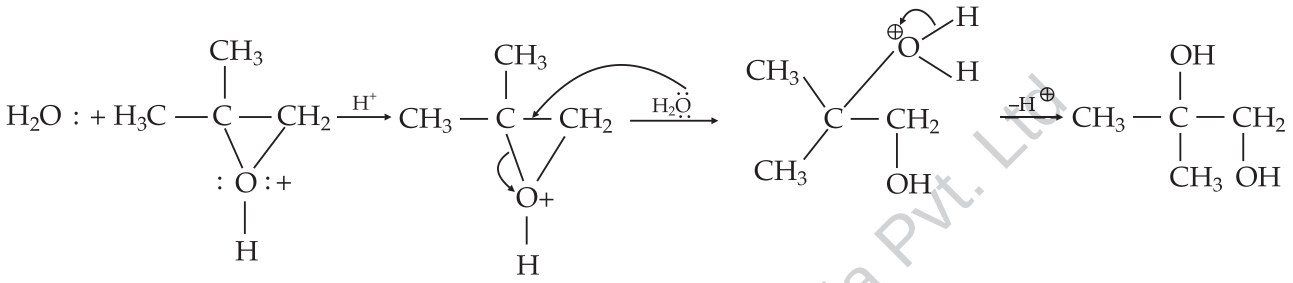
Relative Reactivities of Alkyl Halides in Unimolecular Nucleophilic Substitution (SN^1) Reactions

Relative Reactivities of Alkyl Halides. Formation of the carbocation is the rate determining step in unimolecular nucleophilic substitution (SN^1). Greater the stability, more rapidly is the carbocation formed and, hence, faster is the reaction. Now the relative stability of the carbocations follows the sequence:

Benzyl, allyl > Tertiary > Secondary > Primary > Methyl carbocations.
Therefore, the reactivity of alkyl halides in SN^1 reactions follows the same order, *i.e.*
Benzyl, allyl > Tertiary > Secondary > Primary > Methyl halides.

Example. *2, 2-dimethyl oxirane can be cleaved by acid (H^+). Write the mechanism.*

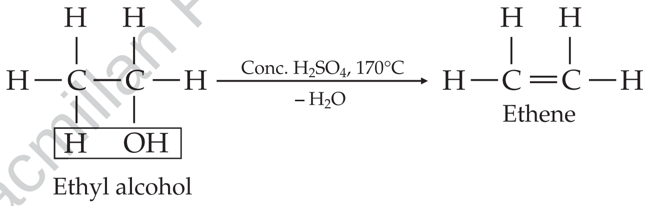
Solution. Acid catalysed SN^2 cleavage.



The leaving group is weakly basic hydroxyl group. The nucleophile is a poor one, water, which attacks the partially positively charged carbon. The reaction has considerable SN^1 character as transition state is stabilized by electronic factor while steric factor has no effect.

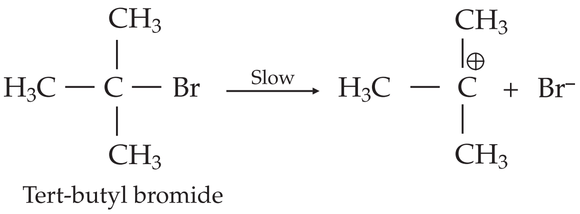
Elimination Reactions

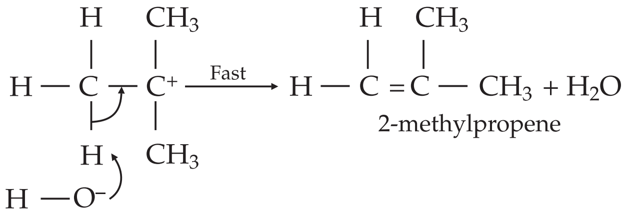
The reactions which are accompanied by the loss of simple molecules like H_2O or HX (X = Cl, Br or I) from the reactant molecules are called **elimination reactions.** Elimination reactions may be viewed as reverse of addition reactions. A multiple bond (double or triple) is introduced in the product as a result of elimination. For example,



Elimination reactions are further classified as E_1 or E_2 reactions.

E_1 Reactions (Elimination Reactions of First Order). These reactions involve a two steps mechanism and are generally given by tertiary halides. The first step involves breaking of carbon-halogen bond heterolytically. The formation of the carbocation is a slow rate-determining step. In the second and first step, the nucleophile abstracts a proton from the β-carbon to form the alkene. Dehydrohalogenation of *tert*-butyl bromide to give 2-methylpropene is an example of E_1 reaction. Its mechanism is given below:





This reaction follows the rate law:

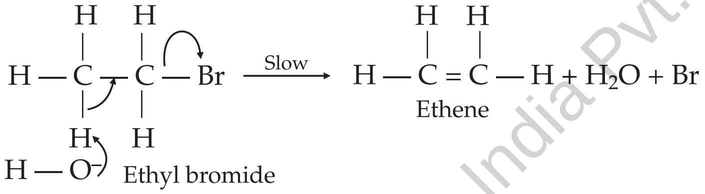
$$\text{Rate} = k\,[\text{Alkyl halide}]$$

As the rate of the reaction depends upon the concentration of only one species, *viz.,* alkyl halide, it is a reaction of first order or E_1 reaction.

E_2 Reactions (Elimination Reactions of Second Order). This type of reaction takes place in one step and are generally given by primary halides. Removal of the proton from β-carbon atom and removal of the halide ion take place simultaneously. The mechanism has been explained by taking the example of dehydrohalogenation of ethyl bromide.

$$C_2H_5Br \xrightarrow[-HBr]{\text{Alc. KOH}} C_2H_4$$

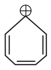
Mechanism

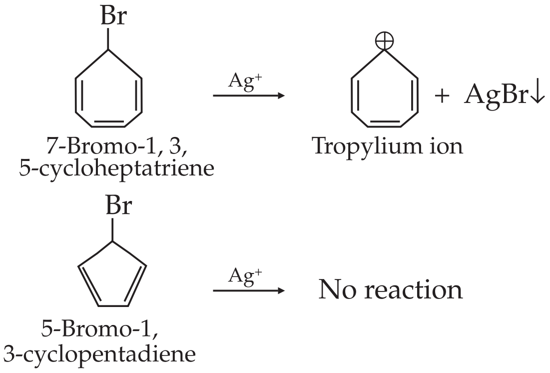


$$\text{Rate of reaction} = k\,[\text{Alkyl halide}]\,[OH^-]$$

As the rate of the reaction depends upon concentration of the two substances, viz. alkyl halide and hydroxyl ion, it is a reaction of second order or E_2 reaction.

Example. *7-bromo-1,3,5–cycloheptatriene exists as an ion whereas 5–bromo–1, 3–cyclopentadiene does not form an ion even in the presence of Ag^+. Explain.*

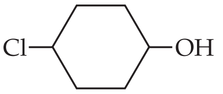
Solution. On ionization, 7–bromo–1, 3, 5–cycloheptatriene gives  (Tropylium ion), which is highly stable as it involves cyclic dispersion of 6 electron clouds which makes it aromatic one. On the other hand, 5–bromo–1, 3–cyclopentadiene may give  (1, 3–cyclopentadienyl cation), which also involves cyclic resonance but of 4 electrons making it an unstable antiaromatic cation.



QUICK SCAN (FOR REVISION)

1. **Vital force theory** was proposed by *Berzelius*. According to this theory, organic compounds consist of living organisms.
2. When ammonium cyanate (NH_4CNO) or a mixture of $NH_4Cl + KCNO$ is heated, an organic compound called urea (NH_2CONH_2) is formed. This reaction is called **Wohler's synthesis**. Vital force theory was thus discarded.
3. The self-linking of carbon atoms through covalent bonds to form long straight or branched chains and rings of different sizes is called **catenation**. This property of carbon is due to strong carbon-carbon bonds.
4. Due to the property of **catenation**, carbon forms a huge number of compounds.
5. Acetic acid was the first organic compound which was synthesized from its elements *i.e.*, C and H by *Kolbe* in 1845.
6. Organic compounds being non-polar are usually **insoluble in water** while inorganic compounds being polar are **soluble in water**.
7. Organic compounds are **covalent** while inorganic compounds are **electrovalent**.
8. The reactions of organic compounds are **molecular in nature** while those of inorganic compounds are **ionic in nature**.
9. Important sources of organic compounds are petroleum, coal, natural gas, plants and animals.
10. Cyclic compounds whose rings are made up of only one kind of atoms, *i.e.* carbon atoms are called **homocyclic or carbocyclic compounds.** Aliphatic cyclic compounds are called **alicyclic compounds.**
11. Organic compounds containing one or more fused or isolated benzene rings and their derivatives are called **benzenoids** or **aromatic compounds,** *e.g.*, benzene, toluene, naphthalene, anthracene, etc.
12. Cyclic compounds containing one or more hetero atoms (usually O, N, S, etc.) are called **heterocyclic compounds,** *e.g.*, furan, pyrrole, thiophene, etc.
13. Most abundant organic compound in nature is cellulose.
14. A homologous series is a family of structurally similar organic compounds, all members of which contain the same functional group and whose consecutive members differ by a CH_2 group. They are prepared by the same general methods of preparation and have almost similar chemical properties. For example, methanol, ethanol, propanol, etc., are the members of a homologous series called **alcohols**.
15. The group of atoms present in a molecule which determines its chemical properties is called a **functional group**, *i.e.* NH_2, OH, NO_2, CHO, COOH, etc.
16. Common name of a compound is derived from its source, property use, etc. These names are being replaced by IUPAC names.
17. When the molecule contains more than one functional group, the one functional group is considered to be principal functional group and all others are considered as substituents.
18. An IUPAC name consists of three parts: *word root, suffix* and *prefix*.
19. **Word root** denotes the number of carbon atoms present in the longest continuous chain of carbon atoms containing the functional group.
20. Prefixes are of two types:
    (*i*) **A primary prefix** *cyclo* is used before the root word to distinguish cyclic from acyclic compounds.
    (*ii*) **A secondary prefix** is used to indicate the nature of secondary functional groups, *i.e.*, functional groups other than the **principal functional group.**
21. Suffixes are of two types:
    (*i*) **Primary suffix** denotes whether the chain is saturated or unsaturated. If saturated, the suffix *ane* is used and if unsaturated, the suffix *ene* for double bond and *yne* for triple bond is used.
    (*ii*) **A secondary suffix** denotes the functional group present in the organic compound.
22. The following order of preferences is used while selecting the principal functional group in poly functional compounds. Sulphonic acids > carboxylic acids > anhydrides > esters > acid chlorides > acid amides > aldehydes > ketones > nitriles > thiols > alcohols > alkyl halides > alkenes > alkynes.
    All the remaining functional groups such as halo, nitro, amino, alkoxy, etc., are treated as **secondary functional groups**.
23. The complete IUPAC name of the organic compounds consists of five parts in the order mentioned below:

Secondary	+	Primary	+	Word	+	Primary	+	Secondary
prefix		prefix		root		suffix		suffix
(s.p.)		(p.p.)		(w.r.)		(p.s.)		(s.s.)

For example, the compound  is named as:

4-chloro	+	cyclo	+	hex	+	an(*e*)	+	1-ol
(s.p.)		(p.p.)		(w.r.)		(p.s.)		(s.s.)

= 4-Chlorocyclohexan-1-ol

It may be noted that locants (number denoting position) for suffixes and prefixes are placed immediately before them.

24. While numbering the carbon atoms of an organic compound the **lowest set of locants** for substituents is always preferred. For example,
   - (*i*) the set of locants (1, 4, 6) is preferred over the set (2, 3, 6) even though both have the same sum of locants, *i.e.* 10.
   - (*ii*) the set of locants (2, 5, 8) is preferred over the set of locants (3, 4, 7) since 2 comes before 3 even though the sum of locants in the former case is 15 while in the latter case, it is 14.

25. When both double and triple bonds are present in a molecule, the numbering of the parent chain is always done from that end which is nearer to the double or the triple bond, *i.e.*

$$\overset{1}{C}H_3\overset{2}{C}H=\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}\equiv\overset{6}{C}\overset{7}{C}H_2\overset{8}{C}H_3$$

(*oct-2-en-5-yne*) and the compound is always named as a derivative of alkyne rather than alkene.

26. If, however, there is a choice in numbering, the double bond is always given preference, *i.e.*

$$H\overset{5}{C}\equiv\overset{4}{C}\overset{3}{C}H_2\overset{2}{C}H=\overset{1}{C}H_2 \text{ (pent-1-en-5-yne).}$$

27. If the branched chain also contains multiple bond and substituents, it is separately numbered.

28. Empirical formula of a substance gives the simplest whole number ratio between the atoms of various elements.

29. Molecular formula gives the actual number of atoms of various elements present in one molecule of the substance.

30. Molecular formula = n × Empirical formula

$$\text{where, } n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

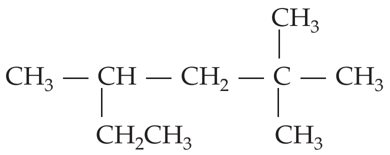
EXERCISES

Very Short Answer Type Questions

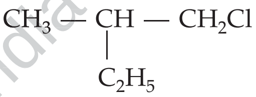
1. What is meant by homologous series?
2. Define the term organic chemistry.
3. What are hydrocarbons?
4. Write the suffixes for the following classes of compounds: Ketone, Esters, Alkyne, Aldehyde.
5. What is catenation?
6. Define the term isomerism.
7. What is an alkyl group? Write the names and formulae of two alkyl groups.
8. Define the term word root and give its significance.
9. Define the term functional group.
10. Name the different types of hydrocarbons.
11. What is the full form of IUPAC?
12. What does DDT stand for?
13. What is the functional group of (*i*) an aldehyde and (*ii*) a nitro compound?
14. What are alicyclic compounds?
15. Give the IUPAC name of the compound: $CH_2=CH-CH(CH_3)_2$.
16. What is LPG?
17. What are aromatic compounds?
18. Give the IUPAC names of the following compounds:

   (*i*) $C_6H_5CH_2CH_2OH$

   (*ii*) $(CH_3)_2CHC\equiv CH$

   (*iii*) 

$$CH_3-\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

   (*iv*) 

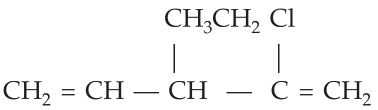
$$CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2Cl$$

   (*v*) $(CH_3)_2CHCH_2CHO$

   (*vi*) CHO.COOH

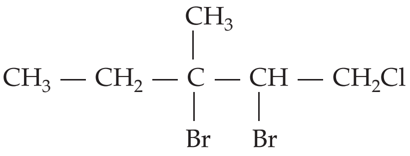
   (*vii*) $BrCH_2CH_2CH_2CH_2CH_2Cl$

   (*viii*) $(CH_3)_3CCH_2CH_2OH$

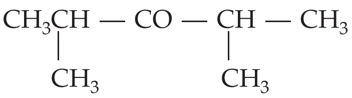
   (*ix*) 

$$CH_2=CH-\overset{\displaystyle CH_3CH_2}{\overset{|}{CH}}-\overset{\displaystyle Cl}{\overset{|}{C}}=CH_2$$

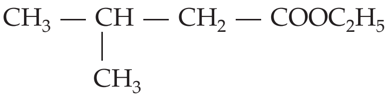
19. Give the IUPAC names of the following compounds:

   (*i*) 

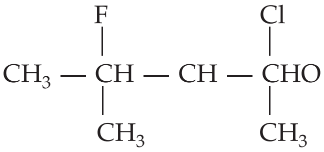
$$CH_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2Cl$$

   (*ii*) 

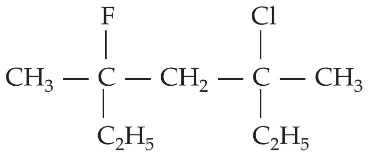
$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}-CO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

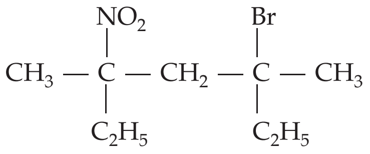
   (*iii*) 

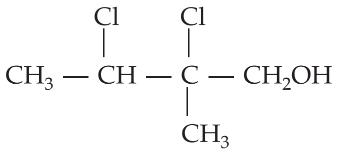
$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-COOC_2H_5$$

   (*iv*) 

$$CH_3-\overset{\displaystyle F}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{CH}}}}-CH-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{CHO}}}}$$

(v) 
$CH_3-\overset{F}{\underset{C_2H_5}{C}}-CH_2-\overset{Cl}{\underset{C_2H_5}{C}}-CH_3$

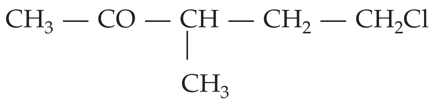
(vi) 
$CH_3-\overset{NO_2}{\underset{C_2H_5}{C}}-CH_2-\overset{Br}{\underset{C_2H_5}{C}}-CH_3$

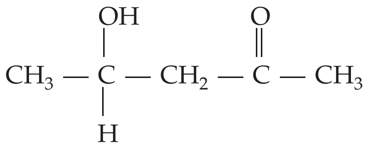
(vii) 
$CH_3-\overset{Cl}{CH}-\overset{Cl}{\underset{CH_3}{C}}-CH_2OH$

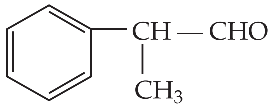
(viii) $CH_3CH = CHCH_2NH_2$

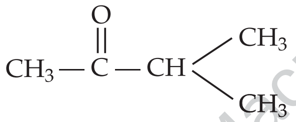
(ix) $CH_2 = CHCN$

20. Write IUPAC names of the following compounds:

(i) 
$CH_3-CO-\underset{CH_3}{CH}-CH_2-CH_2Cl$

(ii) 
$CH_3-\overset{OH}{\underset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(iii) 

(iv) 
$CH_3-\overset{O}{\overset{\|}{C}}-CH\begin{matrix}CH_3\\CH_3\end{matrix}$

Short Answer Type Questions

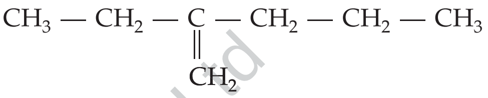
1. What do you understand by the term homologous series? What are the characteristics associated with the members of a homologous series?
2. What are the reasons for the existence of a large number of organic compounds?
3. What are hydrocarbons? Name the different types of hydrocarbons.
4. Draw the structures of the functional group of

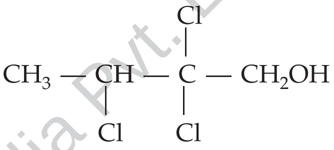
   (i) Aldehydes (ii) Nitro compounds

   (iii) Carboxylic acid (iv) Ethers.
5. Name at least one compound of each of the following classes, write its formula and state its important use:

   (i) Aldehyde (ii) Alcohol

   (iii) Alkyne (iv) Carboxylic acid
6. Define the following terms giving one example of each: (i) Functional group (ii) Isomer (iii) Carbide.
7. What is meant by homologous series? What are its characteristics?
8. What is meant by catenation? Why does carbon exhibit this property to the maximum extent?
9. Give four main reasons to justify why organic chemistry is treated as a special branch of chemistry.
10. What is an alkyl group? Write the names and formulae of alkyl groups obtained from propane.
11. Write the IUPAC names of the following:

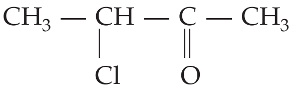
(i) 
$CH_3-CH_2-\underset{CH_2}{\underset{\|}{C}}-CH_2-CH_2-CH_3$

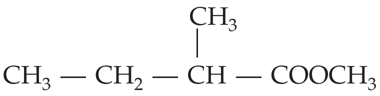
(ii) 
$CH_3-\underset{Cl}{CH}-\overset{Cl}{\underset{Cl}{C}}-CH_2OH$

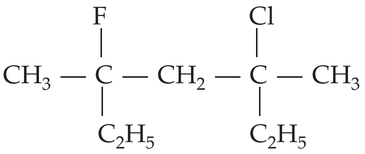
(iii) $CH_2 = CH - CH = CH_2$

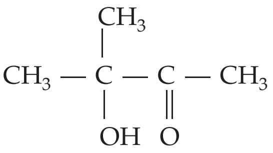
(iv) $(CH_3)_2CHCH(I)CO_2H$

(v) $CH_3 - CH = CH - CHO$

(vi) 
$CH_3-\underset{Cl}{CH}-\underset{O}{\underset{\|}{C}}-CH_3$

(vii) 
$CH_3-CH_2-\overset{CH_3}{CH}-COOCH_3$

(viii) 
$CH_3-\overset{F}{\underset{C_2H_5}{C}}-CH_2-\overset{Cl}{\underset{C_2H_5}{C}}-CH_3$

(ix) 
$CH_3-\overset{CH_3}{\underset{OH}{C}}-\underset{O}{\underset{\|}{C}}-CH_3$

12. Write the structures of the following:

(i) 2-Methyl-2-butanol

(ii) 4-Chloro-2-hexenoic acid

(iii) 2, 2, 4-Trimethyl-3-chloropentane

(iv) 4-Iodo-2-hexenoic acid

(v) Butyne-2

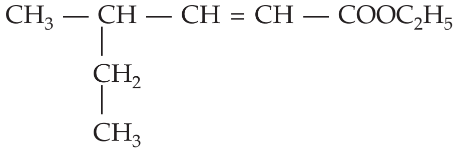
(vi) 3, 5-Dimethyl-4-octanone

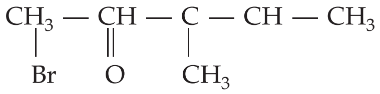
(vii) But-3-en-1-ol

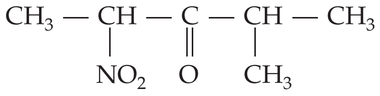
(viii) 2-Chlorobuta-1, 3-diene

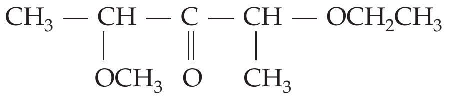
(*ix*) 2-Aminoethan-1-ol
(*x*) 4-Ethyl-5-methylhex-2-ene
(*xi*) 2-Ethylprop-2-en-1-ol
(*xii*) 2, 4-Dimethylhexan-3-one
(*xiii*) 2-Ethoxypropane

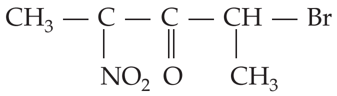
13. Write the IUPAC names of the following compounds:

(*i*) 
$\mathrm{CH_3 - \underset{\substack{|\\CH_2\\|\\CH_3}}{CH} - CH = CH - COOC_2H_5}$

(*ii*) 
$\mathrm{CH_3 - \underset{\substack{|\\Br}}{CH} - \underset{\substack{\|\\O}}{C} - \underset{\substack{|\\CH_3}}{C} - CH - CH_3}$

(*iii*) 
$\mathrm{CH_3 - \underset{\substack{|\\NO_2}}{CH} - \underset{\substack{\|\\O}}{C} - \underset{\substack{|\\CH_3}}{CH} - CH_3}$

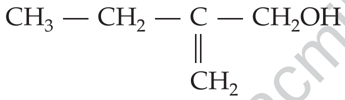
(*iv*) 
$\mathrm{CH_3 - \underset{\substack{|\\OCH_3}}{CH} - \underset{\substack{\|\\O}}{C} - \underset{\substack{|\\CH_3}}{CH} - OCH_2CH_3}$

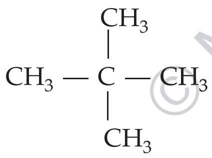
(*v*) 
$\mathrm{CH_3 - \underset{\substack{|\\NO_2}}{C} - \underset{\substack{\|\\O}}{C} - \underset{\substack{|\\CH_3}}{CH} - Br}$

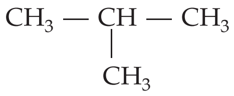
14. Point out the error and write the correct IUPAC names of the following:
(*i*) 1, 5-Pentadiene
(*ii*) 2-Ethyl-2-butene
(*iii*) 2, 3-Dimethyl-3-hexyne
(*iv*) 2-Methyl-3-butanone

15. Give the IUPAC names of the following compounds:

(*i*) $\mathrm{CH_2 = CH - CH_2 - CH_2OH}$

(*ii*) 
$\mathrm{CH_3 - CH_2 - \underset{\substack{\|\\CH_2}}{C} - CH_2OH}$

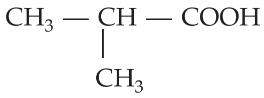
(*iii*) 
$\mathrm{CH_3 - \overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}} - CH_3}$

(*iv*) 
$\mathrm{CH_3 - \underset{\substack{|\\CH_3}}{CH} - CH_3}$

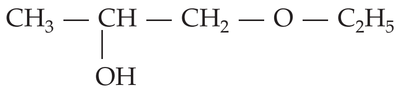
16. Write the IUPAC names of the following compounds:

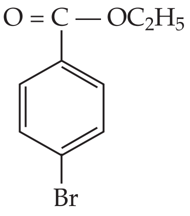
(*i*) $\mathrm{(CH_3)_2CHCH_2CH_3}$

(*ii*) $\mathrm{(C_2H_5)_2CHCH_3}$

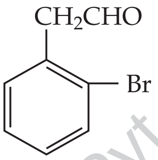
(*iii*) 
$\mathrm{CH_3 - \underset{\substack{|\\CH_3}}{CH} - COOH}$

17. Write the IUPAC names of the following compounds:

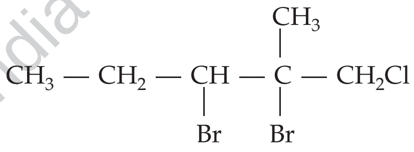
(*i*) 
$\mathrm{CH_3 - \underset{\substack{|\\OH}}{CH} - CH_2 - O - C_2H_5}$

(*ii*) 

(*iii*) 
$\mathrm{CH_3 - \underset{\substack{|\\C_2H_5}}{COCH} - CH_2 - CH_2Cl}$

(*iv*) 

(*v*) $\mathrm{(CH_3)_3COH}$

(*vi*) 
$\mathrm{CH_3 - CH_2 - \underset{\substack{|\\Br}}{CH} - \overset{\substack{CH_3\\|}}{\underset{\substack{|\\Br}}{C}} - CH_2Cl}$

Long Answer Type Questions

1. Why is organic chemistry studied separately from inorganic compounds?
2. Give the procedure for assigning IUPAC names of compounds having a functional group in stepwise sequence.
3. What is aromatic nucleus and side chain? Draw the structures of aryl radicals obtainable from benzene and toluene and name them.
4. Write the structural formulae giving IUPAC names of two members of the following aromatic homologous series. Phenols, Aldehydes, Carboxylic acids, Amides, Esters and Amines.
5. What are alkanes? Describe briefly the procedure to name branched chain alkanes.
6. Explain the isomerism in *di*- and *tri*-derivatives of benzene. Draw the structures of nuclear and side halogen compounds of toluene giving their IUPAC and common names.
7. Give the names and formulae of important compounds belonging to different categories and also give their uses.
8. Name at least two alkanes, alcohols, aldehydes, acids and amines and give their common as well as IUPAC names along with their structures.
9. (*i*) What do you understand by homologous series of compounds?
   (*ii*) Write the formulae of the next two higher homologues of HCHO, $\mathrm{CH_2 = CH_2}$.
   (*iii*) Write the structural formula of $\mathrm{C_4H_{10}C}$.

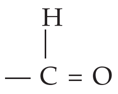
10. Give the name and structural formula of one number of each of the following classes of organic compounds.
   (*i*) An aliphatic alcohol
   (*ii*) An aromatic acid
   (*iii*) An ester of an organic acid
   (*iv*) An alkene
   (*v*) An aliphatic aldehyde.

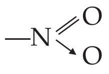
11. (*a*) The molecular formula of a compound is C_3H_8O. Write the structures of all possible isomers and identify the functional groups in each.
   (*b*) Write the structures of two higher homologues of
      (*i*) HCOOH
      (*ii*) $CH_3-CO-CH_3$.

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

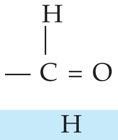
3. Hydrocarbons are organic compounds containing only carbon and hydrogen.
4. One, oate, yne, and al.
5. The property of self-linking of atoms to form chains is called catenation.
10. Alkane, Alkenes, Alkynes, Cycloalkanes, Cycloalkenes, Cycloalkynes and Aromatic hydrocarbons.
11. International Union of Pure and Applied Chemistry.
12. 2, 2-Bis (*p*-chlorophenyl)-1, 1, 1-trichloroethane.

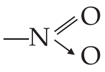
13. (*i*)

$-\overset{\overset{H}{|}}{C}=O$

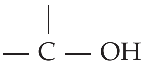
(*ii*)

$-N\begin{smallmatrix}{=}O\\ \searrow O\end{smallmatrix}$

15. 3-Methyl but-1-ene
16. Liquid petroleum gas (It is mixture of butanes)
18. (*i*) 2-Phenylethan-1-ol
   (*ii*) 3-Methylbut-1-yne
   (*iii*) 2,2,4-Trimethylhexane
   (*iv*) 1-Chloro-2-methyl-butane
   (*v*) 3-Methylbutan-1-al
   (*vi*) 2-Oxoethan-1-oic acid
   (*vii*) 1-Bromo-4-Chlorobutane
   (*viii*) 3,3-Dimethylbutan-1-ol
   (*ix*) 2-Chloro-3-ethylpenta-1, 4-diene
19. (*i*) 2,3-Dibromo-1-chloro 3-methylpentane
   (*ii*) 2,4-Dimethylpentan-3-one
   (*iii*) Ethyl 3-methylbutan-1-oate
   (*iv*) 2,3-Dimethylbutan-1-al
   (*v*) 3-Chloro-5-fluoro-3, 5 dimethylheptane
   (*vi*) 3-Bromo-3,5-dimethyl-5-nitroheptane,
   (*vii*) 2,3-Dichloro-2-methylbutan-1-ol
   (*viii*) But-2-en-1-amine
   (*ix*) Prop-2-en-1-nitrile.
20. (*i*) 5-chloro-3-methylpentan-2-one
   (*ii*) 4-Hydroxy pentan-2-one
   (*iii*) 2-Methyl-2-phenylpropanal
   (*iv*) 3-Methyl butan-2-one.

Short Answer Type Questions

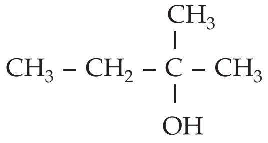
4. (*i*)

$-\underset{H}{\overset{\overset{H}{|}}{C}}=O$

(*ii*)

$-N\begin{smallmatrix}{=}O\\ \searrow O\end{smallmatrix}$

(*iii*)

$-\overset{|}{C}-OH$

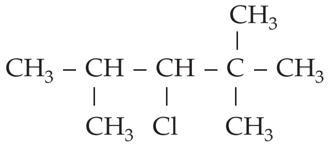
(*iv*) — O —

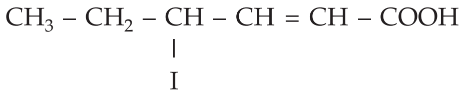
10. (*i*) $CH_3CH_2CH_2$ – (*n*-propyl)
   (*ii*) $CH_3CH–CH_3$ (isopropyl)
11. (*i*) 2-Ethyl-1-pentene
   (*ii*) 2, 2, 3-Trichloro-1-butanol
   (*iii*) 1, 3-Butadiene
   (*iv*) 2-Iodo-3-methylbutanoic acid
   (*v*) 2-Butanal
   (*vi*) 3-Chloro-2-butanone
   (*vii*) Methyl 2-methylbutanoate
   (*viii*) 3-Chloro-5-fluoro-3, 5-dimethylheptane
   (*ix*) 3-Hydroxy-3-methyl-2-butanone

12. (*i*)

$CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

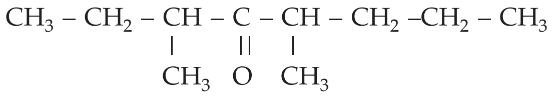
(*ii*)

$CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH-CH-COOH$

(*iii*)

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

(*iv*)

$CH_3-CH_2-\underset{\underset{I}{|}}{CH}-CH=CH-COOH$

(*v*) $CH_3-C\equiv C-CH_3$

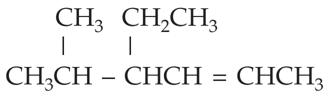
(*vi*)

$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{||}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3$

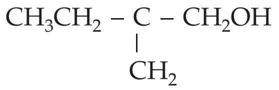
(*vii*) $CH_2=CHCH_2CH_2OH$

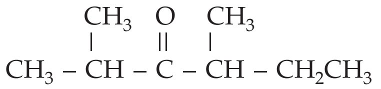
(*viii*)

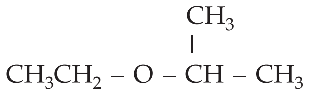
$CH_2=\overset{\overset{Cl}{|}}{C}-CH=CH_2$

(*ix*) $H_2NCH_2CH_2OH$

(*x*)

$CH_3\overset{\overset{CH_3}{|}}{C}H - \overset{\overset{CH_2CH_3}{|}}{C}HCH = CHCH_3$

(*xi*)

$CH_3CH_2 - \underset{\underset{CH_2}{|}}{C} - CH_2OH$

(*xii*)

$CH_3 - \overset{\overset{CH_3}{|}}{C}H - \overset{\overset{O}{\|}}{C} - \overset{\overset{CH_3}{|}}{C}H - CH_2CH_3$

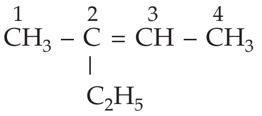
(*xiii*)

$CH_3CH_2 - O - \overset{\overset{CH_3}{|}}{C}H - CH_3$

13. (*i*) Ethyl-4-methylhex-2-enoate
    (*ii*) 2-Bromo-4-methylpentan-3-one
    (*iii*) 2-Nitro-4-methylpentan-3-one
    (*iv*) 2-Ethoxy-4-methoxypentan-3-one
    (*v*) 2-Bromo-4-nitropentan-3-one.
14. (*i*) 1, 5-Pentadiene

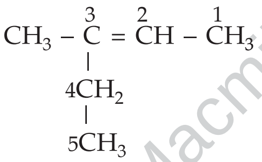
$$H_2\overset{1}{C} = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H = \overset{5}{C}H_2$$

The first double bond is at carbon-1 and the second double bond starts from carbon-4. Therefore, the correct name of the compound should be 1, 4-pentadiene.

(*ii*) 2-Ethyl-2-butene

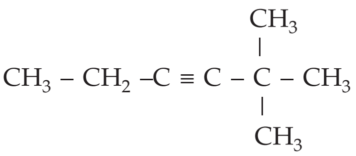

$\overset{1}{C}H_3 - \underset{\underset{C_2H_5}{|}}{\overset{2}{C}} = \overset{3}{C}H - \overset{4}{C}H_3$

The longest chain in this compound contains five carbon atoms as written below:


$CH_3 - \underset{\underset{\underset{\underset{{}_5CH_3}{|}}{{}_4CH_2}}{|}}{\overset{3}{C}} = \overset{2}{C}H - \overset{1}{C}H_3$

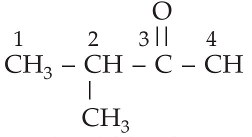
Thus, the correct name should be 3-Methylpent-2-ene

(*iii*) 2-Dimethyl-3-hexyne

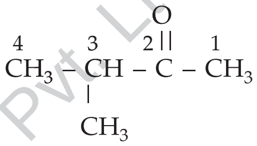

$CH_3 - CH_2 - C \equiv C - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_3$

The correct name is 2, 2-Dimethylhex-3-yne

(*iv*) 2-Methyl-3-butanone


$\overset{1}{C}H_3 - \underset{\underset{CH_3}{|}}{\overset{2}{C}H} - \overset{\overset{O}{\|}}{\overset{3}{C}} - \overset{4}{C}H$

Numbering should be done in such a manner so as to give lower number to the carbonyl carbon as shown alongside.


$\overset{4}{C}H_3 - \underset{\underset{CH_3}{|}}{\overset{3}{C}H} - \overset{\overset{O}{\|}}{\overset{2}{C}} - \overset{1}{C}H_3$

Thus, the correct name should be 3-Methylbutan-2-one

15. (*i*) But-3-en-1-ol
    (*ii*) 2-Ethyl-prop-2-en-1-ol
    (*iii*) 2, 2-dimethylpropane
    (*iv*) 2-Methylpropane
16. (*i*) 2-Methylbutane
    (*ii*) 3-Methylpentane
    (*iii*) 2-Methylpropanoic acid.
17. (*i*) 1-Ethoxypropan-2-ol
    (*ii*) Ethyl 4-bromophenyl methanoate
    (*iii*) 5-chloro-3-ethylpentan-2-one
    (*iv*) 2-Bromophenylethanal
    (*v*) 2-Methylpropan-2-ol
    (*vi*) 2, 3-Dibromo-1-chloro-2-methyl pentane

COMPETITION FILE

SUBJECTIVE PROBLEMS

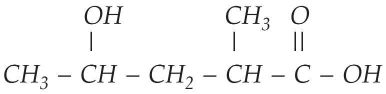
Problem 1. *Pick out the error and write the correct IUPAC names for the following:*

(*i*) *3-Pentyne* (*ii*) *1, 6-Hexadiene*
(*iii*) *2-Ethyl-2-pentene* (*iv*) *1, 2-Dihydroxyethane*
(*v*) *Pent-4-en-1-yne.*

Solution. Correct IUPAC names of the compounds are as follows:

(*i*) Pent-2-yne (*ii*) Hexa-1, 5-diene
(*iii*) 3-Methylhex-3-ene (*iv*) Ethane-1, 2-diol
(*v*) Pent-1-en-4-yne.

Problem 2. *Write the IUPAC name of the following compound, stepwise:*

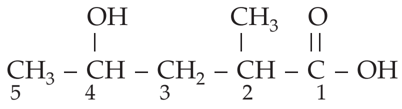

$CH_3 - \overset{\overset{OH}{|}}{C}H - CH_2 - \overset{\overset{CH_3}{|}}{C}H - \overset{\overset{O}{\|}}{C} - OH$

Solution.

Step 1. *Identification of principal functional group.* The compound contains two functional groups, *i.e.* –COOH and –OH. Group –COOH ranks higher in the priority.

Therefore, compound is named as a derivative of a carboxylic acid.

Step 2. *Selection of longest continuous chain.* The longest continuous chain containing COOH group contains five carbon atoms. It is numbered from the –COOH group side.



$$\mathrm{\underset{5}{CH_3} - \underset{4}{\overset{\overset{OH}{|}}{CH}} - \underset{3}{CH_2} - \underset{2}{\overset{\overset{CH_3}{|}}{CH}} - \underset{1}{\overset{\overset{O}{\|}}{C}} - OH}$$

Step 3. *Writing of the parent name.* Since the longest chain contains five carbons, the parent name of the compound is pentanoic acid. The compound will be named as a derivative of pentanoic acid.

Step 4. *Arrangement of substituent names.* The substituents are written in alphabetical order and their positions are identified.

4-Hydroxy-2-methyl

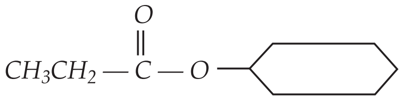
Step 5. *Prefixing substituent names with the parent name.* The name of the compound is:

4-Hydroxy-2-methylpentanoic acid.

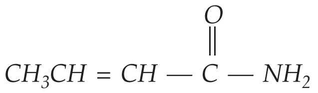
Problem 3. *Give IUPAC names of the following compounds:*

(i) $CH_2 = CH — C \equiv N$

(ii)

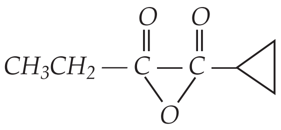


(iii)

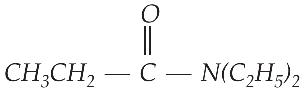


$$CH_3CH = CH — \overset{\overset{O}{\|}}{C} — NH_2$$

(iv)

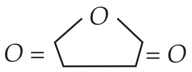


(v)



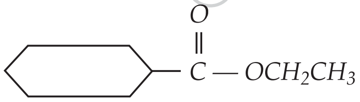
$$CH_3CH_2 — \overset{\overset{O}{\|}}{C} — N(C_2H_5)_2$$

(vi)



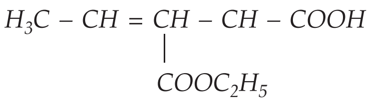
(vii) $(CH_3)_2C(Cl)CH_2CO_2CH_3$

(viii)



(ix) $(CH_3)_3CCOCl$

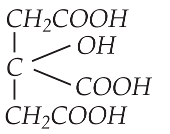
(x)



$$H_3C - CH = CH - \underset{\underset{COOC_2H_5}{|}}{CH} - COOH$$

(xi) $N \equiv CCH_2CH_2CH_2CH_2C \equiv N$

(xii)



Solution. The IUPAC names of the compounds are as follows:

(i) Propenenitrile
(ii) Cyclohexyl propanoate
(iii) 2-Butenamide
(iv) Cyclopropane carboxylic propanoic anhydride
(v) N, N-Diethylpropanamide
(vi) Butanedioic anhydride
(vii) Methyl-3-chloro-3-methylbutanoate
(viii) Ethyl cyclohexyl carboxylate
(ix) 2,2-Dimethylpropanoyl chloride
(x) 2-Carboethoxy-pent-3-enoic acid
(xi) Hexanedinitrile
(xii) 3-Carboxy-3-hydroxy-1, 5-pentanedioc acid

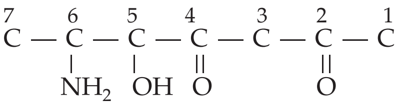
Problem 4. *Write structural formulae of the following compounds stepwise:*

(a) *6-amino 5-hydroxyheptane-2, 4-dione.*
(b) *4-cyno-3-methoxybutanoic acid.*
(c) *N, N-diethyl amino-3-ethoxy, 2-2 difluoro, 4-nitropentane.*

Solution.

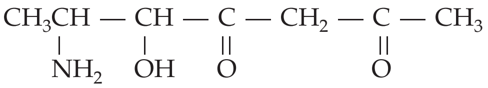
(a) **Step (i)** $C — C — C — C — C — C — C$

Step (ii)



$$\overset{7}{C} — \underset{\underset{NH_2}{|}}{\overset{6}{C}} — \underset{\underset{OH}{|}}{\overset{5}{C}} — \underset{\underset{O}{\|}}{\overset{4}{C}} — \overset{3}{C} — \underset{\underset{O}{\|}}{\overset{2}{C}} — \overset{1}{C}$$

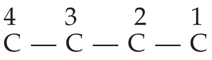
Satisfying the tetravalency of each carbon, the structure is:



$$CH_3\underset{\underset{NH_2}{|}}{CH} — \underset{\underset{OH}{|}}{CH} — \underset{\underset{O}{\|}}{C} — CH_2 — \underset{\underset{O}{\|}}{C} — CH_3$$

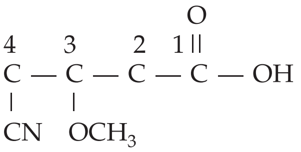
(b) **Step (i)** $C — C — C — C$

Step (ii)



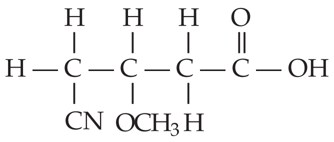
$$\overset{4}{C} — \overset{3}{C} — \overset{2}{C} — \overset{1}{C}$$

Step (iii)



$$\underset{\underset{CN}{|}}{\overset{4}{C}} — \underset{\underset{OCH_3}{|}}{\overset{3}{C}} — \overset{2}{C} — \overset{\overset{O}{\|}}{\overset{1}{C}} — OH$$

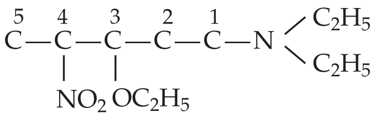
Thus, the compound is



$$H — \underset{\underset{CN}{|}}{\overset{\overset{H}{|}}{C}} — \underset{\underset{OCH_3}{|}}{\overset{\overset{H}{|}}{C}} — \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} — \overset{\overset{O}{\|}}{C} — OH$$

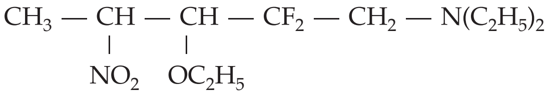
(c) **Step (i)** $C — C — C — C — C$

Step (ii)



$$\overset{5}{C} — \underset{\underset{NO_2}{|}}{\overset{4}{C}} — \underset{\underset{OC_2H_5}{|}}{\overset{3}{C}} — \overset{2}{C} — \overset{1}{C} — N\begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix}$$

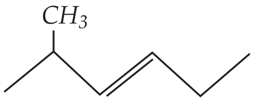
Thus, the compound is



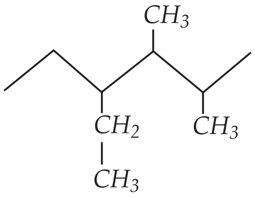
$$CH_3 — \underset{\underset{NO_2}{|}}{CH} — \underset{\underset{OC_2H_5}{|}}{CH} — CF_2 — CH_2 — N(C_2H_5)_2$$

Problem 5. *Give IUPAC names of the following:*

(i)

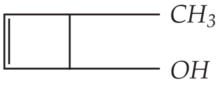


(ii)

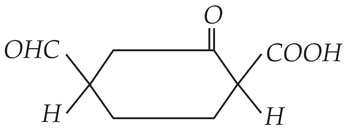


(iii)

(iv)

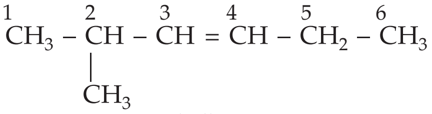


(v)



Solution. The normal structures and IUPAC names corresponding to bond line structures are as follows:

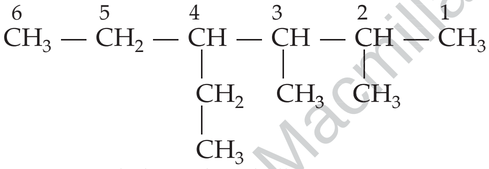
(i)



$$\overset{1}{CH_3} - \underset{\underset{CH_3}{|}}{\overset{2}{CH}} - \overset{3}{CH} = \overset{4}{CH} - \overset{5}{CH_2} - \overset{6}{CH_3}$$

2-Methylhex-3-ene

(ii)



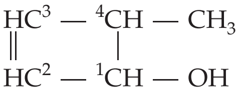
$$\overset{6}{CH_3} — \overset{5}{CH_2} — \underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{\overset{4}{CH}} — \underset{\underset{CH_3}{|}}{\overset{3}{CH}} — \underset{\underset{CH_3}{|}}{\overset{2}{CH}} — \overset{1}{CH_3}$$

4-Ethyl-2, 3-dimethylhexane

(iii) $\overset{7}{H_2C} = \overset{6}{CH} - \overset{5}{CH} = \overset{4}{CH} - \overset{3}{CH} = \overset{2}{CH} - \overset{1}{CHO}$

2, 4, 6-Heptatrienal

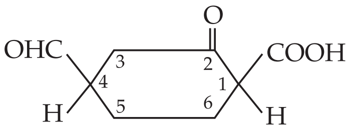
(iv)



$$\begin{array}{l} HC^3 — {}^4CH — CH_3 \\ \| \qquad\quad | \\ HC^2 — {}^1CH — OH \end{array}$$

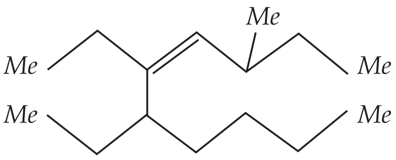
4-Methyl cyclo but-2-en-1-ol

(v)

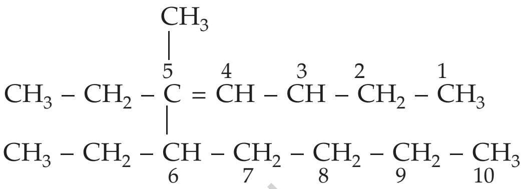


4-Formyl-2-oxocyclohexane-1-carboxylic acid

Problem 6. *Give the IUPAC name of the following compound:*



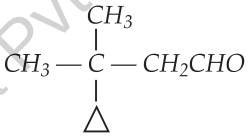
Solution. This is the bond line notation of the compound. Its structure can be drawn as:



$$\begin{array}{l} CH_3 - CH_2 - \overset{\overset{CH_3}{|}}{\overset{5}{C}} = \overset{4}{CH} - \overset{3}{CH} - \overset{2}{CH_2} - \overset{1}{CH_3} \\ \qquad\qquad\quad | \\ CH_3 - CH_2 - \underset{6}{CH} - \underset{7}{CH_2} - \underset{8}{CH_2} - \underset{9}{CH_2} - \underset{10}{CH_3} \end{array}$$

5,6-Diethyl-5-methyl-4-decene

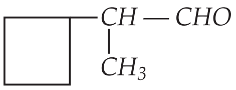
Problem 7. *Give the IUPAC name for the amine.*



Solution. 3-Cyclo propyl-3-methyl butanal

Problem 8. *Give the IUPAC names of the following:*

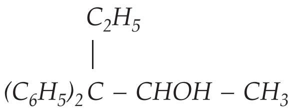
(i)



(ii) $C_6H_5 - CH_2 - C \equiv CH$

(iii) $(CH_3)_2C(CCl_3)_2$

(iv)



$$(C_6H_5)_2\overset{\overset{C_2H_5}{|}}{C} - CHOH - CH_3$$

Solution.

(i) 2-Cyclobutylpropan-1-al,

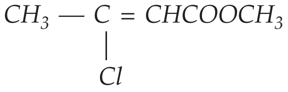
(ii) 3-Phenylprop-1-yne,

(iii) 1, 1, 1, 3, 3, 3-Hexachloro-2, 2-dimethyl- propane,

(iv) 3, 3-Diphenylpentan-2-ol.

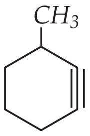
Problem 9. *Write IUPAC name of the following compounds:*

(i)

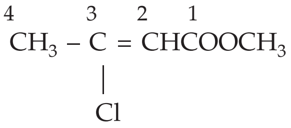


$$CH_3 — \underset{\underset{Cl}{|}}{C} = CHCOOCH_3$$

(ii)

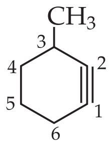


Solution.

(*i*) 

$$\overset{4}{CH_3} - \underset{\displaystyle\overset{|}{Cl}}{\overset{3}{C}} = \overset{2}{C}H\overset{1}{C}OOCH_3$$

Methyl-(3-chloro)-but-2-ene-oate

(*ii*) 

3-Methylcyclohexyne

Problem 10. *The silver salt of an unknown alkyne contains 67.08% of silver. Assuming that no other functional groups are present, what is the structure of alkyne?*

Solution.

$\because$ 67.08 g silver ≡ 100 g silver salt of alkyne

$\therefore$ 108 g silver = $\frac{100 \times 108}{67.08}$ g

≡ 161 g silver salt of alkyne

RC ≡ CH is equal to RC ≡ CAg – Ag + H

$\therefore$ Molar mass of alkyne ≡ Molar mass of silver salt of alkyne – 108 + 1

or Molar mass of alkyne ≡ 161 – 108 + 1 ≡ 54 g

The general formula of alkyne is C_nH_{2n-2}

$\therefore$ $12n + 2n - 2 = 54$ or $14n - 2 = 54$

or $14n = 56$ or $n = 4$.

Thus, alkyne is C_4H_6, *i.e.* 1—Butyne. It structural formula is

$$CH_3–CH_2–C \equiv CH.$$

Problem 11. *Compound (A) with molecular weight 108 contained 88.89% C and 11.11% H. It gave white precipitate with ammoniacal silver nitrate. Complete hydrogenation of (A) gave another compound (B) with molecular weight 112. Oxidation of (X) gave an acid with equivalent weight 128. Decarboxylation of this acid gave cyclohexane. Give structures of (A) and (B) and write the equations of the reactions involved.*

Solution. Calculation of empirical formula

Elements	*Percentage*	*Atomic ratio*	*Simplest ratio*	*Simple whole no. ratio*
C	88.89	$\frac{88.89}{12}$ = 7.4	$\frac{7.4}{7.4} = 1$	2
H	11.11	$\frac{11.11}{1}$ = 11.11	$\frac{11.11}{7.4} = 1.5$	3

Empirical formula: C_2H_3.

Calculation of molecular formula

$\therefore$ Empirical formula = C_2H_3

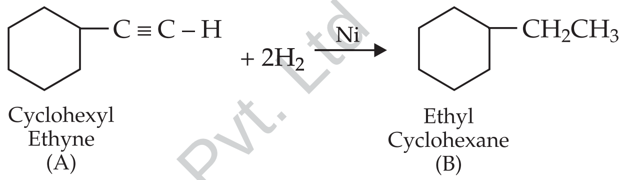
Empirical formula wt. = 2 × 12 + 1 × 3 = 27

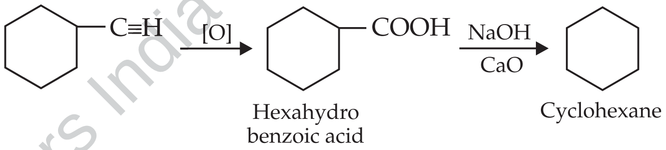
Molecular wt. = 108

$$n = \frac{108}{27} = 4$$

$\therefore$ Molecular formula = $(C_2H_3)_4C_8H_{12}$ (A)

As the hydrocarbon (A) gives white ppt. with $AgNO_3$ it should be an alkyne which on hydrogenation should give C_8H_{16} (B) having molecular weight 112. Oxidation of (A) gave an acid having equivalent weight 128 which on decarboxylation gave cyclohexane. Hence, (A) is a hydrocarbon having six membered ring and an unsaturated side chain. The structures of A and B and the reactions involved are:





Problem 12. *An acid (A) contains carbon = 40.7%, hydrogen = 5.1% and its silver salt contains 65.1% silver. The ethyl ester of (A) has V.D. of 87. What structure (A) may have? How would you distinguish between isomers?*

Solution. (*i*) Determination of the empirical formula of A

Elements	*Relative no. of element*	*Simplest ratio*	*Whole no. ratio*
C	$\frac{40.7}{12} = 3.39$	1	2
H	$\frac{5.1}{1} = 5.1$	1.5	3
O	$\frac{54.2}{16} = 3.4$	1	2

$\therefore$ Empirical formula of the acid is $C_2H_3O_2$.

(*ii*) Determination of the molecular formula

$$\frac{\text{Wt. of silver salt}}{\text{Wt. of silver}} = \frac{\text{Eq. wt. of silver salt}}{\text{Eq. wt. of silver}}$$

$$\frac{100}{65.1} = \frac{\text{Eq. wt. of silver salt}}{108}$$

$\therefore$ Eq. wt. of silver salt = $\frac{100}{65.1} \times 108 = 165.89$

Eq. wt. of the acid = 165.89 – 108 + 1

= 58.89

Molecular weight of ethyl ester = 87 × 2 = 174

The acid is dibasic because molecular weight of ethyl group is only 29.

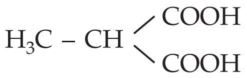
Thus, molecular weight of the acid = 58.89 × 2

= 117.78

∴ Empirical formula weight = 59

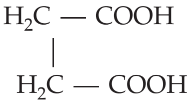
∴ Mol. formula of acid = $(C_2H_3O_2)_2 = C_4H_6O_4$

Thus, the acid (A) is



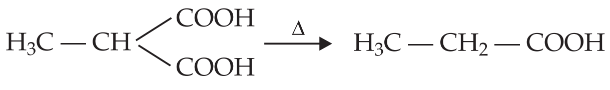
$H_3C-CH(COOH)_2$

The isomer of A is

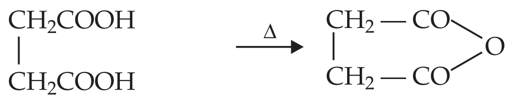


$HOOC-CH_2-CH_2-COOH$

The two isomers may be distinguished by the action of heat.



Methyl malonic acid (A) Propanoic acid



Succinic acid (B) Succinic Anhydride

Problem 13. *An acid of molecular mass 104 contains 34.6% carbon and 3.85% hydrogen. 3.812 mg of the acid required 7.33 cm³ of 0.01 N NaOH for neutralization. Suggest a structure for the acid.*

Solution.

(*i*) Percentage of carbon = 34.6%

(*ii*) Percentage of hydrogen = 3.85%

(*iii*) Percentage of oxygen = 100 – (34.6 + 3.85)

= 100 – 38.45 = 61.55%

(*iv*) **To derive empirical formula**

Element	Percentage	*Relative no. of atoms*	*Simplest ratio*	*Simplest whole no. ratio*
C	34.6	$\frac{34.6}{12} = 2.88$	$\frac{2.88}{2.88} = 1$	3
H	3.85	$\frac{3.85}{1} = 3.85$	$\frac{3.85}{2.88} = 1.33$	4
O	61.55	$\frac{61.55}{16} = 3.85$	$\frac{3.85}{2.88} = 1.33$	4

Empirical formula: $C_3H_4O_4$

(*v*) **Molecular formula:**

7.33 cm³ of 0.01 N NaOH required acid = 0.0038 g

1000 cm³ of 1 N NaOH will require acid

$$= \frac{0.0038 \times 1000}{7.33 \times 0.01} = 52 \text{ g}$$

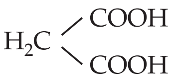
But 1000 mL of 1 N NaOH solution contain 1 gram equivalent of the base which must react with a gram equivalent of the acid.

∴ Equivalent weight of the acid = 52

Molecular mass of the acid = 104

$$\text{Basicity of acid} = \frac{104}{52} = 2$$

The acid is a dibasic acid. Therefore, the structural formula of the acid must be



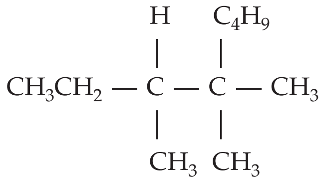
$H_2C(COOH)_2$

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. The IUPAC name of $CH_3OC_2H_5$ is
   (*a*) Methyl ethyl ether (*b*) Ethyl methyl ether
   (*c*) Methoxyethane (*d*) Ethoxymethane
2. $CH_3CH_2CH_2CH(CH=CH_2)CH_2CH_2CH_3$ is
   (*a*) 4-Ethenylheptane (*b*) 3-*n*-Propyl-1-hexene
   (*c*) 4-Ethenylhexane (*d*) 3-Ethenylheptane
   (*e*) Non-4-ene
3. The IUPAC name of *tert*-butyl chloride is
   (*a*) 4-Chlorobutane
   (*b*) 2-Chlorobutane
   (*c*) 1-Chloro-3-methylpropane
   (*d*) 2-Chloro-2-methylpropane
4. The IUPAC name of acraldehyde is
   (*a*) Prop-2-en-1-al (*b*) Propenylaldehyde
   (*c*) But-2-en-1-al (*d*) Propenal
5. The IUPAC name of

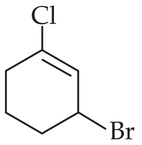


$CH_3CH_2-C(H)(CH_3)-C(C_4H_9)(CH_3)-CH_3$

   (*a*) 3, 4, 4-Trimethylheptane
   (*b*) 3, 4, 4-Trimethyloctane
   (*c*) 2-Butyl-2-methyl-3-ethylbutane
   (*d*) 2-Ethyl-3, 3-dimethylheptane

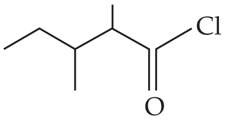
6. The IUPAC name of $CH_3CH=CHCOOC_2H_5$ is
   (*a*) Ethyl but-1-enoate
   (*b*) Ethyl but-2-enoate
   (*c*) Ethyl prop-2-enoate
   (*d*) None of these

7. The IUPAC name of the compound shown below is



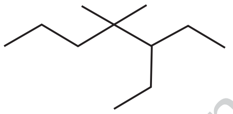
(*a*) 2-bromo-6-chlorocyclohex-1-ene
(*b*) 6-bromo-2-chlorocyclohexene
(*c*) 3-bromo-1-chlorocyclohexene
(*d*) 1-bromo-3-chlorocyclohexene

8. The IUPAC name of C_6H_5COCl is
(*a*) chlorobenzyl ketone
(*b*) benzene chloroketone
(*c*) benzene carbonyl chloride
(*d*) chlorophenyl ketone.

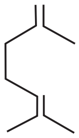
9. The IUPAC name of  is

(*a*) 2,3-dimethylpentanoyl chloride
(*b*) 3,4-dimethylpentanoyl chloride
(*c*) 1-chloro-1-oxo-2,3-dimethylpentane
(*d*) 2-ethyl-3-methylbutanoyl chloride

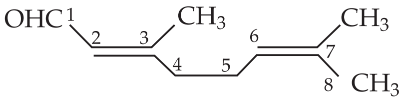
10. The general molecular formula, which represents the homologous series of alkanols is
(*a*) $C_nH_{2n+2}O$ (*b*) $C_nH_{2n}O_2$
(*c*) $C_nH_{2n}O$ (*d*) $C_nH_{2n+1}O$.

11. The IUPAC name of  is

(*a*) 3-ethyl-4-4-dimethylheptane
(*b*) 1,1-diethyl-2,2-dimethylpentane
(*c*) 4,4-dimethyl-5,5-diethylpentane
(*d*) 5,5-diethyl-4,4-dimethylpentane

12. The correct IUPAC name of the compound  is
(*a*) 1, 1, 5-Trimethyl-1, 6-hexadiene
(*b*) 2, 6-Dimethyl-2, 6-heptadiene
(*c*) 2, 6-Dimethyl-1, 5-heptadiene
(*d*) None of the above.

13. Assign IUPAC name for the compound

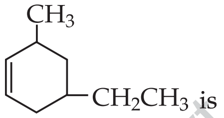


(*a*) 3, 7-Dimethylhepta-2, 6-dien-1-al
(*b*) 3, 7-Dimethylocta-2-6-dien-1-al
(*c*) 2, 6-Dimethylocta-2, 6-dien-1-al
(*d*) 3, 7-Dimethylocta-2, 6-dienal

14. What is the IUPAC name of the compound
—CONH — C_6H_5?
(*a*) Phenyl benzamide
(*b*) N-Cyclohexyl benzamide
(*c*) N-phenyl cyclohexane carboxamide or cyclohexane carboxanilide
(*d*) None of the above

15. The compound norborane is known by which of the following names?
(*a*) Bicyclo-2-[2. 2. 2] octane
(*b*) Bicyclo-[2. 2. 1] octane
(*c*) Bicyclo-[1. 2. 1] octane
(*d*) Bicyclo-[1. 1. 1] octane

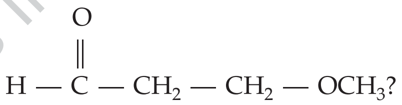
16. The systematic name of the compound



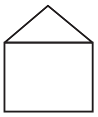
is

(*a*) 1-Methyl-5-ethylcyclohex-2-ene
(*b*) 5-Ethyl-3-methylcyclohex-1-ene
(*c*) 4-Ethyl-6-methylcyclohex-1-ene
(*d*) 1-Ethyl-5-methylcyclohex-1-ene

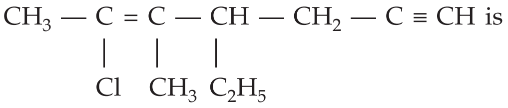
17. What is the IUPAC name of


$$H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-OCH_3?$$

(*a*) 2-Formyl methoxy ethane
(*b*) Methoxy propanal
(*c*) 2-Methoxy propanal
(*d*) 3-Methoxy propanal

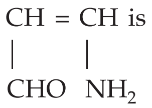
18. The IUPAC name of the compound  is
(*a*) Bicyclo (2, 1, 0) pentane
(*b*) 1, 2-Cyclopropyl cyclobutane
(*c*) Cyclo pentane (4, 3) annulene
(*d*) 1, 2-Methylene cyclobutane

19. The IUPAC name of


$$CH_3-\underset{\displaystyle Cl}{\underset{|}{C}}=\underset{\displaystyle CH_3}{\underset{|}{C}}-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2-C\equiv CH \text{ is}$$

(*a*) 6-Chloro-4-ethyl-5-methyl hept-5-en-1-yne
(*b*) 6-Chloro-4-ethyl-5-methyl-hept-1-yn-5-ene
(*c*) 2-Chloro-4-ethyl-3-methyl-hept-2-ene-6-yne
(*d*) 2-Chloro-4-ethyl-3-methyl hept-6-yn-2-ene

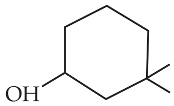
20. The name of


$$\underset{\displaystyle CHO}{\underset{|}{CH}}=\underset{\displaystyle NH_2}{\underset{|}{CH}} \text{ is}$$

(*a*) 1-Aminoprop-2-enal
(*b*) 3-Aminoprop-2-enal

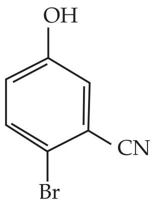
(*c*) 1-Amino-2-formylethene
(*d*) 3-Amino-1-oxoprop-2-ene

21. The IUPAC name of the following compound is



(*a*) 3, 3-Dimethyl-1-hydroxy cyclohexane
(*b*) 1, 1-Dimethyl-3-hydroxy cyclohexane
(*c*) 3, 3-Dimethyl-1-cyclohexanol
(*d*) 1, 1-Dimethyl-3-cyclohexanol

22. The IUPAC name of the following compound is



(*a*) 4–bromo–3–cyanophenol
(*b*) 2–bromo–5–hydroxybenzonitrile
(*c*) 2–cyano–4–hydroxybromobenzene
(*d*) 6–bromo–3–hydroxybenzonitrile

23. The IUPAC name of the compound having the formula $CH \equiv C - CH = CH_2$ is
(*a*) 1–butyne–3–ene (*b*) but–1–yne–3–ene
(*c*) 1–butene–3–yne (*d*) 3–butene–1–yne

24. The IUPAC name of neopentane is
(*a*) 2–methylbutane
(*b*) 2, 2–dimethylpropane
(*c*) 2–methylpropane
(*d*) 2, 2–dimethylbutane

25. The IUPAC name of the compound $CH_3CH = CH \equiv CH$ is
(*a*) Pent–4–yn–2–ene (*b*) Pent–3–en–1–yne
(*c*) Pent–2–en–4–yne (*d*) Pent–1–yn–3–ene

26. The number of atoms in Cr and O are 4.8×10^{10} and 9.6×10^{10} respectively. Its empirical formula is
(*a*) Cr_2O_3 (*b*) CrO_2
(*c*) Cr_2O_8 (*d*) None

27. Empirical formula of a hydrocarbon containing 80% carbon and 20% hydrogen is
(*a*) CH (*b*) CH_2
(*c*) CH_3 (*d*) CH_4

28. An organic compound containing C, H and N gave the following analysis. What would be its empirical formula? C = 40%, H = 13.33%, N = 46.67%.
(*a*) C_2H_7N (*b*) $C_2H_7N_2$
(*c*) CH_4N (*d*) CH_5N

29. On analysis, a compound was found to contain 50% of element A (at. mass 12.5) and 50% of element B (at. mass 37.5). The simplest formula of the compound is:
(*a*) AB (*b*) A_2B
(*c*) A_3B (*d*) A_2B_3

30. An organic compound containing C, H and N gave the following analysis: C = 40%, H = 13.34% and N = 46.67%. Its empirical formula would be
(*a*) CHN (*b*) C_2H_2N
(*c*) CH_4N (*d*) C_2H_7N

31. Empirical formula of a compound is CH_2O. If its molecular weight is 180, then the molecular formula of the compound is
(*a*) $C_6H_{12}O_6$ (*b*) $C_5H_{10}O_5$
(*c*) $C_3H_6O_3$ (*d*) $C_4H_8O_4$

32. Which of the following has molecular weight of 92?
(*a*) Toluene (*b*) Benzene
(*c*) Ethylene (*d*) Propene

33. Empirical formula of a compound is CH_2O. If its vapour density is 90, then the molecular formula of the compound is
(*a*) $C_5H_{10}O_5$ (*b*) $C_3H_6O_3$
(*c*) $C_6H_{12}O_6$ (*d*) $C_4H_8O_4$

34. An organic compound contains 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Molecular formula of the compound is
(*a*) $C_3H_5O_2$ (*b*) $C_6H_{10}O_4$
(*c*) $C_3H_{10}O_2$ (*d*) $C_4H_{10}O_2$

35. The empirical formula of an acid is CH_2O_2, the probable molecular formula of the simplest acid may be
(*a*) CH_2O (*b*) CH_2O_2
(*c*) $C_2H_4O_2$ (*d*) $C_3H_6O_4$

(B) Fill in the Blanks

Fill in the blank spaces:

1. A very pure form of amorphous carbon is called ....
2. Hexane is an .... compound while benzene is an .... compound.
3. Each member of a .... series differs from its adjacent member by a common difference of ....
4. Aliphatic cyclic compounds are called .... compounds.
5. Compounds of carbon and a metal are called ....
6. The isomer with a methyl group attached to the second carbon in alkane is given the prefix ....
7. IUPAC stands for ....

8. One recently discovered allotrope of carbon (*e.g.*, C_{60}) is commonly known as ....
9. The IUPAC name of succinic acid is ....

(C) True/False Statements

Write T for true and F for false statements:

1. LPG is mainly propane.
2. The IUPAC names of various classes of organic compounds are derived from alkenes.
3. Organic compounds contain ionic linkages.
4. Propanoic acid and methyl ethanoate are isomers.
5. The general IUPAC name for the compounds having general formula $RCONH_2$ is amino-alkane.
6. The large number of organic compounds is due to catenation.
7. The first organic compound was synthesized in laboratory by Wohler.
8. Hexane is an alicyclic hydrocarbon.

(D) Assertion-Reason Type Questions

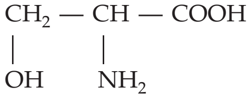
The question below (1 to 4) consist of an Assertion (A) in column 1 and the Reasons (R) in column 2. Use the following key to choose the appropriate answer.

(*a*) Both the *Assertion* and *Reason* are *correct* and the *Reason* is the correct *explanation* of the *Assertion*.

(*b*) Both the *Assertion* and the *Reason* are *correct* but the *Reason* is *not* the correct *explanation* of the *Assertion*.

(*c*) The *Assertion* is correct but the *Reason* is *incorrect*.

(*d*) The *Assertion* is *incorrect* but the *Reason* is *correct*.

Assertion (Column 1)	**Reason (Column 2)**
1. Organic compounds contain electrovalent linkage.	1. Buckminsterfullerene is the recently discovered allotrope of carbon.
2. Compounds of a metal with carbon are called carbides.	2. IUPAC name for the compound  $\underset{OH}{CH_2}-\underset{NH_2}{CH}-COOH$ is 1-Hydroxy-2-amino propan-3-oic acid.
3. Organic compounds show the property of catenation.	3. Carbon-carbon bond is associated with high bond energy.
4. Any two successive members of a homolo-groups series differ by $-CH_2$ group.	4. Most of the organic compounds can be obtained from animal or plant origin.

(E) Matching Questions

Match the items of Column I with appropriate items of Column II:

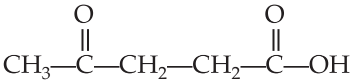
Column I	**Column II**
1. Allotropes	*a*. Dimethyl ether and ethyl alcohol
2. Homologues	*b*. Diamond and graphite
3. Isomers	*c*. Methanal and ethanal
4. Freon	*d*. C_5H_{10}
5. Alicyclic compound	*e*. CF_2Cl_2

SOME ADDITIONAL QUESTIONS

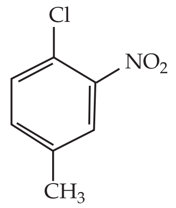
I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. Which of the following is the correct IUPAC name?
   (*a*) 3-Ethyl-4, 4-dimethylheptane
   (*b*) 4, 4-Dimethyl-3-ethylheptane
   (*c*) 5-Ethyl-4, 4-dimethylheptane
   (*d*) 4, 4-Bis(methyl)-3-ethylheptane

2. The IUPAC name for  $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$ is
   (*a*) 1-hydroxypentane-1, 4-dione
   (*b*) 1, 4-dioxopentanol
   (*c*) l-carboxybutan-3-one
   (*d*) 4-oxopentanoic acid

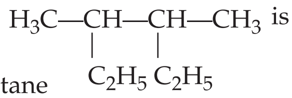
3. The IUPAC name for



   (*a*) 1-Chloro-2-nitro-4-methylbenzene
   (*b*) l-Chloro-4-methyl-2-nitrobenzene
   (*c*) 2-Chloro-1-nitro-5-rnethylbenzene
   (*d*) *m*-Nitro-p-chlorotoluene

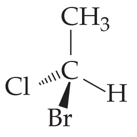
4. Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with asterisk is most electronegative?
   (*a*) $CH_3-CH_2-{}^{*}CH_2-CH_3$
   (*b*) $CH_3-{}^{*}CH\equiv CH-CH_3$
   (*c*) $CH_3-CH_2-C\equiv {}^{*}CH$
   (*d*) $CH_3-CH_2-CH\equiv {}^{*}CH_2$

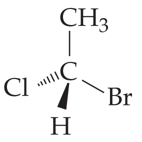
5. In which of the following, functional group isomerism is not possible?
   - (*a*) Alcohols
   - (*b*) Aldehydes
   - (*c*) Alkyl halides
   - (*d*) Cyanides

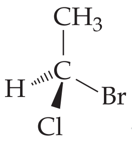
6. Correct IUPAC name for  $H_3C—CH(C_2H_5)—CH(C_2H_5)—CH_3$ is
   - (*a*) 2-ethyl-3-methylpentane
   - (*b*) 3, 4-dimethylhexane
   - (*c*) 2-*sec*-butylbutane
   - (*d*) 2, 3-dimethylbutane

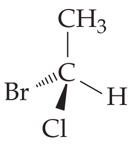
7. Which of the following compounds contain all the carbon atoms in the same hybridisation state?
   - (*a*) $H — C \equiv C — C \equiv C — H$
   - (*b*) $CH_3 — C \equiv C — CH_3$
   - (*c*) $CH_2 = C = CH_2$
   - (*d*) $CH_2 = CH — CH = CH_2$

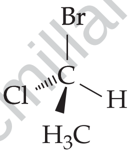
8. In which of the following representations given below spatial arrangement of group/atom different from that given in structure 'A'?


(A)

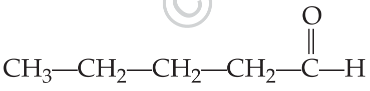
(*a*) 

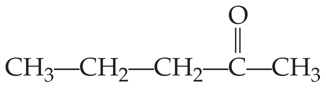
(*b*) 

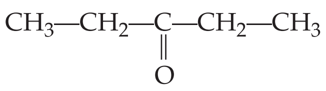
(*c*) 

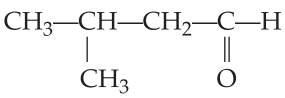
(*d*) 

Note: *Consider the following four compounds for answering questions 9 and 10.*

I.  $CH_3—CH_2—CH_2—CH_2—C(=O)—H$

II.  $CH_3—CH_2—CH_2—C(=O)—CH_3$

III.  $CH_3—CH_2—C(=O)—CH_2—CH_3$

IV.  $CH_3—CH(CH_3)—CH_2—C(=O)—H$

9. Which of the following pairs are position isomers?
   - (*a*) I and II
   - (*b*) II and III
   - (*c*) II and IV
   - (*d*) III and IV

10. Which of the following pairs are **not** functional group isomers?
    - (*a*) II and III
    - (*b*) II and IV
    - (*c*) I and IV
    - (*d*) I and II

11. Which of the following compounds have tertiary hydrogen atoms?
    - (*a*) $(CH_3)_3CCH_2CH_3$
    - (*b*) $(CH_3)_2CHCH_2CH_3$
    - (*c*) $(CH_3)_2CHCH(CH_3)_2$
    - (*d*) $(CH_3)_3CH$

12. Which of the following forms a homologous series?
    - (*a*) Ethane, ethylene, acetylene
    - (*b*) Ethane, propane, butanone
    - (*c*) Methanal, ethanal, propanal
    - (*d*) Butane, 2-methylbutane, 2, 3-dimethylbutane

13. The huge number of organic compounds occur due to the fact that
    - (*a*) carbon is tetravalent
    - (*b*) carbon possesses property of catenation
    - (*c*) carbon compounds exhibit isomerism
    - (*d*) carbon can form multiple bonds with O, N and S.

14. Which of the following compounds have secondary carbon atoms?
    - (*a*) Cyclohexane
    - (*b*) 2, 3-Dimethylbutane
    - (*c*) 2-Methylpentane
    - (*d*) Neo-pentane

II. Assertion-Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

1. ***Assertion (A):*** Pent-1-ene and pent-2-ene are position isomers.

   Reason (R): Position isomers differ in the position of functional group or a substituent.
   - (*i*) Both A and R are correct and R is the correct explanation of A.
   - (*ii*) Both A and R are correct but R is not the correct explanation of A.
   - (*iii*) Both A and R are not correct.
   - (*iv*) A is not correct but R is correct.

2. ***Assertion (A):*** All the carbon atoms in $H_2C = C = CH_2$ are sp^2 hybridised.

Reason (R): In this molecule all the carbon atoms are attached to each other by double bonds.

(*i*) Both A and R are correct and R is the correct explanation of A.

(*ii*) Both A and R are correct but R is not the correct explanation of A.

(*iii*) Both A and R are not correct.

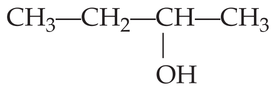
(*iv*) A is not correct but R is correct.

III. Short Answer Type Questions

Note: *Consider structures I to VII and answer the questions 1-4.*

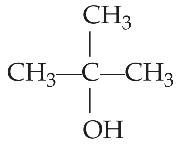
I. $CH_3 — CH_2 — CH_2 — CH_2 — OH$

II.



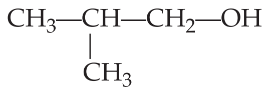
$CH_3—CH_2—\underset{\large OH}{\underset{|}{CH}}—CH_3$

III.



$CH_3—\overset{\large CH_3}{\overset{|}{\underset{\large OH}{\underset{|}{C}}}}—CH_3$

IV.

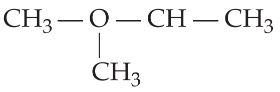


$CH_3—\underset{\large CH_3}{\underset{|}{CH}}—CH_2—OH$

V. $CH_3 — CH_2 — O — CH_2 — CH_3$

VI. $CH_3 — O — CH_2 — CH_2 — CH_3$

VII.

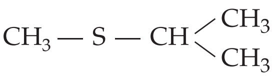


$CH_3 — O — \underset{\large CH_3}{\underset{|}{CH}} — CH_3$

1. Which of the above compounds form pairs of metamers?
2. Identify the pairs of compounds which are functional group isomers.
3. Identify the pairs of compounds that represents position isomerism.
4. Identify the pairs of compounds that represents chain isomerism.
5. Compounds with same molecular formula but differing in their structures are said to be structural isomers. What type of structural isomerism is shown by

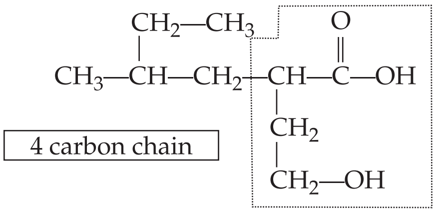
$CH_3 — S — CH_2 — CH_2 — CH_3$

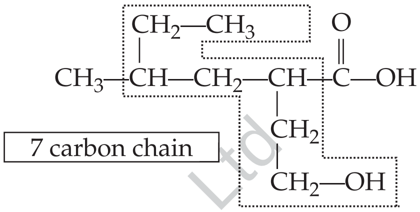
and

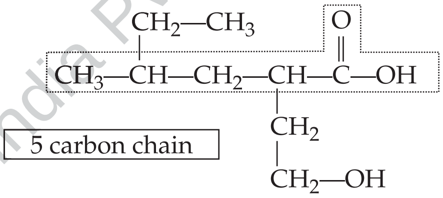


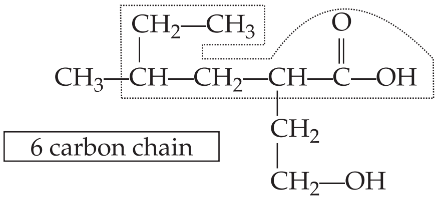
$CH_3 — S — CH\begin{matrix} ^{\diagup CH_3} \\ _{\diagdown CH_3} \end{matrix}$

6. Which of the following selected chains is correct to name the given compound according to IUPAC system?

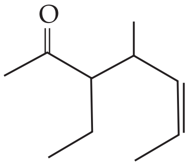


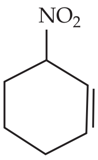






7. Name the compounds whose line formulae are given below:


(*i*)


(*ii*)

8. Write structural formulae for compounds named as:
   (*a*) 1-Bromoheptane
   (*b*) 5-Bromoheptanoic acid

ANSWERS

(A) Multiple Choice Questions

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

(B) Fill in the Blanks

1. sugar charcoal 2. aliphatic, aromatic 3. homologous, CH_2 4. alicyclic
5. carbides 6. iso 7. International Union of Pure and Applied Chemistry
8. Buckminster Fullerene 9. butanedioic acid

(C) True/False Statements

1. F 2. F 3. F 4. T 5. F 6. T 7. T 8. F

(D) Assertion-Reason Type Questions

I. 1. (*d*) 2. (*c*) 3. (*a*) 4. (*b*)

(E) Matching Questions

1. (*b*) 2. (*c*) 3. (*a*) 4. (*e*) 5. (*d*)

Some Additional Questions

I. Multiple Choice Questions

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

II. Assertion-Reason Type Questions

1. (*i*) 2. (*iv*)

11

CHAPTER

Hydrocarbons: Alkanes, Alkenes and Alkynes

LEARNING OBJECTIVES

Alkanes

- Structure, bonding, isomerism and nomenclature
  - Write the general formula for alkanes (C_nH_{2n+2}) and the correct formulae for any aliphatic alkane.
  - Describe the tetrahedral shape around each carbon atom in an alkane molecule using sp^3 hybridisation.
  - Explain that the principle type of isomerism in alkanes is structural isomerism and draw and name structural isomers for alkanes with the same chemical fourmula e.g. C_6H_{14}.
- Substitution reactions of alkanes
  - Describe the reactions of alkanes with chlorine.
  - Explain the mechanism of free radical substitution for the reaction of alkanes with chlorine (initiation, propagation and termination).

Alkenes

- Structure, bonding and isomerism
  - Explain the general formula of alkenes (C_nH_{2n}) and write correct formulae for any aliphatic alkene.
  - Apply the IUPAC rules to the nomenclature of simple alkenes.
  - Explain the alkenes are unsaturated hydrocarbons.
  - Explain that the $C=C$ is planar and describe the overlap of adjacent *p*-orbitals to form a p-bond using sp^2 hybridisation.
  - Explain that the p-bond is an area of high electron density.
  - Explain that alkenes exhibit E-Z isomerism because of the restricted rotation about the $C=C$ double bond.
  - Draw structure of E and Z isomers for simple alkenes.
- Addition reaction of alkenes
  - Describe the reactions of alkenes with Br_2, H_2SO_4 and HCl.
  - Explain the mechanism of electrophilic addition for the reaction of alkenes with Br_2, H_2SO_4 and HCl.
  - Explain that bromine can be used as a test for unsaturation.
  - Predict, using Markovnikov's rule, the products of addition of HCl to unsynmmetrical alkenes.
  - Explain the pattern of addition of HCl to unsymmetrical alkenes referring to the relative stabilities of primary, secondary and tertiary carbocation intermediates.
  - State the reaction conditions and equation for the industrial production of ethanol from ethene.
  - Describe how margarine is manufactured by catalytic hydrogenation of unsaturated vegetable oil.
- Polymerisation
  - Describe the addition polymerisation of alkenes, for examples, like the formation of poly(ethene), poly(propene), polytetrafluoroethene (PTFE), polyvinylchloride (PVC), polystyrene and natural and synthetic rubber.

  - State uses of polymers e.g. poly(ethene), poly(propene), polytetrafluorethene (PTFE), and polyvinylchloride (PVC).
  - Identify the repeating unit, the monomer unit, using the structure of the polymer.

Alkynes

- Structure, bonding and isomerism
  - State the general formula of alkynes (C_nH_{2n-2}) and write correct formulae for any alkyne.
  - Apply the IUPAC rules to the nomenclature of simple alkynes.
  - Explain that alkynes are unsaturated hydrocarbons.
  - Explain that the shape of ethyne is linear and describe the overlap of adjacent p-orbitals to form a 2p-bond by sp hybridisation.
- Source of ethyne
  - Describe the preparation of ethyne from natural gas.
  - State the uses of ethyne in oxy-acetylene torches and the manufacture of a variety of organic compounds.
- Addition reaction of alkynes
  - Describe the reactions of alkynes with H_2, Br_2 and HCl.
  - Explain the mechanism of electrophilic addition for the reaction of alkynes with H_2, Br_2, and HCl.
  - Compare and contrast the reactions of alkanes, alkenes and alkynes.

11.1 INTRODUCTION

Hydrocarbons are the parent organic compounds. All other compounds are considered to be derived from these hydrocarbons. Petroleum and natural gases are mixtures of hydrocarbons. LPG that we use for cooking is a mixture of butane and pentane. Marsh gas that occurs in mines is a hydrocarbon. Acetylene which is used as an illuminant and in welding is again a hydrocarbon. Halogen substituted hydrocarbons such as methylene dichloride, chloroform, iodoform and carbon tetrachloride are important compounds which find varied applications in the laboratory and industry. In this chapter, we shall discuss shapes and structures of hydrocarbons.

11.2 CLASSIFICATION OF HYDROCARBONS

On the basis of structure, hydrocarbons are divided broadly into the following two types:

1. *Acyclic or open chain hydrocarbons*
2. *Cyclic or closed chain hydrocarbons*

1. **Acyclic or Open Chain Hydrocarbons.** These compounds contain open chains of carbon atoms in their molecules. They are also called **aliphatic hydrocarbons**. They are further classified into three categories: (*i*) Alkanes, (*ii*) Alkenes, (*iii*) Alkynes.

An alkane *has only carbon-carbon single bond.* For example,

$CH_3 — CH_3$
Ethane

$CH_3 — CH_2 — CH_3$
Propane

$CH_3 - CH_2 - CH_2 - CH_3$
n-Butane

$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$
n-Hexane

An alkene *has at least one carbon-carbon double bond.* For example,

$CH_2 = CH_2$
Ethene

$CH_3 - CH = CH_2$
Propene

$CH_3 - CH = CH - CH_3$
But-2-ene

$CH_2 = CH - CH = CH_2$
1, 3-Butadiene

An alkyne *has at least one carbon-carbon triple bond.* For example,

$CH \equiv CH$ Ethyne

$CH_3 - C \equiv CH$ Propyne

$CH_3 - C \equiv C - CH_3$ But-2-yne

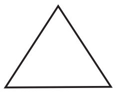
2. Cyclic or Closed Chain Hydrocarbons. Compounds containing closed chains or rings of carbon atoms in their molecules are called cyclic compounds. There are two types of cyclic compounds.

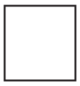
(*i*) *Alicyclic hydrocarbons*

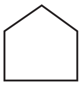
(*ii*) *Aromatic hydrocarbons*

(*a*) Alicyclic hydrocarbons. Hydrocarbons containing a ring of three or more carbon atoms and having properties similar to those of aliphatic hydrocarbons are called **alicyclic hydrocarbons**. Different types of alicyclic compounds are given below:

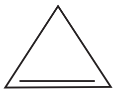
Cycloalkanes. *Saturated alicyclic hydrocarbons in which all the carbon atoms are joined by single covalent bonds are called* **cycloalkanes**. For example,

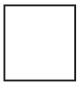

Cyclopropane

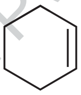

Cyclobutane


Cyclopentane

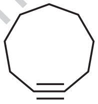
Cycloalkenes. *Unsaturated alicyclic hydrocarbons which contain a carbon-carbon double bond are called* **cycloalkenes**. For example,


Cyclopropene

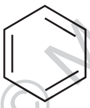

Cyclobutene

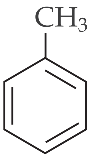

Cyclohexene

Cycloalkynes. *Unsaturated alicyclic hydrocarbons which contain one carbon-carbon triple bond are called* **cycloalkynes**. Compounds containing less than nine carbon atoms are unstable. Cyclononyne, which is a stable compound has the following structure:

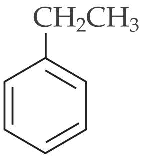

Cyclononyne

(*b*) Aromatic hydrocarbons – Arenes. *Hydrocarbons and their alkyl derivatives which contain one or more benzene rings either fused or isolated in their molecules are called* **aromatic hydrocarbons**. They are also called **arenes (aromatic alkenes)**. For example,

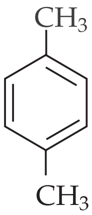

Benzene



Toluene

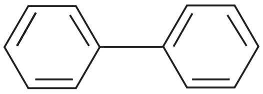


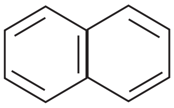
Ethylbenzene

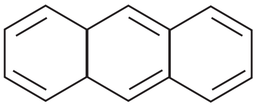


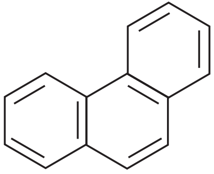
p-Xylene

Arenes may also contain two or more rings either separated or fused. For example,


Diphenyl


Naphthalene


Anthracene


Phenanthrene

All these arenes are also called *benzenoid compounds,* since they possess the characteristics of benzene. We will discuss about aromatic hydrocarbons in chapter 14.

11.3 CLASSIFICATION OF ALIPHATIC HYDROCARBONS ALKANES

Saturated hydrocarbons, *i.e.* hydrocarbons containing carbon-carbon single bonds can be either acyclic or cyclic. The *acyclic hydrocarbons are called* **paraffins**. They are relatively unreactive towards most of the reagents. In the IUPAC system, they are called **alkanes**. Their general formula is C_nH_{2n+2} where n = 1, 2, 3, ..., etc.

Cyclic saturated hydrocarbons are called **cycloalkanes** or **cycloparaffins**. Their general formula is C_nH_{2n} (*if monocyclic*) or C_nH_{2n-2} (*if bicyclic*) and so on. Here, n = 3, 4, 5, ..., etc., since a ring cannot be constructed with less than three carbon atoms.

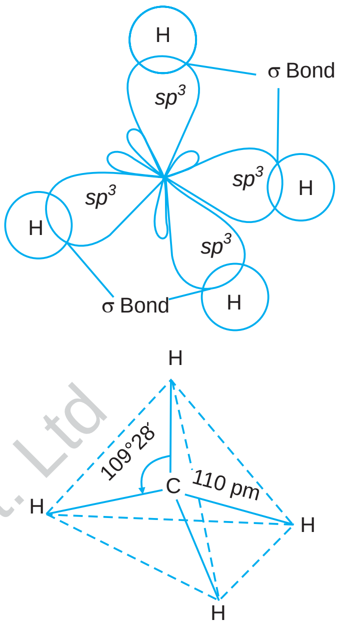


Fig. 11.1: *Orbital structure of methane*

Structure of alkanes. Alkanes contain only carbon-carbon and carbon-hydrogen single bonds, therefore, carbon in alkanes is sp^3-hybridized. Since a sp^3-hybridized carbon has four half-filled sp^3-orbitals, therefore it forms four σ-bonds. These four bonds are directed towards the corners of a regular tetrahedron, with the angle between any two adjacent bonds as 109° 28′ (*tetrahedral angle*).

Structure of methane (CH_4). In this molecule, carbon lies in the centre of the tetrahedron while the four hydrogens are present at the corners or vertices of the regular tetrahedron. This implies that each face of the tetrahedron is an equilateral triangle and has three bonds as shown in Fig. 11.1.

Simple representations of methane are given in Fig. 11.2 (*a*) and 11.2 (*b*).

In Fig. 11.2 (*a*), the thick solid (or heavy) line indicates a C–H bond lying above the plane of the paper (projecting towards the reader), a normal or ordinary line shows a C–H bond lying in the plane of the paper while the two dotted lines represent the C–H bonds lying below the plane of the paper.

Such a representation of a molecule in space is called a **spatial formula**.

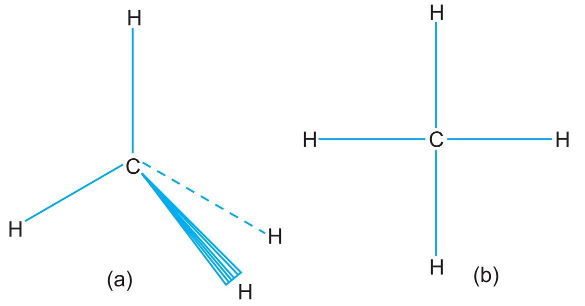


Fig. 11.2: *(a) Spatial formula of methane*
(b) Graphic formula of methane

Fig. 11.2 (*b*) is a two dimensional representation of a methane molecule. Such a representation is usually called as **graphic formula**. Such representation does not reveal the true geometry of the molecule but they are commonly used for most purposes since they are easy to draw.

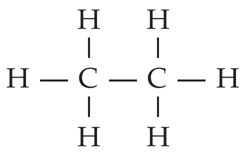
Orbital structure of ethane. (Structure of carbon-carbon single bond).

In the formation of ethane,

(*i*) One sp^3 hybrid of each of the two carbon atoms overlap axially to form a C–C sigma bond.

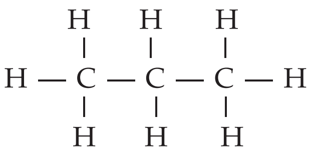
(*ii*) The remaining three sp^3 hybrid orbitals of each carbon atom overlap with the 1*s* orbital of hydrogen atom to form six C–H bonds, as shown in Fig. 11.3.

We can represent ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) by the following graphic formulae:



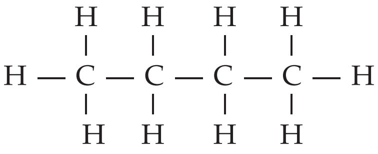
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & \text{—} & C & \text{—} & C & \text{—} & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Ethane



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & \text{—} & C & \text{—} & C & \text{—} & C & \text{—} & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

Propane



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & \text{—} & C & \text{—} & C & \text{—} & C & \text{—} & C & \text{—} & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

n-Butane

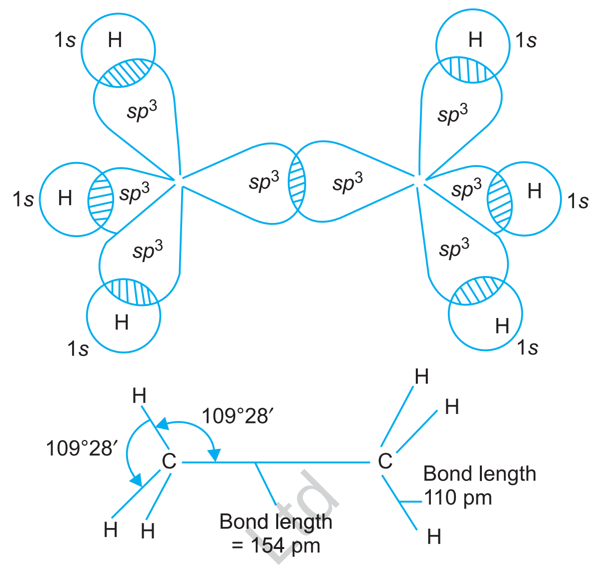


Fig. 11.3: *Orbital structure of ethane*

Still simpler representations for hydrocarbons are used, as given below:

$CH_3 — CH_3$
Ethane

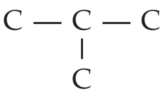
$CH_3 — CH_2 — CH_3$
Propane

$CH_3 — CH_2 — CH_2 — CH_3$
n-Butane

11.4 STRUCTURAL ISOMERISM IN ALKANES

In the first three members of the alkane family, the carbon atoms are linked to each other to form straight chains (C — C or C — C — C). However, in the next member butane (C_4H_{10}), there is a scope for branching *i.e.* there may be a straight chain or branched chain of carbon atoms as shown below:

C — C — C — C
(Straight chain)

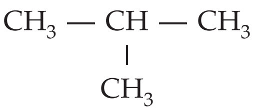


$$\begin{array}{ccccc} C & \text{—} & C & \text{—} & C \\ & & | & & \\ & & C & & \end{array}$$

(Branched chain)

The alkanes corresponding to these structures are called butane (*n*-butane) and 2-Methylpropane (isobutane).

$H_3C — CH_2 — CH_2 — CH_3$
n-butane



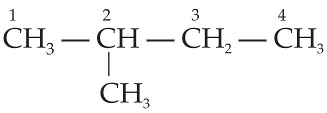
$$\begin{array}{ccccc} CH_3 & \text{—} & CH & \text{—} & CH_3 \\ & & | & & \\ & & CH_3 & & \end{array}$$

iso-butane

These are the examples of the **chain** isomers which may be defined as *the compounds having the same molecular formula but differing in the nature of the chains of the carbon atoms (straight or branched).*

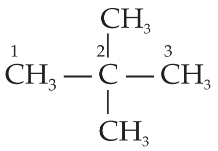
It may be noted that as the number of the carbon atoms in a molecule increases, the extent of branching, also increases accordingly. Thus, pentane (C_5H_{12}) has three chain isomers given below:

$CH_3 — CH_2 — CH_2 — CH_2 — CH_3$
Pentane



$$\begin{array}{ccccccc} \overset{1}{CH_3} & \text{—} & \overset{2}{CH} & \text{—} & \overset{3}{CH_2} & \text{—} & \overset{4}{CH_3} \\ & & | & & & & \\ & & CH_3 & & & & \end{array}$$

2–Methylbutane
(Isopentane)



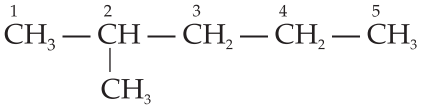
$$\begin{array}{ccccc} & & CH_3 & & \\ & & {}^{2}| & & \\ \overset{1}{CH_3} & \text{—} & C & \text{—} & \overset{3}{CH_3} \\ & & | & & \\ & & CH_3 & & \end{array}$$

2, 2–Dimethylpropane
(Neopentane)

Similarly, hexane (C_6H_{14}) has five chain isomers which are listed as follows:

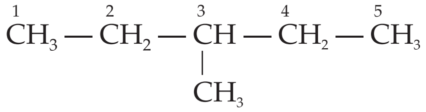
(*i*) $\mathrm{CH_3-CH_2-CH_2-CH_2-CH_2-CH_3}$

Hexane

(*ii*) 

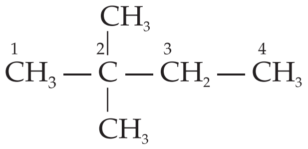
$$\overset{1}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{CH}}}-\overset{3}{\mathrm{CH_2}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_3}}$$

2–Methylpentane

(*iii*) 

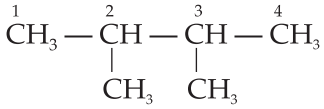
$$\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH_2}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{3}{\mathrm{CH}}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_3}}$$

3–Methylpentane

(*iv*) 

$$\overset{1}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{C}}}}-\overset{3}{\mathrm{CH_2}}-\overset{4}{\mathrm{CH_3}}$$

2, 2–Dimethylbutane

(*v*) 

$$\overset{1}{\mathrm{CH_3}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{2}{\mathrm{CH}}}-\underset{\underset{\mathrm{CH_3}}{|}}{\overset{3}{\mathrm{CH}}}-\overset{4}{\mathrm{CH_3}}$$

2, 3–Dimethylbutane

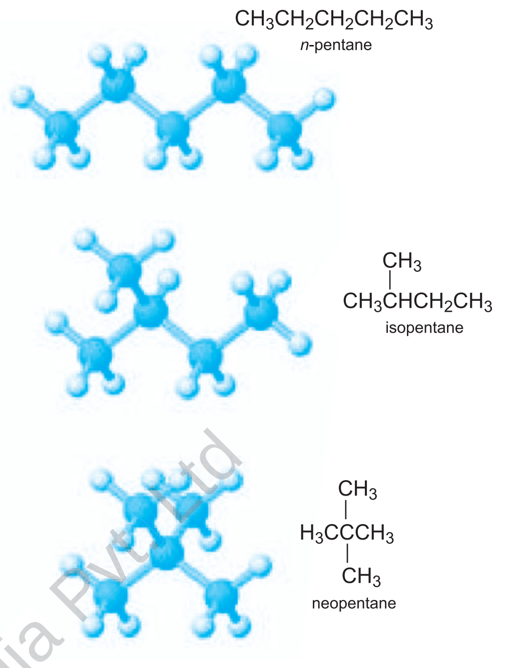


Fig. 11.4: *Isomers of pentane*

11.5 PREPARATION OF ALKANES

Some methods for preparation of alkanes are discussed below:

1. **From Alkyl Halides.** Alkanes can be obtained from alkyl halides by any one of the following methods:

   (*i*) **Using Grignard reagents.** Alkyl halides react with magnesium metal in presence of dry ethoxyethane (diethyl ether) to form alkylmagnesium halides. These are commonly known as **Grignard reagents**.

$$\underset{\text{Alkyl halide}}{\mathrm{R-X}} + \mathrm{Mg} \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{\mathrm{R-Mg-X}}$$

e.g.,

$$\underset{\substack{\text{Bromoethane}\\(\textit{Ethyl bromide})}}{\mathrm{CH_3CH_2-Br}} + \mathrm{Mg} \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Ethylmagnesium}\\\text{bromide}}}{\mathrm{CH_3CH_2MgBr}}$$

Grignard reagents readily react with compounds containing *active hydrogen* such as water, acids, alcohols, ammonia, amines, etc., to form alkanes. For example,

$$\underset{\substack{\text{Ethylmagnesium}\\\text{bromide}}}{\mathrm{CH_3CH_2MgBr}} + \mathrm{H_2O} \longrightarrow \underset{\text{Ethane}}{\mathrm{CH_3CH_3}} + \mathrm{Mg(OH)Br}$$

$$\underset{\substack{\text{Methylmagnesium}\\\text{iodide}}}{\mathrm{CH_3MgI}} + \underset{\text{Methanol}}{\mathrm{CH_3OH}} \longrightarrow \underset{\text{Methane}}{\mathrm{CH_4}} + \mathrm{Mg(OCH_3)I}$$

   (*ii*) **Wurtz reaction.** When an alkyl halide is treated with metallic sodium in the presence of dry diethyl ether, a symmetrical alkane, containing double the number of carbon atoms present in the alkyl group, is formed. *This reaction is known as* **Wurtz reaction**. For example,

$$\underset{\text{Alkyl halide}}{\mathrm{R-}}\boxed{\mathrm{X + 2Na + X}}\mathrm{-R} \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{\mathrm{R-R}} + \mathrm{2NaX}$$

$$\underset{\substack{\text{Bromomethane}\\ (\textit{Methyl bromide})}}{CH_3 - \boxed{Br + 2Na + Br} - CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2NaBr$$

$$\underset{\substack{\text{Iodoethane}\\ (\textit{Ethyl iodide})}}{CH_3CH_2 - \boxed{I + 2Na + I} - CH_2CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2 - CH_2CH_3} + 2NaI$$

However, if two different alkyl halides are used to prepare an alkane a mixture of three alkanes is actually produced. This is due to the reason that the two alkyl halides also react amongst themselves giving a mixture of three alkanes as illustrated below:

$$\underset{\substack{\text{Iodomethane}\\ (\textit{Methyl iodide})}}{CH_3 - I} + 2Na + \underset{\substack{\text{Iodoethane}\\ (\textit{Ethyl iodide})}}{I - CH_2CH_3} \xrightarrow{\text{Dry ether}} \underset{\text{Propane}}{CH_3 - CH_2CH_3} + 2NaI$$

$$CH_3 - I + 2Na + I - CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3 - CH_3} + 2NaI$$

$$CH_3CH_2 - I + 2Na + I - CH_2CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{CH_3CH_2 - CH_2CH_3} + 2NaI$$

Thus, Wurtz reaction is used for the synthesis of only symmetrical alkanes and not for the preparation of unsymmetrical alkanes, i.e. alkanes containing odd number of carbon atoms.

(iii) **Reduction of alkyl halides.** Reduction of alkyl halides with nascent hydrogen produces alkanes. *Nascent hydrogen* is obtained from a suitable metal and an acid, such as Zn and HCl, Sn and HCl, etc., or with Zn-Cu couple and alcohol. Molecular hydrogen in the presence of a catalyst such as Pt or Pd can also bring about reduction.

$$Zn + 2HCl \longrightarrow ZnCl_2 + \underset{\text{Nascent hydrogen}}{2(H)}$$

$$\underset{\text{Alkyl halide}}{R - X} + 2(H) \longrightarrow \underset{\text{Alkane}}{R - H} + HX$$

e.g.,

$$\underset{\substack{\text{Bromoethane}\\ (\textit{Ethyl bromide})}}{CH_3 - CH_2 - Br} + 2(H) \longrightarrow \underset{\text{Ethane}}{CH_3 - CH_3} + HBr$$

$$\underset{\text{Bromoethane}}{CH_3 - CH_2 - Br} + H_2 \xrightarrow{\text{Pt or Pd}} \underset{\text{Ethane}}{CH_3 - CH_3} + HBr$$

Reduction of alkyl halides can also be carried out with red phosphorus and hydroiodic acid at 420 K.

$$\underset{\substack{\text{Iodoethane}\\ (\textit{Ethyl iodide})}}{CH_3CH_2 - I} + HI \xrightarrow{\text{420 K/red P}} \underset{\text{Ethane}}{CH_3 - CH_3} + I_2$$

Red phosphorus removes the iodine liberated in the reaction, as shown below:

$$2P + 3I_2 \longrightarrow 2PI_3$$

This prevents iodine from reacting back with the alkane to give alkyl halide.

2. **From Alcohols.** Hot hydroiodic acid and red phosphorus reduce alcohols to hydrocarbons.

$$ROH + 2HI \xrightarrow{\text{Red P}} RH + H_2O + I_2$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + 2HI \xrightarrow{\text{Red P}} C_2H_6 + H_2O + I_2$$

3. **From Aldehydes.** Reduction of aldehydes using Zn/HCl gives hydrocarbons.

$$\mathrm{Zn} + 2\mathrm{HCl} \longrightarrow \mathrm{ZnCl_2} + \underset{\text{Nascent hydrogen}}{2[\mathrm{H}]}$$

Nascent hydrogen produced carries out reduction

$$\mathrm{R-CHO} + 4[\mathrm{H}] \xrightarrow{\mathrm{Zn/HCl}} \mathrm{RCH_3} + \mathrm{H_2O}$$

$$\underset{\text{Acetaldehyde}}{\mathrm{CH_3-CHO}} + 4[\mathrm{H}] \xrightarrow{\mathrm{Zn/HCl}} \underset{\text{Ethane}}{\mathrm{CH_3CH_3}} + \mathrm{H_2O}$$

4. **From Carboxylic Acids.** Carboxylic acids can be converted into alkanes by decarboxylation. Carboxylic acid on heating with soda lime (NaOH + CaO in the ratio of 3 : 1) at about 630 K, loses a molecule of CO_2 and an alkane with one carbon atom less than the carboxylic acid is obtained.

$$\underset{\text{Carboxylic acid}}{\mathrm{R-COOH}} + \mathrm{NaOH} \longrightarrow \mathrm{R-COONa} + \mathrm{H_2O}$$

$$\mathrm{R-COONa} + \mathrm{NaOH} \xrightarrow{\mathrm{CaO,\ 630\ K}} \underset{\text{Alkane}}{\mathrm{R-H}} + \mathrm{Na_2CO_3}$$

$$\underset{\text{Acetic acid}}{\mathrm{CH_3COOH}} + \mathrm{NaOH} \longrightarrow \underset{\text{Sod. acetate}}{\mathrm{CH_3COONa}} + \mathrm{H_2O}$$

$$\mathrm{CH_3COONa} + \mathrm{NaOH} \xrightarrow{\mathrm{CaO,\ 630\ K}} \underset{\text{Methane}}{\mathrm{CH_4}} + \mathrm{Na_2CO_3}$$

$$\underset{\text{Propionic acid}}{\mathrm{CH_3CH_2COOH}} + 2\mathrm{NaOH} \xrightarrow[\mathrm{630\ K}]{\mathrm{CaO}} \underset{\text{Ethane}}{\mathrm{CH_3-CH_3}} + \mathrm{Na_2CO_3} + \mathrm{H_2O}$$

The purpose of CaO in soda lime is to keep NaOH dry since it is highly *hygroscopic* in nature. Set-up of the apparatus used for the preparation of methane in laboratory is shown in Fig. 11.5. It is prepared by heating a mixture of sodium acetate and soda lime in a copper tube and the methane produced is collected by the downward displacement of water.

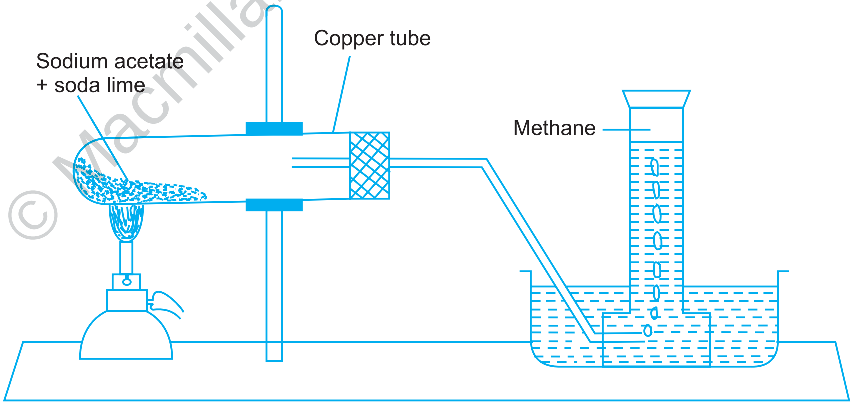


Fig. 11.5: Laboratory preparation of methane – Decarboxylation

5. **From Unsaturated Hydrocarbons.** Alkenes and alkynes add one and two molecules of hydrogen respectively, in presence of a catalyst such as finely divided nickel, platinum or palladium at 523–573 K, to form alkanes. This reaction is commonly referred to as **Sabatier and Senderen's reduction**.

$$\underset{\substack{\text{Ethene}\\(\textit{Ethylene})}}{CH_2 = CH_2} + H_2 \xrightarrow[523-573\ K]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{CH_3 - CH_3}$$

$$\underset{\substack{\text{Ethyne}\\(\textit{Acetylene})}}{CH \equiv CH} + 2H_2 \xrightarrow[523-573\ K]{\text{Ni or Pt or Pd}} \underset{\text{Ethane}}{CH_3 - CH_3}$$

This reaction is used in the manufacture of *Vanaspati Ghee* from edible vegetable oils.

6. By the Action of Water on Aluminium Carbide or Beryllium Carbide

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + \underset{\text{Methane}}{3CH_4}$$

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

This reaction can be conveniently used for preparing methane in the laboratory. Aluminium carbide is taken in a flask fitted with a delivery tube and a dropping funnel. Dilute hydrochloric acid is taken in the dropping funnel and is added to aluminium carbide dropwise. Methane gas is collected by downward displacement of water as shown in Fig. 11.6.

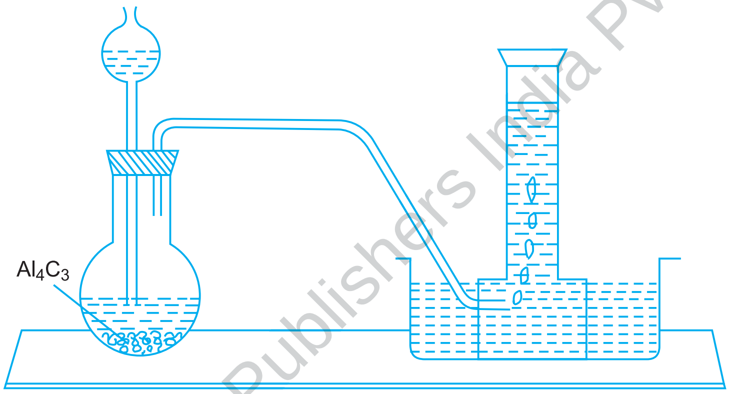


Fig. 11.6: *Laboratory preparation of methane — using aluminium carbide*

11.6 PHYSICAL PROPERTIES OF ALKANES

1. **Physical State.** The first four members of alkanes (methane, ethane, propane and butane) are colourless and odourless gases. The next thirteen members from C_5 to C_{17} are colourless volatile liquids while higher members from C_{18} onwards are waxy solids at ordinary temperature.
2. **Density.** The densities of alkanes increase with increase in their molecular masses. All alkanes are lighter than water.
3. **Solubility.** Hydrocarbons are nonpolar compounds and so in keeping with the popular rule *"like dissolves like"*, they are insoluble in polar solvent such as water but are soluble in non-polar solvents such as benzene, ether, carbon tetrachloride, etc. Solubility increases with increase in their molecular masses.
4. **Boiling Point.** The boiling points of *n*-alkanes increase gradually with increase in molecular mass (Fig. 11.7).

   The increase in boiling point can be explained in terms of intermolecular forces of attraction. Alkanes are nonpolar compounds and have only weak van der Waals' forces of attraction between the molecules. These forces act along the surface of the molecules and their magnitude increases with their increase in the surface area. As the molecular size of alkane increases, the surface area increases, and therefore, the boiling point also increases.

It is observed that *branched-chain isomers*, in general, have lower boiling points than the corresponding straight chain isomers. For example, the boiling points of *n*-pentane, isopentane and neopentane (two branches) are 309, 301 and 282.5 K respectively. This is because in branched chain molecules, the molecules tend to be spherical and so available surface area for intermolecular attraction is decreased and hence the boiling point gets lowered. Greater the branching, lower will be the boiling point.

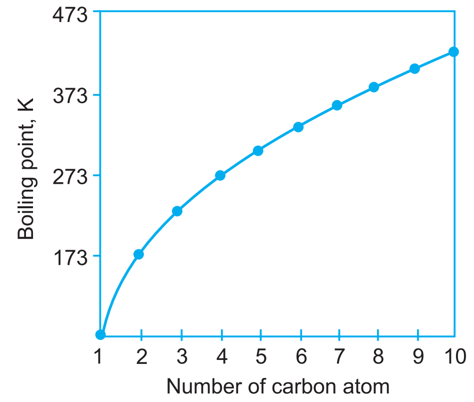
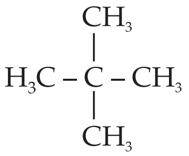


Fig. 11.7: *Increase in b.p. with increase in C-atoms of alkanes*

$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$,

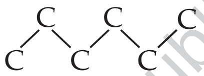
n-Pentane
(b.p. 309 K)

Isopentane
(b.p. 310 K)

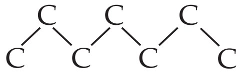


Neopentane
(b.p. 282.5 K)

5. **Melting Point.** The melting point of alkanes increases with molecular size but the variation is not regular because it depends on how the molecules are packed in the crystal. Generally alkanes with an even number of carbon atoms have higher melting points than the adjacent lower and higher alkanes having an odd number of carbon atoms. This is due to the fact that alkanes with an even number of carbon atoms have their terminal carbon atoms on the opposite side of the chain while odd numbered carbon atoms alkanes have their terminal carbon atoms on the same side of the chain as shown below:



Even numbered C-chain



Odd numbered C-chain

Alkanes with even number of carbon atoms have greater probability to fit in closely together in the crystal so as to permit greater intermolecular attraction and, therefore, have slightly, higher melting points than the previous lower and next higher alkanes having odd number of carbon atoms. Such type of variation in melting points is known as **alternating effect**. For example, the melting point of ethane (101 K) is higher than both the lower member methane (90 K) and higher member propane (86 K).

It may be noted that alternation effect which is found in melting points of alkanes is not found in their boiling points. This is because in their solid state, the positions and shapes of molecules are fixed while in their liquids, these parameters keep on changing as a result of collisions.

11.7 CHEMICAL PROPERTIES OF ALKANES

Alkanes are chemically inert under ordinary conditions. The inertness of alkanes can be explained as follows:

(*i*) Since alkane molecules do not contain any lone pair electrons, they fail to react with Lewis acids.

(*ii*) Carbon (2.5) and hydrogen (2.1) have nearly the same electronegativity, therefore, the carbon-hydrogen bonds are only slightly polarized. Consequently, they are nonpolar in nature and are generally not affected by most bases such as NaOH, KOH.

(*iii*) The bond angles in alkanes is 109° 28´, which is due to sp^3 hybridization of carbon atoms. Since there is no deviation from normal tetrahedral angle, there is no angle strain. Thus, alkanes are quite stable and hence less reactive towards common reagents.

(*iv*) Alkanes are saturated hydrocarbons having strong C–C (347.19 kJ mole^{-1}) and C–H (414.12 kJ mol^{-1}) bonds. These bonds are not easily broken by any of the oxidizing agents such as $KMnO_4$, $K_2Cr_2O_7$ or reducing agents such as lithium-aluminium hydride, sodium borohydride, etc.

However, under strong conditions alkanes do react. Important reactions of alkanes are discussed below:

1. **Halogenation.** The process of replacement of hydrogen atom of an alkane by a halogen atom is known as *halogenation* of alkanes. The order of reactivity of halogens towards alkanes is $F_2 > Cl_2 > Br_2 > I_2$.

(*i*) **Fluorination.** Fluorine reacts violently with alkanes with cleavage of carbon skeleton of alkanes to form a mixture of carbon-fluorinated alkanes and hydrofluoric acid.

$$\underset{\text{Methane}}{CH_4} \xrightarrow{F_2} C + HF + (CH_3F + CH_2F_2 + CHF_3 + CF_4 + C_2F_6 + C_3F_8)$$

In fact, the reaction is highly exothermic. A tremendous amount of energy is liberated in the fission of the organic molecule. But the reaction can be controlled by diluting fluorine with nitrogen and carrying out the reaction in a metal tube packed with copper gauze at a temperature of 420–620 K.

(*ii*) **Chlorination**

(*a*) **Chlorination of methane.** Methane reacts with chlorine in the presence of diffused sunlight or when heated to 520–670 K. Hydrogen atoms are replaced by chlorine atoms one by one.

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow{h\nu} \underset{\substack{\text{Methyl chloride} \\ (\textit{Chloromethane})}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \longrightarrow \underset{\substack{\text{Methylene chloride} \\ (\textit{Dichloromethane})}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow \underset{\substack{\text{Chloroform} \\ (\textit{Trichloromethane})}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \longrightarrow \underset{\substack{\text{Carbon tetrachloride} \\ (\textit{Tetrachloromethane})}}{CCl_4} + HCl$$

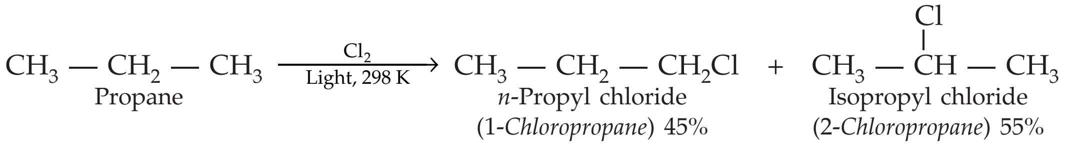
[For free radical mechanism of chlorination refer to chapter 10.]

In the presence of direct sunlight, the reaction is very explosive leading to the formation of carbon and HCl.

$$CH_4 + 2Cl_2 \xrightarrow{\text{Direct sunlight}} C + 4HCl$$

(*b*) **Chlorination of higher members.** Halogenations of higher alkanes yields a mixture of various isomeric products.

$$C_2H_6 \xrightarrow[\text{Light, 298 K}]{Cl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + HCl$$



$$\underset{\text{Propane}}{CH_3 — CH_2 — CH_3} \xrightarrow[\text{Light, 298 K}]{Cl_2} \underset{\substack{n\text{-Propyl chloride} \\ (1\text{-}\textit{Chloropropane})\ 45\%}}{CH_3 — CH_2 — CH_2Cl} + \underset{\substack{\text{Isopropyl chloride} \\ (2\text{-}\textit{Chloropropane})\ 55\%}}{CH_3 — \overset{\overset{\large Cl}{|}}{CH} — CH_3}$$

The ease of substitution of a hydrogen atom by a halogen atom is in the order:

tertiary > secondary > primary

(*iii*) Bromination. Bromination takes place slower than chlorination.

$$\underset{\text{Methane}}{CH_4} \xrightarrow[-HBr]{Br_2,\ \text{Light}} \underset{\substack{\text{Methyl}\\\text{bromide}}}{CH_3Br} \xrightarrow[-HBr]{Br_2,\ \text{Light}} \underset{\substack{\text{Methylene}\\\text{bromide}}}{CH_2Br_2} \xrightarrow[-HBr]{Br_2,\ \text{Light}} \underset{\substack{\text{Bromo}\\\text{form}}}{CHBr_3} \xrightarrow[-HBr]{Br_2,\ \text{Light}} \underset{\substack{\text{Carbon}\\\text{tetrabromide}}}{CBr_4}$$

(*iv*) Iodination. The reaction with iodine is extremely reversible.

$$CH_4 + I_2 \rightleftharpoons \underset{\text{Methyl Iodide}}{CH_3I} + HI$$

Iodination is, therefore, carried out in the presence of an oxidizing agent such as iodic acid or nitric oxide which converts hydrogen iodide formed into iodine and thus eliminates possibility of reversible reaction.

$$5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$$

2. Nitration. *The process of replacement of hydrogen atom of alkanes by nitro group (–NO_2) is called nitration of alkanes.*

Nitration of alkanes can be carried out by two different methods.

(*i*) Liquid phase nitration

(*ii*) Vapour phase nitration

(*i*) Liquid phase nitration. This method is used for nitration of higher alkanes. In this method alkane is heated with fuming HNO_3 at 413 K under pressure.

$$\underset{\text{Hexane}}{C_6H_{13}}\boxed{H + HO}\underset{\substack{\text{Fuming}\\\text{nitric acid}}}{—NO_2} \xrightarrow[\text{High pressure, (40 hrs.)}]{413\text{ K}} \underset{\text{Nitrohexane}}{C_6H_{13}NO_2} + H_2O$$

(*ii*) Vapour phase nitration. This method is used for nitration of lower alkanes. In this method, the alkane is heated with conc. HNO_3 at 670–750 K.

$$\underset{\text{Methane}}{CH_3}—\boxed{H + HO}—NO_2 \xrightarrow{750\text{ K}} \underset{\text{Nitromethane}}{CH_3NO_2} + H_2O$$

$$\underset{\text{Ethane}}{C_2H_5}—\boxed{H + HO}—NO_2 \xrightarrow{725\text{ K}} \underset{\text{Nitroethane}}{C_2H_5NO_2} + H_2O$$

3. Sulphonation. *The process in which hydrogen atom of alkanes is replaced with sulphonic acid group* (–SO_3H) *is known as* **sulphonation**.

Only higher alkanes (hexane onwards) undergo sulphonation. Alkane is heated with fuming sulphuric acid or oleum or pyrosulphuric acid, $H_2S_2O_7$ which is a mixture of conc. H_2SO_4 and SO_3 gas to give alkane sulphonic acid. For example,

$$\underset{\text{Hexane}}{C_6H_{13}}—\boxed{H + HO}—\underset{\substack{\text{Sulphuric}\\\text{acid}}}{SO_3H} \xrightarrow{SO_3} \underset{\substack{\text{Hexanesulphonic}\\\text{acid}}}{C_6H_{13}SO_3H} + H_2O$$

4. Oxidation

(*i*) Complete combustion or complete oxidation. Alkanes burn in excess of air or oxygen to give carbon dioxide and water. A large quantity of heat is evolved during the process. This makes alkanes a valuable fuels.

$$\underset{\text{Methane}}{CH_4\ (g)} + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (g);\ \Delta H = -890.0\text{ kJ}$$

$$\underset{\text{Ethane}}{C_2H_6\ (g)} + \frac{7}{2}O_2\ (g) \rightarrow 2CO_2\ (g) + 3H_2O\ (g);\ \Delta H = -1560.0\text{ kJ}$$

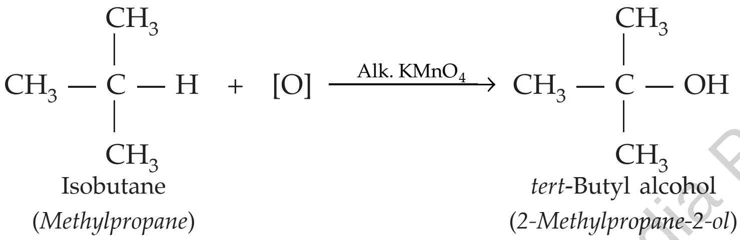
(ii) **Incomplete combustion.** On heating in a limited supply of air or oxygen, **carbon black** (a variety of carbon which is used in the manufacture of printer ink, black paint, polishes, and rubber tyres) is obtained. Carbon black obtained from methane is called *lamp black*.

(iii) **Controlled oxidation.** When heated in a controlled supply of air or oxygen at high temperature under high pressure in the presence of a catalyst such as copper, molybdenum oxide, manganese acetate; alkanes are oxidised to alcohols and aldehydes.

$$\underset{\text{Methane}}{2CH_4} + O_2 \xrightarrow[\text{473 K}]{\text{Cu tube, 100 atm,}} \underset{\text{Methyl alcohol}}{2CH_3OH}$$

$$CH_4 + O_2 \xrightarrow[\text{Oxide}]{\text{Molybdenum}} \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

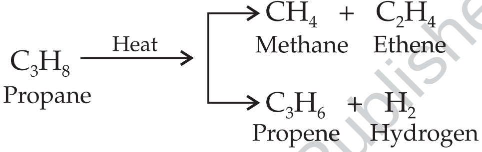
(iv) **Chemical oxidation.** Alkanes containing tertiary hydrogen atom are oxidized by strong oxidizing agents such as $KMnO_4$ and $K_2Cr_2O_7$ to corresponding alcohols. For example,



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-H + [O] \xrightarrow{\text{Alk. KMnO}_4} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH$$

Isobutane (*Methylpropane*) → *tert*-Butyl alcohol (*2-Methylpropane-2-ol*)

5. **Thermal Decomposition or Pyrolysis or Cracking.** Alkanes on heating to a high temperature (700–800 K) or to a slightly lower temperature in the presence of alumina or silica catalysts crack into smaller fragments. For example,



The process of cracking involves the breaking of C–C as well as C–H bonds. The reaction follows a free radical mechanism.

The cracking process is of prime importance for the manufacture of gasoline from high boiling fractions of petroleum such as fuel oil or lubricating oils. It is also used for the production of oil gas from kerosene.

11.8 ALKENES

Acyclic (open chain) unsaturated hydrocarbons containing a carbon-carbon double bond are called **alkenes**. They are also called **olefins** (Greek: olefiant – oil forming) since the lower members of this class such as ethene (ethylene), propene (propylene), etc. produce oily products on reaction with halogens such as chlorine and bromine. General formula of olefins is C_nH_{2n} where, $n = 2, 3, 4, ...$, etc.

11.8.1 Structure of Alkenes

Consider the structure of ethene, the simplest alkene. Each carbon in ethene (ethylene), is sp^2-hybridized. sp^2-hybridized carbon has three sp^2-orbitals which lie in a plane inclined to one another at an angle of 120°. The unhybridized $2p_z$-orbital is perpendicular to the plane containing sp^2-orbitals.

Now one of the three sp^2-hybrid orbitals of each carbon overlap mutually along their internuclear axis to form C–C, σ-bond. The remaining two sp^2-orbitals of each carbon overlap with 1*s*-orbitals of two hydrogen atoms to form in all four C–H, σ-bonds.

As all the three sp^2-orbitals of each carbon lie in a plane, *the two carbon atoms and the four hydrogen atoms all lie in the same plane*.

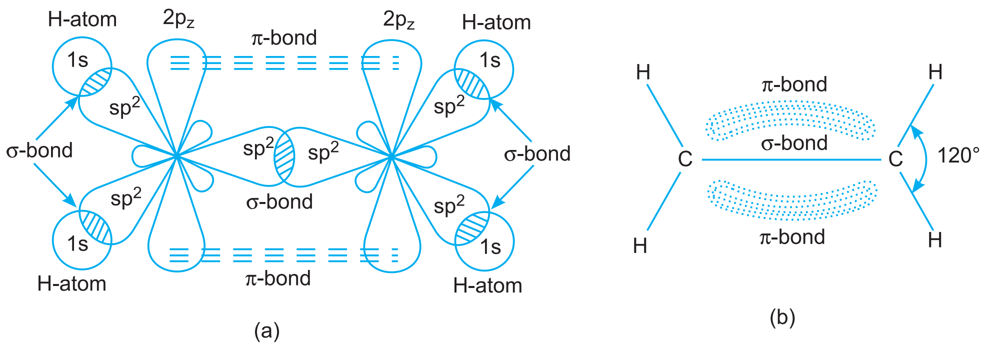


Fig. 11.8: *(a) Orbital structure of ethene (b) π-electron cloud consists of two equal halves; one lying above and other below the plane of carbon and hydrogen atoms*

Each carbon atom is now left with one unhybridized $2p_z$-orbital which is perpendicular to the plane of carbon and hydrogen atoms. These two $2p_z$-orbitals are parallel and hence *overlap sideways* to form a π-bond (Fig. 11.8*a*).

The electron cloud of the π-bond consists of two equal halves; one lying above and other below the plane of carbon and hydrogen atoms (Fig. 11.8*b*).

There are two types of bonds in carbon-carbon double bond, *i.e.* a σ-bond and a π-bond.

The bond energies for the carbon-carbon single bond (σ-bond) and carbon carbon double bond (one-bond + one-bond) have been determined to be 347 kJ mol^{-1} and 598 kJ mol^{-1} respectively giving a bond energy of (598 – 347) = 251 kJ mol^{-1} to the π-bond. Thus a *π-bond is a weaker bond than the σ-bond*. Being weaker, a π-bond easily breaks in chemical reactions. Therefore, *it is this π-bond which is responsible for the chemical reactivity of alkenes.*

A carbon-carbon double bond is shorter (134 pm) as compared to carbon-carbon single bond length of 154 pm. This is due to the fact that a sp^2-orbital is smaller in size than a sp^3-orbital. Furthermore, the sideways overlapping of *p*-orbitals also brings the two carbon atoms closer.

11.8.2 Nomenclature

Nomenclature of alkenes is explained in the form of Table 11.1.

Table 11.1

S. No.	*Structure*	*Common name*	*IUPAC name*
1.	$CH_2 = CH_2$	Ethylene	Ethene
2.	$CH_3CH = CH_2$	Propylene	Propene
3.	$CH_3CH_2CH = CH_2$	β-butylene	But-1-ene
4.	$CH_3CH = CH — CH_3$	α-butylene	But-2-ene
5.	$\underset{\displaystyle CH_3}{\underset{\vert}{CH_3 — C}} = CH_2$	Isobutylene	2-Methylpropene

11.8.3 Isomerism in Alkenes

Alkenes show the following types of isomerism:

(*i*) **Position Isomerism.** *Alkenes which have the same molecular formula but differ from one another in the position of a double bond are called* **position isomers** *and the phenomenon is called* **position isomerism**. Position isomerism is a kind of structural isomerism.

But-1-ene and but-2-ene are position isomers of each other. Both have the molecular formula C_4H_8.

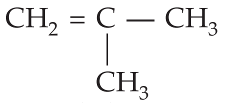
$$\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H = \overset{1}{C}H_2 \qquad \overset{4}{C}H_3 - \overset{3}{C}H = \overset{2}{C}H - \overset{1}{C}H_3$$

But-1-ene But-2-ene

(*ii*) **Chain Isomerism.** *Alkenes which have the same molecular formula but have different arrangements of the carbon chain are called* **chain isomers**. For example, But-1-ene and 2-Methylpropene are chain isomers of each other as they differ in the structure of carbon-chain.

$$CH_2 = CH - CH_2 - CH_3$$

But-1-ene



$$CH_2 = C(CH_3) - CH_3$$

2-Methylpropene

(*iii*) **Geometrical Isomerism (Hindered rotation around carbon-carbon double bond).** A double bond consists of a σ-bond and a π-bond (Fig. 11.9). The π-bond is formed by sideways overlapping of unhybridized *p*-orbitals of two carbon atoms above and below the plane of carbon atoms. Breaking of a π-bond requires 251 kJ mol^{-1} of energy which is not easily available at room temperature. Consequently, the rotation about a carbon-carbon double bond is not free and is *strongly hindered or restricted.* Due to this hindered rotation, the relative positions of atoms or groups attached to the carbon atoms of the double bond get fixed.

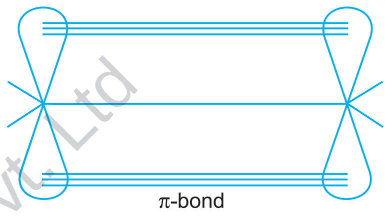
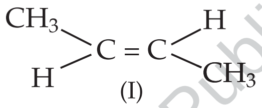


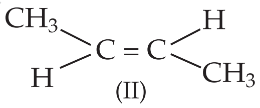
Fig. 11.9: *Rotation about a carbon-carbon double bond*

Many substituted alkenes can exist in two distinct isomers which differ from each other only in the relative positions of atoms or groups in space around the double bond. For example, but-2-ene can exist in the following two forms:



(I)

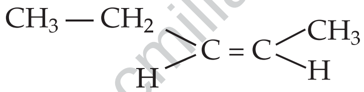
cis-But-2-ene



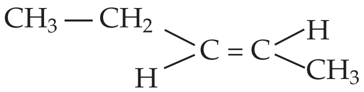
(II)

trans-But-2-ene

Pent-2-ene exists in the form of three isomers, two of which are geometrical isomers (*cis-trans*).

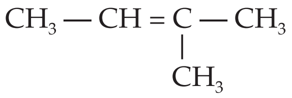


cis-Pent-2-ene



trans-Pent-2-ene

The third isomer of Pent-2-ene is:



$$CH_3 - CH = C(CH_3) - CH_3$$

2-Methylbut-2-ene

These isomers have the same structural formulae but differ in the relative spatial arrangement of hydrogen atoms and methyl groups around the double bond.

Isomers which have the same structural formulae but differ in the relative spatial arrangement of atoms or groups around the double bond are called **geometrical isomers** *and the phenomenon is called* **geometrical isomerism**. *Geometrical isomerism is a type of space or stereoisomerism.*

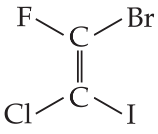
The isomer (I), in which the similar atoms or groups lie on the same side of the double bond is called the *cis*-isomer whereas the isomer (II) in which the similar atoms or groups lie on the opposite sides of the double bond is called the *trans*-isomer. Thus, geometrical isomerism is also known as ***cis-trans*** **isomerism**.

11.8.4 E and Z System of Nomenclature

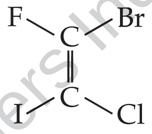
The *cis* and *trans*- designation can be used only for the compounds in which two doubly bonded carbon atoms are having similar atoms or groups *e.g.*, of the type $C_{AB} = C_{AB}$. But, when the two doubly bonded carbon atoms are having different atoms or groups attached to them, *e.g.*, of the type $C_{AB} = C_{DE}$; it is not possible to assign them *cis* or *trans* configurations. To overcome this difficulty, a more general system for designating the configuration of geometric isomers has been adopted. This system developed by Cahn, Ingold and Prelog is known as *E* and *Z* system and is based on priority of attached groups. Priority of an atom attached to carbon is determined by the atomic mass of the atom. Higher the atomic mass, greater is the priority. In the case of groups attached to carbon, the atomic mass of the atom of the group directly linked to ethylenic carbon is considered. The atoms or groups attached to each carbon of the double bond, are assigned first and second priority. If the atoms or groups having higher priority attached to two carbons are on the same side of double bond the configuration is designated as *Z* (derived from German word *Zusammen* meaning together) and if the atoms or groups of higher priority are on the opposite side of the double bond, the configuration is designated as *E* (derived from German word *-entgegen* meaning across or opposite).

Priorities of atoms or groups are determined in the same way as for R and S configurations of optical isomers. At. masses or atomic numbers of atoms directly linked with ethylenic carbon atoms are taken into consideration.

Let us consider an example in which two doubly bonded atoms are attached to four different halogens such as $C_{BrF} = C_{ICl}$. Br is having higher priority over F and I is having higher priority over Cl (due to their higher atomic numbers). The isomer in which Br and I are on the same side of double bond will be called *Z* and the isomer in which Br and I are on the opposite sides of double bond will be called *E*.

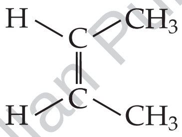


Z-isomer

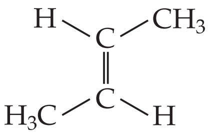


E-isomer

In the same way *cis* and *trans* isomers of 2-butene can be called Z and E but-2-enes respectively.



Z-2-Butene



E-2-Butene

11.9 PREPARATION OF ALKENES

Methods of preparation of alkenes are described as below:

1. **From Alkyl Halides.** Alkyl halides on dehydrohalogenation give alkenes. *Dehydrohalogenation means removal of halogen acids such as HCl, HBr, HI, etc.* This reaction is carried out by heating an alkyl halide with an alcoholic solution of potassium hydroxide. For example,

$$\underset{\text{Ethyl iodide}}{CH_3CH_2 - I} + KOH\ (alc.) \xrightarrow{353-363\ K} \underset{\text{Ethylene}}{CH_2 = CH_2} + KI + H_2O$$

$$\underset{n\text{-Propyl bromide}}{CH_3CH_2CH_2 - Br} + KOH\ (alc.) \xrightarrow{353-363\ K} \underset{\text{Propylene}}{CH_3CH = CH_2} + KBr + H_2O$$

This process of removal of a molecule of a halogen acid (HCl, HBr or HI) from a haloalkane to form an alkene is called **dehydrohalogenation**.

In dehydrohalogenation, hydrogen is lost from the carbon atom adjacent to that carrying the halogen. This reaction is also referred to as *β*-**elimination**.

The order of reactivity for different types of alkyl halides is:

Tertiary > Secondary > Primary

Primary alkyl halides are found to be least reactive. Therefore, this does not constitute a good method for the preparation of ethylene (ethene).

For a given alkyl group, the ease of dehydrogenation for different alkyl halides is in the order:

Iodide > Bromide > Chloride

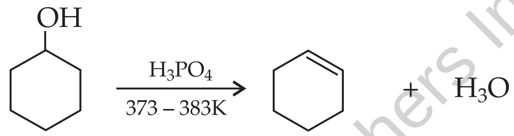
2. **From Alcohols.** Alcohols on dehydration (removal of water) give alkenes.

This dehydration is usually carried out by heating a suitable alcohol with either alumina or with mineral acids such as conc. H_2SO_4 or H_3PO_4. For example,

$$\underset{\substack{\text{Ethanol}\\ (\textit{Ethyl alcohol})}}{CH_3CH_2OH} \xrightarrow[623-633\text{ K}]{Al_2O_3} \underset{\substack{\text{Ethene}\\ (\textit{Ethylene})}}{CH_2 = CH_2} + H_2O$$

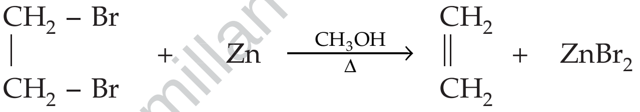
$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[440\text{ K}]{95\%\ H_2SO_4} \underset{\text{Ethene}}{CH_2 = CH_2} + H_2O$$

$$\underset{\text{1-Propanol}}{CH_3CH_2CH_2OH} \xrightarrow[623-633\text{ K}]{Al_2O_3} \underset{\text{Propene}}{CH_3CH = CH_2} + H_2O$$



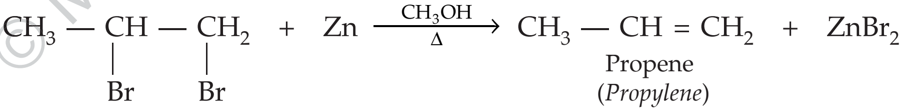
Cyclohexanol Cyclohexene

3. **From Dihaloalkanes.** Dihalogen derivatives of alkanes in which the two halogen atoms are present on adjacent carbon atoms are called **vicinal** or **1, 2-dihaloalkanes**. Alkenes can be obtained by heating a suitable 1, 2-dihaloalkane with zinc dust in methanol as solvent. For example,



$$\begin{matrix} CH_2 - Br \\ | \\ CH_2 - Br \end{matrix} + Zn \xrightarrow[\Delta]{CH_3OH} \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + ZnBr_2$$

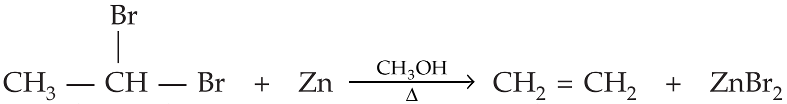
1, 2-Dibromoethane (*Ethylene dibromide*) Ethene (*Ethylene*)



$$\underset{\substack{\text{1, 2-Dibromopropane}\\ (\textit{Propylene dibromide})}}{CH_3 - \underset{Br}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH_2}}} + Zn \xrightarrow[\Delta]{CH_3OH} \underset{\substack{\text{Propene}\\ (\textit{Propylene})}}{CH_3 - CH = CH_2} + ZnBr_2$$

1, 2-Dibromopropane (*Propylene dibromide*)

This process of removal of a molecule of halogen from a dihaloalkane to form an alkene is called **dehalogenation**. Dihaloalkane containing both halogens on the same carbon (gem-dihalides) also undergo dehalogenation when heated with zinc dust in methanol.



$$\underset{\substack{\text{1, 1-Dibromoethane}\\ (\textit{Ethylidene dibromide})}}{CH_3 - \overset{\overset{Br}{|}}{CH} - Br} + Zn \xrightarrow[\Delta]{CH_3OH} \underset{\text{Ethene}}{CH_2 = CH_2} + ZnBr_2$$

1, 1-Dibromoethane (*Ethylidene dibromide*)

4. **By Partial Hydrogenation of Alkynes.** When hydrogen gas is passed over alkyne in the presence of palladium based on barium sulphate in xylene solution at 473 K, alkene is obtained. Further, hydrogenation of alkene to alkane is hindered because of the poisoning of catalyst by barium sulphate.

$$\underset{\substack{\text{Acetylene}\\(\textit{Ethyne})}}{CH \equiv CH} + H_2 \xrightarrow[473\text{ K}]{Pd/BaSO_4} \underset{\substack{\text{Ethylene}\\(\textit{Ethene})}}{CH_2 = CH_2}$$

Palladium poisoned by barium salts is called **Lindlar's catalyst**.

11.9.1 Laboratory Preparation of Ethene

Ethene is prepared by dehydration of C_2H_5OH with conc. H_2SO_4 at 440 K. A mixture of ethanol and conc. H_2SO_4 in the ratio of 1 : 2 by volume is taken in a dropping funnel and added into a round bottomed flask containing anhydrous $Al_2(SO_4)_3$ and sand. $Al_2(SO_4)_3$ catalyses the reaction whereas sand is used to avoid frothing and spurting during the process.

The reaction mixture is heated to 440 K. Ethene is produced which is collected over water as shown in Fig. 11.10. Ethene thus produced contains impurities of SO_2 (formed by the reduction of H_2SO_4) and CO_2 (formed by the oxidation of ethanol). Impure ethene is passed through a solution of caustic soda which absorbs CO_2 and SO_2 and pure gas is obtained.

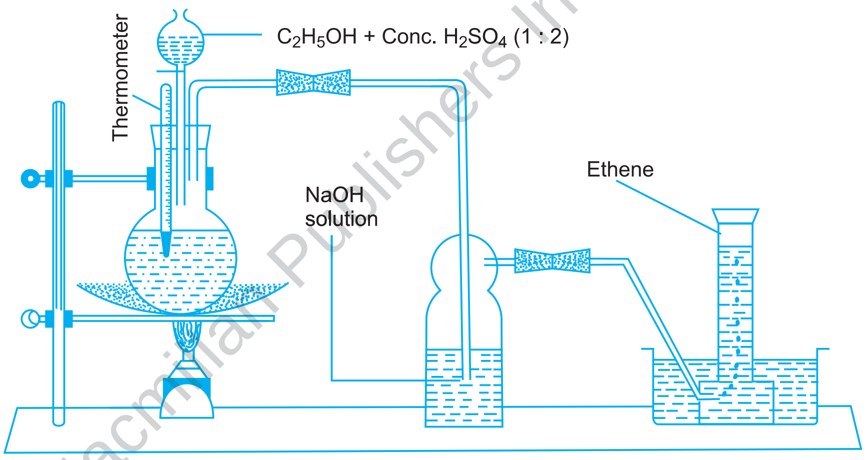


Fig. 11.10: *Laboratory preparation of ethene*

11.10 PHYSICAL PROPERTIES OF ALKENES

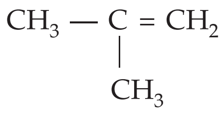
1. **Physical state.** The first three members ($C_2 – C_4$) are colourless gases, next fourteen members ($C_5 – C_{18}$) are liquids while higher members are solids at room temperature.
2. **Density.** Alkenes are lighter than water. Densities of alkenes gradually increase with the increase in the molecular mass.
3. **Solubility.** They are insoluble in water but soluble in non-polar solvents such as ether, benzene, etc.
4. **Boiling points.**
   (*i*) Boiling points increase with the increase in the molecular masses. It has been observed that there is an increase of 20–30°C for the addition of each methylene unit.

(*ii*) Branched-chain alkenes exhibit lower boiling points than straight-chain alkenes. For example, b.p. of *cis*-2-butene (277 K) is higher than that of methyl propene (266 K).

$CH_3 - CH = CH - CH_3$

cis-2-Butene

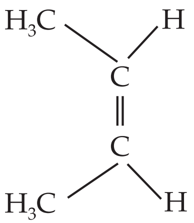
(b.p. 277 K)



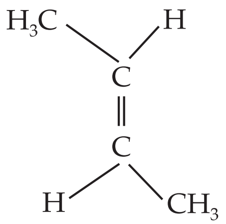
$$CH_3 - \underset{\substack{|\\ CH_3}}{C} = CH_2$$

Methyl propene

(*iii*) *cis*-alkenes possess higher boiling points than *trans*-alkenes. This is due to the greater dipole moment of *cis*-alkenes resulting in stronger intermolecular attractions. On the other hand *trans*-alkenes having almost zero dipole moment experiences weaker intermolecular attractions.



cis–2–Butene
b.p. 277 K
m.p. 134 K



trans–2–Butene
b.p. 274 K
m.p. 167 K

(*iv*) In general, alkenes have higher boiling points than corresponding alkanes. This is due to the greater polarity on the molecules on account of the presence of π (pi) electrons.

5. Melting points.

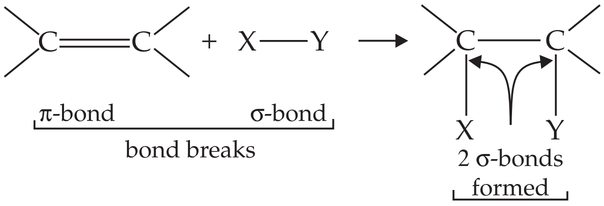
(*i*) Melting points of alkenes increase with the increase in the molecular mass.

(*ii*) Alkenes show alternation effect, where the m.p. of an alkene with even carbon atoms is higher than the melting points of the next lower and next higher alkenes containing odd number of carbon atoms.

(*iii*) In alkenes, however, which exhibit geometrical isomerism, melting points depend on the symmetry of the molecule. For example, the more symmetrical *trans*-2 butane has higher melting point than the less symmetrical *cis*-2 butene. This is because the less symmetrical molecules fit poorly in the crystal lattice.

11.11 CHEMICAL PROPERTIES OF ALKENES

A carbon-carbon double bond – C = C – consists of a strong σ-bond and a weak π-bond. Reactivity of alkene is due to the presence of weak π-bond. When double bond is attacked by chemical reagents, π-bond breaks up rather easily and two new sigma bonds are formed.



Thus, alkenes mainly undergo addition reactions.

In a double bond, there is an electron cloud above and below the plane of the molecule. These electrons are loosely held by the carbon nuclei compared to σ-electrons. These π-electrons are easily available to the electron seeking reagents called **electrophiles**. Thus, majority of the reactions of carbon-carbon double bond are those in which the attacking reagents are electrophilic reagents.

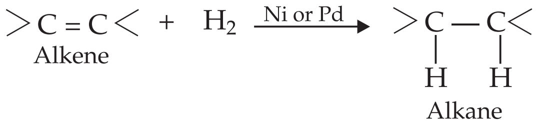
Some important reactions of alkenes are discussed below:

A. ELECTROPHILIC ADDITION REACTIONS

The addition reactions initiated by electrophiles are called **electrophilic addition reactions**. Some electrophilic addition reactions of alkenes are discussed below:

1. Addition of Hydrogen (Hydrogenation).

Alkenes react with hydrogen in the presence of finely-divided nickel at 523–573 K (**Sabatier and Senderen's reaction**) or palladium or platinum at room temp. (298 K) to form alkanes.



$$\underset{\text{Alkene}}{>C=C<} + H_2 \xrightarrow{\text{Ni or Pd}} \underset{\text{Alkane}}{>\underset{H}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}<}$$

Examples:

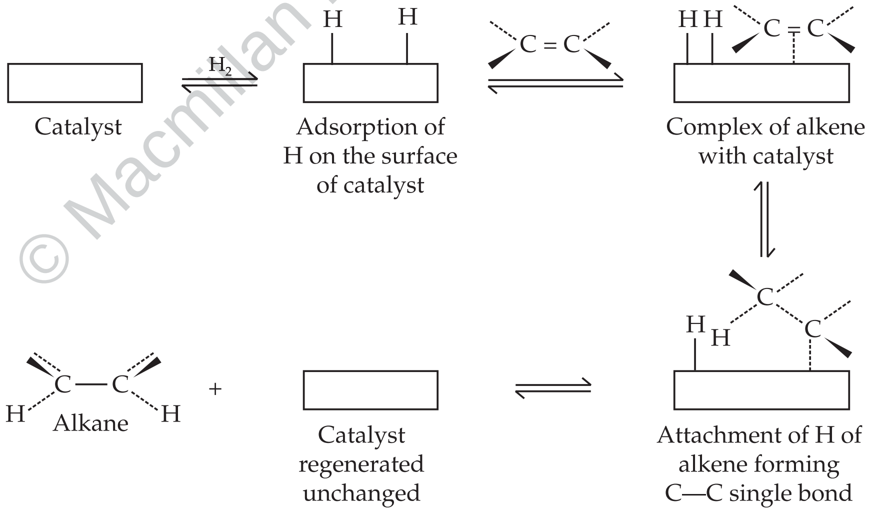
(*i*) $\underset{\substack{\text{Ethylene}\\(\textit{Ethene})}}{H_2C=CH_2} + H_2 \xrightarrow{\text{Ni or Pd}} \underset{\text{Ethane}}{H_3C-CH_3}$

(*ii*) $\underset{\substack{\text{Propylene}\\(\textit{Propene})}}{CH_3-CH=CH_2} + H_2 \xrightarrow[\text{or Pt}]{\text{Ni or Pd}} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$

Hydrogenation of alkenes is of industrial importance: Vanaspati/margarine in the solid form is obtained by passing H_2 gas through hot oils in the presence of nickel powder. Oils (liquids) contain carbon-carbon double bonds which get converted to carbon-carbon single bonds, providing solid fats, known as vanaspati or margarine.

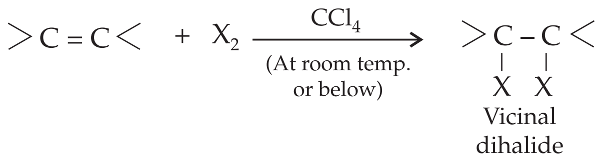
Hydrogenation of alkenes is an exothermic reaction. The quantity of heat evolved when one molecule of unsaturated compound is hydrogenated is known as **heat of hydrogenation**.

Mechanism of Addition of Hydrogen: Hydrogenation of alkenes is a *cis*-addition process. Catalyst has a big role to play in the reaction as illustrated below.



Hydrogen molecule gets adsorbed on the surface of the catalyst using the vacant *d*-orbitals of the catalyst metal. Then the alkene molecule is adsorbed through π-electrons. Then the adsorbed H-atom is transferred to the same face of unsaturated compound giving ***cis*-addition** product. The product is desorbed from the catalyst surface to make way for the addition of more alkene molecules on the surface. This process continues till the hydrogenation process is complete.

2. **Addition of Halogens.** Halogens combine with alkenes to form dihalides in an inert solvent such as carbon tetrachloride and in the absence of light.



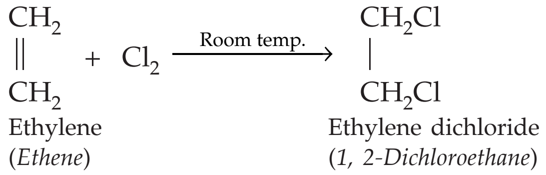
$$>C=C< + X_2 \xrightarrow[\text{(At room temp. or below)}]{CCl_4} >\underset{X}{\underset{|}{C}}-\underset{X}{\underset{|}{C}}<$$

Vicinal dihalide

The decreasing order of reactivity of halogens is $F_2 > Cl_2 > Br_2 > I_2$.

(*i*) **With fluorine.** Reaction with fluorine is violent resulting in fragmentation of the molecule. We cannot obtain vicinal difluorides by this method.

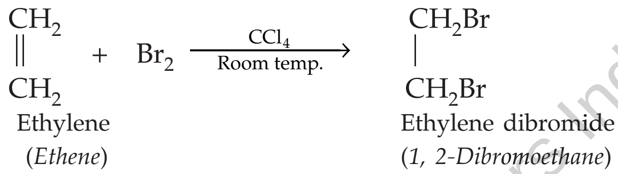
(*ii*) **With chlorine**



$$CH_2{=}CH_2 + Cl_2 \xrightarrow{\text{Room temp.}} CH_2Cl-CH_2Cl$$

Ethylene (*Ethene*) Ethylene dichloride (*1, 2-Dichloroethane*)

(*iii*) **With bromine.** When ethylene is treated with Br_2 in CCl_4 (or in water), the orange solution gets decolourized.



$$CH_2{=}CH_2 + Br_2 \xrightarrow[\text{Room temp.}]{CCl_4} CH_2Br-CH_2Br$$

Ethylene (*Ethene*) Ethylene dibromide (*1, 2-Dibromoethane*)

This reaction is used as a test of unsaturation.

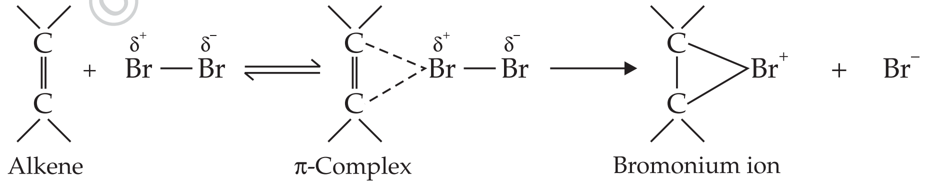
(*iv*) **With iodine.** Addition of iodine takes place slowly and vicinal di-iodide formed is unstable.

Mechanism of Halogenation: Halogenation of an alkene takes place by electrophilic addition mechanism. A halogen molecule (Cl_2, Br_2 or I_2) is non-polar in nature. But when this molecule approaches the alkene molecule, the π bonds have the effect of polarising the halogen molecule. The positive end of the polarised halogen molecule is attached to one ethylenic carbon atom with the simultaneous attachment of the negative end to the second ethylenic carbon atom forming a halonium ion, with the release of halide ion. The halide ion then attacks the halonium ion from the back side to avoid steric hindrance, thus giving rise to a dihalide. The steps of the mechanism are shown as under, by taking the example of bromination.

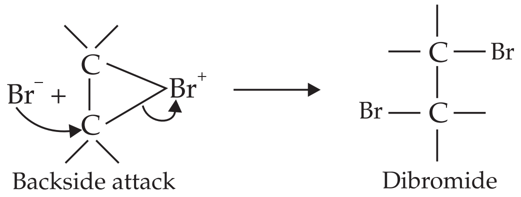
$$Br-Br \xrightarrow[\text{cloud}]{\pi\text{ Electron}} \overset{\delta^+}{Br}-\overset{\delta^-}{Br}$$

Polarised bromine molecule

Step 1.



Step 2.



In the π-complex, there is only electrostatic attraction between the polarised bromine molecule and the alkene, there is no actual bonding.

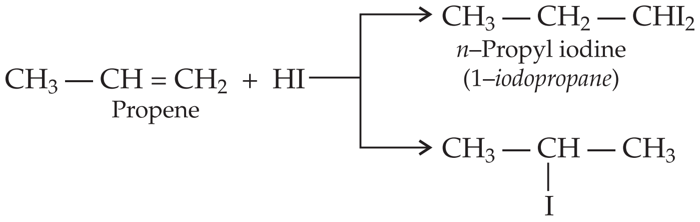
3. **Addition of Halogen Acids.** Alkenes react with strong aqueous solution of halogen acids to form alkyl halides. The order of reactivity of the halogen acids is HI > HBr > HCl.

$$\underset{\substack{\text{Ethylene}\\(\textit{Ethene})}}{CH_2 = CH_2} + HI \rightarrow \underset{\substack{\text{Ethyl iodide}\\(\textit{Iodoethane})}}{CH_3CH_2I}$$

Markownikoff's Rule

The addition of unsymmetrical reagents such as halogen acids (HX) which consist of two different atoms or groups to an unsymmetrical alkene say propene may yield two different products depending upon how the addition takes place. For example, when HI adds to propene, the two possible products are:

Markownikoff



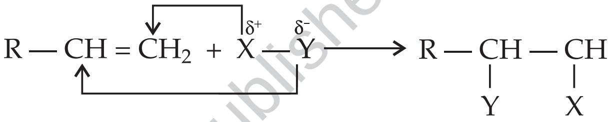
$$\underset{\text{Propene}}{CH_3-CH=CH_2} + HI \rightarrow \begin{cases} CH_3-CH_2-CHI_2 \\ CH_3-\underset{|\atop I}{CH}-CH_3 \end{cases}$$

n–Propyl iodine
(1–*iodopropane*)

Isopropyl iodine
(2–*iodopropane*)

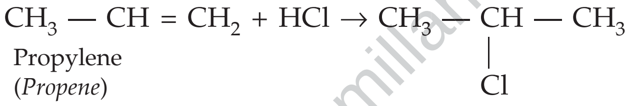
It is, however, observed that out of the two products, isopropyl iodide is the major product (90%).

Whenever addition across an unsymmetrical double bond (– HC = CH –) takes place, the negative part of the addendum, i.e. the molecule to be added goes to the carbon atom of double bond with the smaller number of hydrogen atoms. This is the statement of Markownikoff's rule. It is represented as follows:



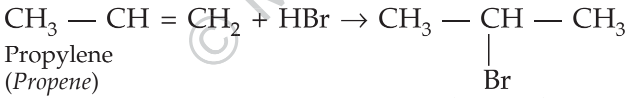
$$R-CH=CH_2 + \overset{\delta^+}{X}-\overset{\delta^-}{Y} \longrightarrow R-\underset{|\atop Y}{CH}-\underset{|\atop X}{CH}$$

This is further illustrated with the help of following examples:



(*i*) $\underset{\substack{\text{Propylene}\\(\textit{Propene})}}{CH_3-CH=CH_2} + HCl \rightarrow CH_3-\underset{|\atop Cl}{CH}-CH_3$

Isopropyl chloride
(2-*Chloropropane*)



(*ii*) $\underset{\substack{\text{Propylene}\\(\textit{Propene})}}{CH_3-CH=CH_2} + HBr \rightarrow CH_3-\underset{|\atop Br}{CH}-CH_3$

Isopropyl Bromide
(2-*Bromopropane*)

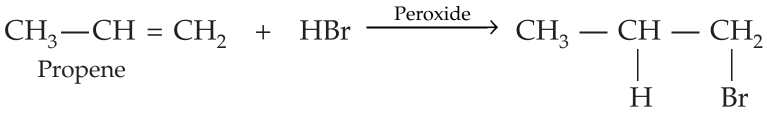
Modern Concept of Markownikoff's rule

Addition of a molecule to an alkene involves the formation of a carbocation as intermediate product. When a symmetrical molecule is added to an unsymmetrical molecule, the addition takes place in such a manner so as to give the stable carbocation. A stable carbocation is formed when the negative part of the adding molecule (say Cl in HCl) attaches itself to the carbon atom containing lower number of hydrogen atoms attached to it.

Kharasch in his laboratory

It can also be stated that a stable carbocation is formed when the positive part of the adding molecule (say H in HCl) attaches itself to the carbon containing greater number of hydrogen atoms attached to it.

Peroxide effect or Kharasch effect (Anti-Markownikoff addition). Addition of HBr to unsymmetrical alkenes in presence of organic peroxides takes place against the Markownikoff's rule. For example, addition of HBr to propene in presence of organic peroxides gives 1 bromopropane instead of 2-bromopropane. This is known as **peroxide effect or Kharasch effect**.



$$CH_3-CH=CH_2 + HBr \xrightarrow{\text{Peroxide}} \underset{\displaystyle H}{\underset{|}{CH_3-CH}}-\underset{\displaystyle Br}{\underset{|}{CH_2}}$$

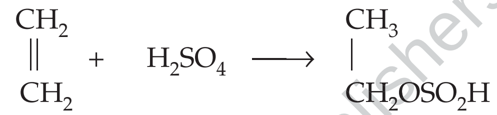
Propene

1-Bromopropane
(major product)

This is because, in the presence of organic peroxides, the reaction proceeds through free radical mechanism. In the absence of peroxides, it takes place through electrophilic mechanism.

It is important to note that peroxide effect or Kharasch effect is observed only with HBr and not with other halogen acids. This is because H–F and H–Cl bonds being stronger than H–Br bond are not decomposed by organic peroxides to form free radicals. On the other hand, although HI breaks easily into free radicals, the iodine radicals owing to bigger size are not much reactive to add on a double bond but recombine to form iodine molecule.

4. **Addition of Sulphuric Acid.** When alkene is bubbled through concentrated sulphuric acid, alkyl hydrogen sulphate is formed. For example,

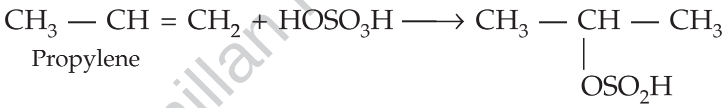


$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + H_2SO_4 \longrightarrow \begin{matrix} CH_3 \\ | \\ CH_2OSO_2H \end{matrix}$$

Ethylene

Ethyl hydrogen sulphate

In case of unsymmetrical alkenes, the addition of sulphuric acid follows Markownikoff's rule:



$$CH_3-CH=CH_2 + HOSO_3H \longrightarrow CH_3-\underset{\displaystyle OSO_2H}{\underset{|}{CH}}-CH_3$$

Propylene

Isopropyl hydrogen
sulphate

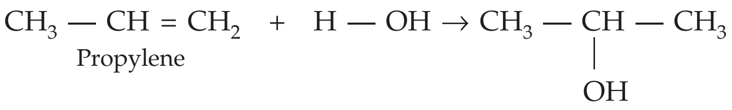
(*i*) The product isopropyl hydrogen sulphate when heated gives back alkene. *The reaction is, therefore, used for the separation of alkene from the gaseous mixture.*

(*ii*) Alkyl hydrogen sulphates on warming with water form *alcohols*.

$$\underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2HSO_4} + HOH \xrightarrow{\text{warm}} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + H_2SO_4$$

5. **Addition of Water (Hydration of alkenes).** Water adds to alkenes in presence of acids to form alcohols. Addition to the double bond takes place according to Markownikoff's rule. For example,

$$\underset{\text{Ethene}}{CH_2=CH_2} + H-OH \xrightarrow[\text{515 K}]{H^+} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$



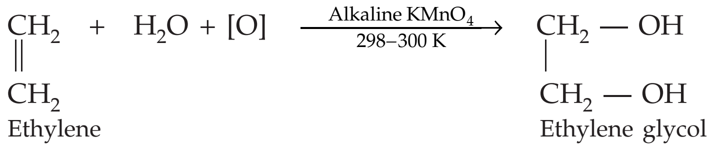
$$CH_3-CH=CH_2 + H-OH \rightarrow CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

Propylene

Isopropyl alcohol
(major product)

B. OXIDATION REACTIONS

1. **Oxidation with Cold Alkaline $KMnO_4$ (Baeyer's reagent).** When ethylene is passed through dilute solution of alkaline $KMnO_4$ it gets decolourised and ethylene is oxidized to glycol (*Hydroxylation*).

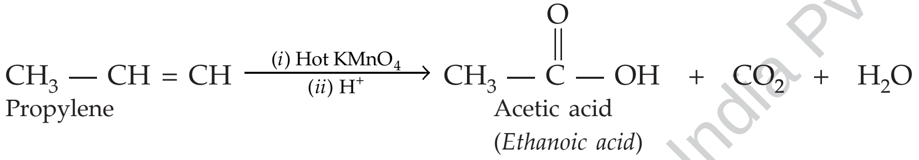


$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + H_2O + [O] \xrightarrow[298\text{–}300\ K]{\text{Alkaline } KMnO_4} \underset{\text{Ethylene glycol}}{CH_2(OH){-}CH_2(OH)}$$

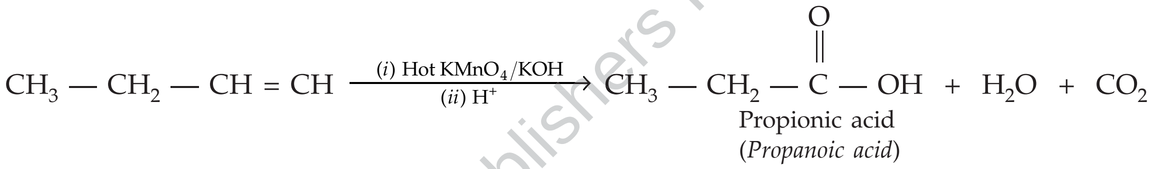
Decolourization of $KMnO_4$ (or Baeyer's reagent), is, therefore, used as a test for the presence of double bond in an unknown organic compound. This test is known as **Baeyer's test**.

2. **Oxidation with Hot Alkaline $KMnO_4$ (oxidative cleavage of alkenes).** When an alkene is heated with concentrated solution of alkaline $KMnO_4$, cleavage of the C = C bond takes place resulting in the formation of ketones and/or carboxylic acids and CO_2.
   (*i*) Terminal = CH_2 is oxidized to CO_2.
   (*ii*) If there is a hydrogen attached to the double bonded carbon atom, it is oxidized to –COOH.
   (*iii*) If there is no hydrogen attached to the double bonded carbon atom, it is oxidized to ketone.

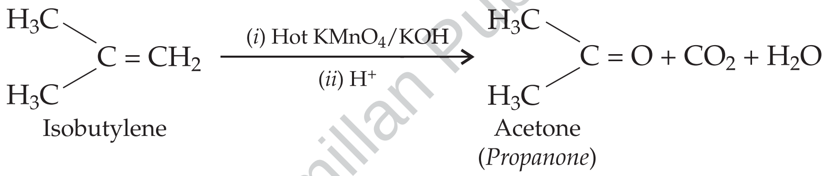
   It is illustrated by the examples given below.

(*a*) 

$$\underset{\text{Propylene}}{CH_3-CH=CH_2} \xrightarrow[(ii)\ H^+]{(i)\ \text{Hot } KMnO_4} \underset{\substack{\text{Acetic acid}\\(\textit{Ethanoic acid})}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + CO_2 + H_2O$$

(*b*) 

$$CH_3-CH_2-CH=CH_2 \xrightarrow[(ii)\ H^+]{(i)\ \text{Hot } KMnO_4/KOH} \underset{\substack{\text{Propionic acid}\\(\textit{Propanoic acid})}}{CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + H_2O + CO_2$$

(*c*) 

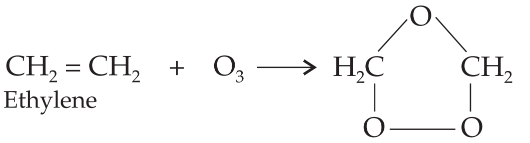
Isobutylene

Acetone

(*Propanone*)

Thus, by identifying the products formed on oxidation with alkaline $KMnO_4$ it is possible to locate the position of the double bond in an unknown alkene molecule.

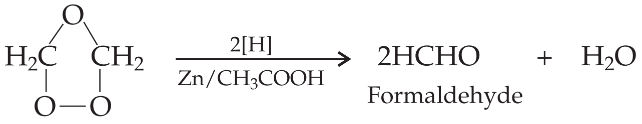
3. **Oxidation with Ozone (Ozonolysis).** When ozone is passed through a solution of ethylene in an inert solvent such as carbon tetrachloride at low temperature, an ozonide is obtained.



Ethylene

Ethylene ozonide

The ozonides on reduction with zinc and acetic acid or hydrogen in the presence of a metal catalyst (Pt or Pd) or on boiling with water containing traces of zinc dust decomposes to give carbonyl compounds, aldehydes and/or ketones. The fission of the molecule takes place at the position of the double bond.



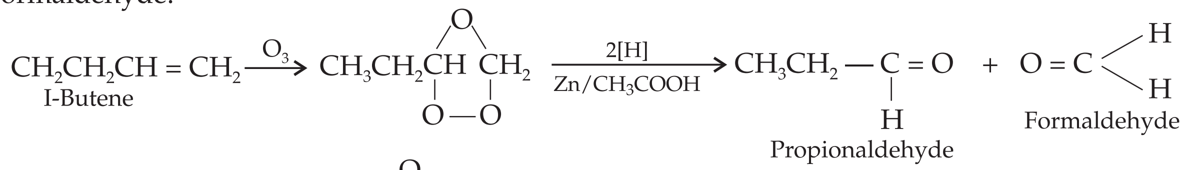
Ethylene ozonide

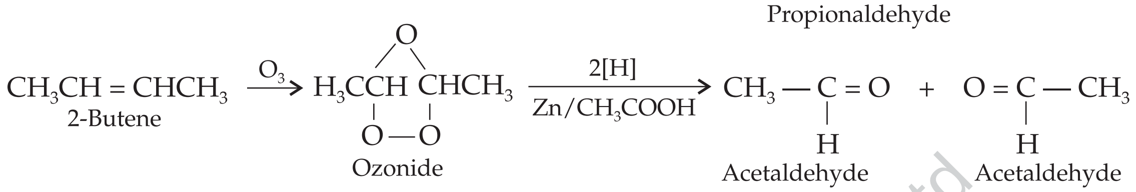
Formaldehyde

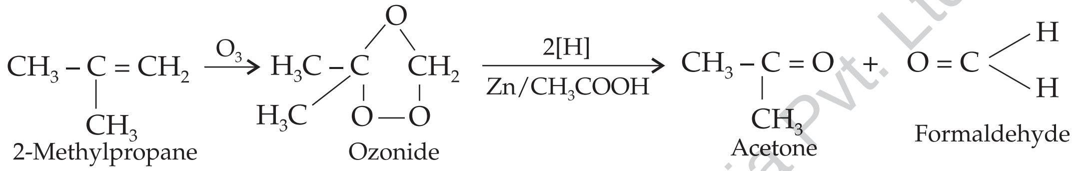
The process of formation of ozonide and its decomposition to give carbonyl compounds is known as **ozonolysis**. Ozonolysis can help to locate the position of double bond in an unknown alkene. For example, different isomers of butene can be identified by examining the products formed on ozonolysis.

Thus, 1-butene on ozonolysis forms a mixture of propionaldehyde and formaldehyde.

2-Butene forms only acetaldehyde whereas isobutylene (2-Methylpropene) forms a mixture of acetone and formaldehyde.

(*i*)


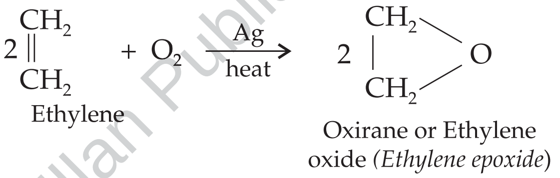
(*ii*)


(*iii*)


4. **Combustion.** Alkenes burnt in air to form carbon dioxide and water. They burn with a yellow, sooty flame. This reaction is exothermic.

$$\underset{\text{Ethylene}}{C_2H_4\,(g)} + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 2H_2O\,(l) + 1410.60\,\text{kJ}$$

5. **Catalytic Oxidation.** A mixture of ethylene and air when passed over silver at 525–625 K, gives ethylene oxide.



C. SUBSTITUTION REACTIONS

Alkenes give substitution reactions at high temperature. Chlorine or bromine replaces hydrogen of the alkyl group at about 773 K without breaking the double bond. *If the alkyl group contains more than one carbon atom, then the substitution occurs at the carbon next to the double bond.* For example,

$$\underset{\text{Propene}}{CH_3CH = CH_2} + Cl_2 \xrightarrow{773\text{ K}} \underset{\substack{\text{3-chloropropene}\\(\textit{Allyl chloride})}}{Cl.CH_2CH = CH_2} + HCl$$

$$\underset{\text{1-Butene}}{CH_3CH_2CH = CH_2} + Cl_2 \xrightarrow{773\text{ K}} \underset{\text{3-chloro-1-butene}}{CH_3CH(Cl)CH = CH_2} + HCl$$

D. POLYMERIZATION

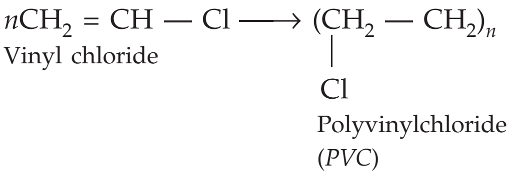
A large number of simple molecules (monomers) combine to form large molecules called macromolecules or polymers. This process is known as **polymerization**.

1. When ethylene is heated with traces of oxygen (0.01%) at 373 K under high pressure, it forms the polymers known as *polyethylene* or *polythene*,

$$\underset{\substack{\text{Ethylene}\\(\textit{Ethene})}}{nCH_2 = CH} \xrightarrow{373\text{ K, High pressure}} \underset{\substack{\text{Polyethylene}\\(\textit{Polythene})}}{(-CH_2-CH_2-)_n}$$

where, *n* is the degree of polymerization. Its value is 100 or more. Polythene is flexible and tough polymer, that is, water resistant and has excellent insulating properties.

2. Substituted ethenes on polymerization give a variety of substances. For example,



$$nCH_2=CH-Cl \longrightarrow (\underset{\underset{Cl}{|}}{CH_2-CH_2})_n$$

Vinyl chloride

Polyvinylchloride (*PVC*)

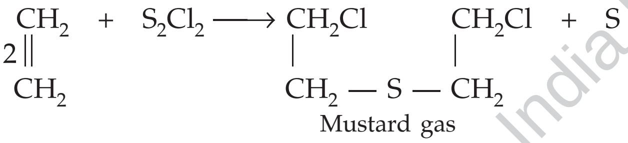
Plastic bottles, raincoats, pipes, etc., are made of PVC.

3. Tetrafluoro derivative of ethene polymerises to teflon,

$$\underset{\text{Tetra fluoroethene}}{nCF_2=CF_2} \longrightarrow \underset{\substack{\text{Poly tetrafluoroethene}\\ (\textit{PTFE, Teflon})}}{(CF_2-CF_2)_n}$$

Due to its thermal stability and chemical inertness, teflon is used in non-stick utensils. It is also used in the manufacture of chemically resistant pipes.

4. Ethylene on treatment with sulphur monochloride, S_2Cl_2 gives a poisonous gas known as mustard gas,



$$2\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + S_2Cl_2 \longrightarrow \begin{array}{ccccc}CH_2Cl & & & & CH_2Cl\\ | & & & & |\\ CH_2 & - & S & - & CH_2\end{array} + S$$

Mustard gas

11.12 POLYMERIZATION

Polymers *may be defined as substances made up of giant molecules of high molecular mass, each molecule of which consists of a very large number of simple molecules joined together through covalent bonds in a regular manner.*

11.12.1 Terms Used in Polymers

Monomers. The simple molecules which combine with one another repetitively to form the polymers are called **monomers.**

Repeat Unit. Consider the case of polyethylene polymer. It is made from polymerizing ethylene as shown below:

$$nCH_2=CH_2 \xrightarrow{\text{Polymerization}} (-CH_2-CH_2-)_n$$

Thus, we find that ethyene ($CH_2=CH_2$) is not the repeat unit in the polymer. Repeat unit is $-CH_2-CH_2-$ which is repeated over and over again to produce the polymer. Thus, **repeat unit** *is the smallest chain which is repeated to provide the polymer.*

Degree of Polymerization. It is the number of times a repeat unit is contained in the polymer molecule. In the above example of polyethylene, *n* denotes the degree of polymerization. Usually, *n* is very large, of the order of a few thousands or tens of thousand.

11.12.2 Homopolymers and Copolymers

Depending upon the nature of the repeating structural unit, polymers are divided into two categories:

(*i*) **Homopolymers.** *Polymers whose repeat unit is derived from only one type of monomer units are of ethylene molecules, the repeat unit, i.e.* $-CH_2-CH_2-$ is derived from only one type of monomer, *i.e.*, ethylene.

$$\underset{\substack{\text{Ethylene}\\ (\textit{Monomer})}}{nCH_2=CH_2} \xrightarrow{\text{Polymerization}} \underset{\substack{\text{Polyethylene}\\ (\textit{Polymer})}}{(-CH_2-CH_2-)_n}$$

Polypropylene, polyvinyl chloride (PVC), polyisoprene, neoprene (polychloroprene), polyacrylonitrile (PAN), nylon-6, polybutadiene, teflon (polytetrafluoroethylene), etc. are other examples of homopolymers.

(ii) **Copolymers.** Polymers whose repeat units are derived from two or more types of monomer units are called **copolymers.** For example, in case of nylon 66, the repeat unit, *i.e.*

$$—NH—(CH_2)_6—NH—CO—(CH_2)_4—CO—$$

is derived from two monomer units, *i.e.* hexamethylene diamine and adipic acid.

$$\underset{\substack{\text{Hexamethylenediamine}\\(\textit{Monomer})}}{nH_2N—(CH_2)_6—NH_2} + \underset{\substack{\text{Adipic acid}\\(\textit{Monomer})}}{nHOOC—(CH_2)_4—COOH}$$

$$\Big\downarrow \text{Polymerization}$$

$$\underset{\text{Nylon-66 }(\textit{Polymer})}{[—NH—(CH_2)_6—NH—CO—(CH_2)_4—CO—]_n} + nH_2O$$

Buna-S, polyesters, bakelite, melamine-formaldehyde polymer, etc. are other examples of copolymers.

11.13 CLASSIFICATION OF POLYMERS BASED UPON SOURCE

Depending upon the source from which they are obtained, polymers are broadly divided into two classes:
(1) *Natural polymers* and (2) *Synthetic polymers.*

1. **Natural Polymers.** Polymers which are obtained from animals and plants are called **natural polymers.** Starch, cellulose, proteins, nucleic acids and natural rubber are some examples of this type of polymers. A brief description of these natural polymers is given below:

Starch. It is a polymers of α-glucose. It is the chief food reserve of the plants and is made up of two fractions — amylose and amylopectin. Amylose is a *linear polymer* of α-glucose.

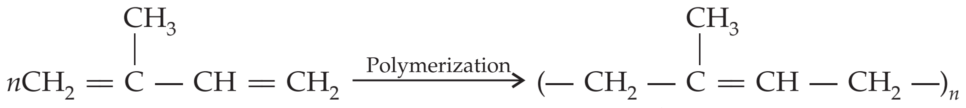
Cellulose. It is a polymer of β-glucose. It is the chief structural material of the plants and is obtained from wood and cotton. About 50% of wood is cellulose, cotton contains about 90% to 95% cellulose.

Both starch and cellulose are made by plants from glucose produced during *photosynthesis.*

> **Chemotrophs and Phototrophs**
>
> Chemotrophs are organisms that obtain energy by the oxidation of electron-donating molecules in their environment. These molecules can be organic (organotrophs) or inorganic (lithotrophs). The chemotroph definition is in contrast to phototrophs which utilize solar energy.

Proteins. Proteins are polypeptides or polyamides. These polymers contain a large number of α-amino acids joined together through peptide (NH–CO) bonds in a particular sequence. These are either long chain or cross-linked polymers.

Natural rubber. It is prepared from latex which, in turn, is obtained from rubber trees. It is a polymer of the hydrocarbon isoprene (2-methyl-1, 3-butadiene). Polymerization is illustrated as under:



$$nCH_2{=}\overset{\overset{\large CH_3}{|}}{C}—CH{=}CH_2 \xrightarrow{\text{Polymerization}} (—CH_2—\overset{\overset{\large CH_3}{|}}{C}{=}CH—CH_2—)_n$$

Isoprene (*2-Methly-1, 3-butadiene*)

Polyisoprene (*Natural rubber*)

2. **Synthetic Polymers.** Polymers which are made in the laboratory or industry are called synthetic polymers. Natural rubber swells and loses elasticity after prolonged exposure to petrol and motor oil. Stability and melting points of many natural polymers are such that they cannot be melted and cast into desired shapes. Further, natural fibres such as cotton, wool, silk, etc., cannot meet the increasing demands. All these needs led man to synthesize polymers in the laboratory and industry. Some important

synthetic polymers are: polyethylene, polystyrene, polyvinyl chloride (PVC), bakelite, nylon and dacron.

11.14 CLASSIFICATION OF POLYMERS BASED UPON STRUCTURE

On the basis of structure, polymers are classified into three types:

1. **Linear Polymers.** In such polymers, the monomers are joined together to form long straight chains of polymer molecules. The various polymeric chains are then stacked over one another to give a well packed structure (Fig. 11.11 *a*). *Linear polymers have high melting points, high densities and high tensile strength because of close packing of chains.* Nylon and polyesters are the examples of linear polymers.
2. **Branched-chain Polymers.** In such polymers, the monomer units not only combine to form the linear chain but also form branches along the main chain (Fig. 11.11 *b*).

   These polymer molecules do not pack well because of branches. As a result, branched chain polymers have lower melting points, densities and tensile strength compared to linear polymers. An important example of a branched-chain polymer is low density polythene.

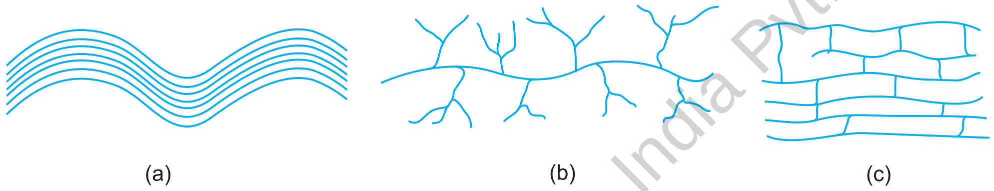


Fig. 11.11: *Different structures of polymers (a) linear structure, (b) branched-chain structure and (c) three-dimensional network structure*

3. **Three-dimensional Network Polymers.** In such polymers, the linear polymer chains formed initially are joined together to form a three-dimensional network structure (Fig. 11.11 *c*). Because of the presence of crosslinks, these polymers are also called **cross-linked polymers.** These polymers are hard, rigid and brittle. Bakelite, urea-formaldehyde polymer and melamine-formaldehyde polymer are some examples of this class.

11.15 CLASSIFICATION OF POLYMERS BASED ON SYNTHESIS

Polymerization mainly occurs by two modes:

1. *Addition polymerization*
2. *Condensation polymerization*

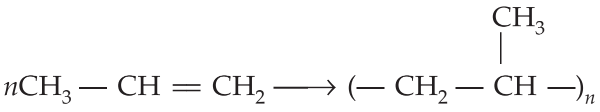
Corresponding to these two modes of synthesis, polymers have been classified into two types:

1. *Addition polymers*
2. *Condensation polymers*

1. **Addition Polymerization.** In this type of polymerization, the molecules of the same or different monomers simply add to one another in repetition leading to the formation of a polymer in which the molecular formula of the repeat unit is the same as that of the monomer. The polymers thus formed are called **addition polymers.**

   Addition polymerization generally occurs among molecules containing double bonds.

$$\underset{\text{Ethylene}}{nCH_2 = CH_2} \longrightarrow \underset{\text{Polyethylene}}{(-CH_2-CH_2)_n}$$

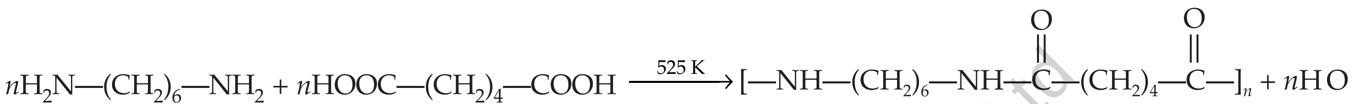


$$n\mathrm{CH_3-CH=CH_2} \longrightarrow (\mathrm{-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-})_n$$

Propylene Polypropylene

2. **Condensation Polymerization.** In this type of polymerization, a large number of monomer molecules combine together usually with the loss of simple molecules such as water, alcohol, ammonia, carbon dioxide, hydrogen chloride, etc., to form a polymer in which the molecular formula of the repeat is not the same as that of the monomer. The polymers thus formed are called **condensation polymers.** Condensation polymerization generally occurs between monomers containing bifunctional compounds.

   Nylon-66, obtained by the condensation of two monomers, *i.e.* hexamethylenediamine and adipic acid, each containing two functional groups with the loss of water molecules, is an example of condensation polymer.



$$n\mathrm{H_2N{-}(CH_2)_6{-}NH_2} + n\mathrm{HOOC{-}(CH_2)_4{-}COOH} \xrightarrow{525\ \mathrm{K}} [\mathrm{-NH{-}(CH_2)_6{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}}]_n + n\mathrm{H\,O}$$

Hexamethylenediamine Adipic acid Nylon-66

Terylene and bakelite are other examples of condensation polymers.

11.16 CLASSIFICATION OF POLYMERS BASED UPON INTERMOLECULAR FORCES

Depending upon the magnitude of intermolecular forces, polymers have been divided into the following four categories:

(*i*) **Elastomers.** Elastomers are those polymers in which the intermolecular forces of attraction between the polymer chains are the weakest.

Elastomers are amorphous polymers having high degree of elasticity. They have the ability to stretch out many times their normal length and return to their original position when the force is withdrawn. These polymers consist of randomly coiled molecular chains of irregular shape having a few cross links (Fig. 11.12). When the force is applied, these coiled chains open out and the polymer is stretched. Since the van der Waal's forces of attraction between the polymer chains are very weak, these cannot maintain this stretched form. Therefore, as soon as the force is withdrawn, the polymer chains returns to its original coiled state. Thus, we observe that weak *van der Waals' forces of attraction allow the polymer chains to be stretched on applying the force but the cross-links bring the polymer back to the original position when the force is withdrawn.* The most important example of an elastomer is natural rubber.

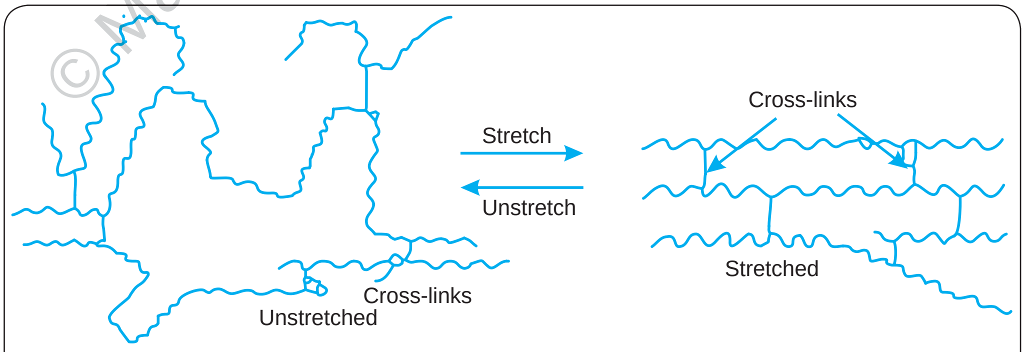


Fig. 11.12: *Unstretched and stretched forms of an elastomer*

Vulcanization. Properties like tensile strength, elasticity and resistance to abrasion of natural rubber can be improved by a process called **vulcanization.** It consists of heating rubber with 3%–5% sulphur. During vulcanization, sulphur cross-links between polymer chains are introduced (Fig. 11.13). The

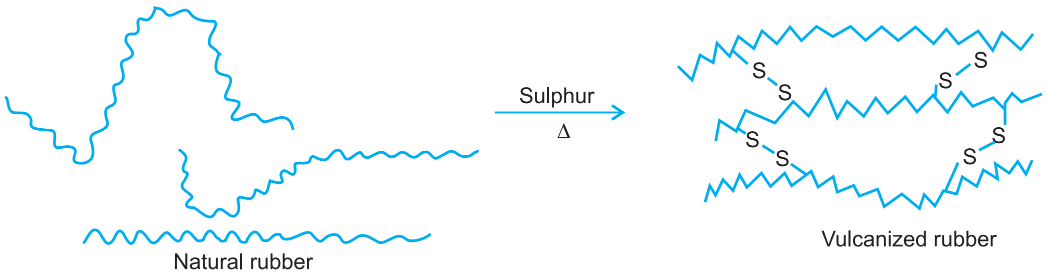


Fig. 11.13: *In vulcanized rubber, the polymer chains are held together by polysulphide bridges or cross-links*

Charles Goodyear

process of vulcanization was discovered by Charles' Goodyear in 1839. Goodyear is now a famous brand of automobile tyres and tubes. Fig. 11.13 given above illustrates how sulphur cross-links between the polymer chains are formed.

(ii) **Fibres.** Polymers having the strongest intermolecular forces of attraction are called **fibres.** These forces are either due to H-bonding or dipole-dipole interactions. In case of nylons the intermolecular forces are due to H-bonding (Fig. 11.14) while in polyesters and polyacrylonitrile they are due to powerful dipole-dipole interactions between the polar carbonyl (C=O) groups and, between carbonyl and cyano (–C ≡ N) groups respectively.

Fibres show high tensile strength and minimum elasticity due to strong intermolecular forces.

The molecules of these polymers are long, thin and thread-like and hence polymer chains can be easily packed over one another. As a result, they have high melting points and low solubility.

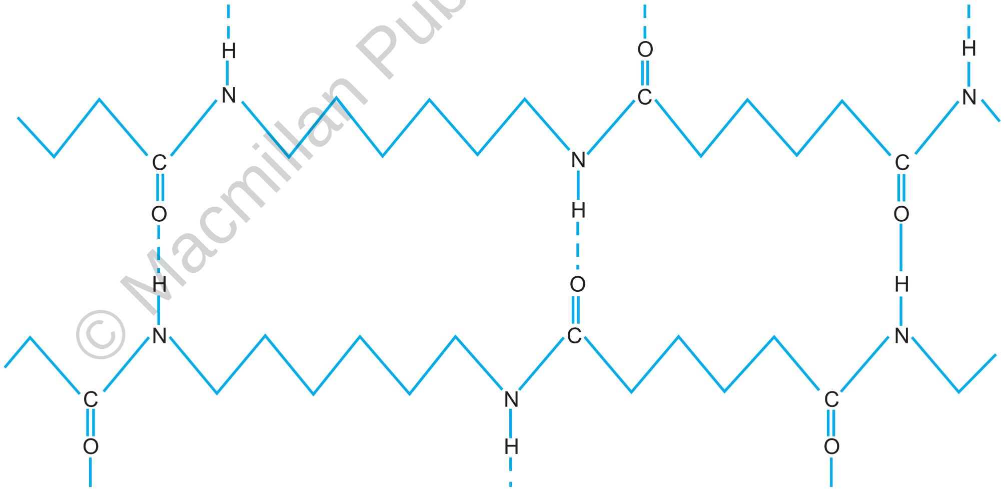


Fig. 11.14: *Hydrogen bonding in Nylon-66*

(iii) **Thermoplastics.** Thermoplastics are those polymers in which the intermolecular forces of attraction are in between those of elastomers and fibres. These polymers which are linear in shape and hard at room temperature, become soft and viscous on heating and again become rigid on cooling. The process of softening and cooling can be repeated as many times as desired without any change in properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases, etc. Thermoplastics have little or no cross linking and, hence, the individual polymer chains can slip past

one another on heating. Some common examples of thermoplastics are: polythene, polystyrene, polyvinyl chloride, teflon, polyvinyl acetate and polyacrylonitrile.

Plasticizers. Those plastics which do not soften easily on heating can be made soft by the addition of certain organic compounds called **plasticizers.** Dialkylphthalates or cresyl phosphates are the commonly used platicizers.

(iv) **Thermosetting Polymers.** Thermosetting polymers are semifluid substances with low molecular weights which on heating in a mould, undergo change in chemical composition to give a hard, infusible and insoluble mass. This hardening on heating takes place due to extensive cross-linking between different polymer chains to give a three-dimensional network solid (Fig. 11.15).

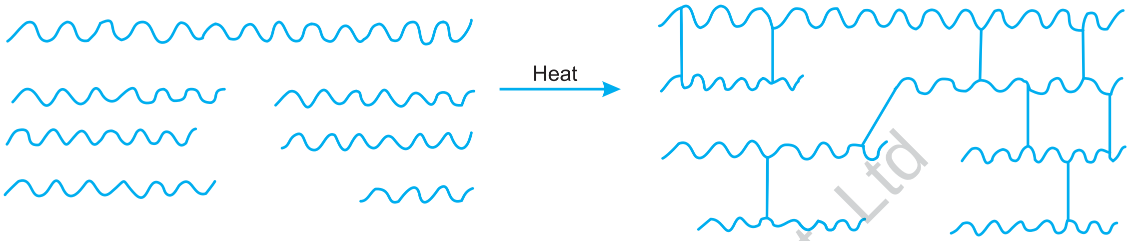


Fig. 11.15: *Conversion of uncross-linked polymer into highly cross-linked thermosetting*

Thus, a **thermoplastic polymer** *can be melted again and again without any change, while a* **thermosetting polymer** *can be heated only once when it permanently sets into a solid which cannot be remelted and reworked.* Some examples of thermosetting polymers are: phenol-formaldehyde (bakelite), urea-formaldehyde and melamine-formaldehyde.

11.17 ADDITION POLYMERS

Various polymers of this category are discussed below:

1. **Low Density Polythene.** In this polymer, the repeat unit is $—CH_2–CH_2—$. It is manufactured by heating ethylene to 473 K under a pressure of 1500 atmospheres in the presence of a trace of oxygen. This polymerizaton occurs by a free-radical mechanism initiated by oxygen.

$$n\mathrm{CH_2=CH_2} \xrightarrow[\text{Traces of oxygen}]{\text{473 K, 1500 atm.}} \underset{\text{Polythene}}{(—\mathrm{CH_2}—\mathrm{CH_2}—)_n}$$

The polythene, thus, produced has a molecular mass of about 20,000 and has a *branched structure.* These branched polythene molecules do not pack well and hence this type of polythene has a low density (0.92 g/cm^3) and a low melting point (384 K). That is, why polythene prepared by free-radical polymerization is called low density polythene.

Properties and Uses. Low density polythene is a *transparent polymer* of moderate tensile strength and high toughness. It is chemically inert and is a poor conductor of electricity.

It is widely used as a packaging material (in the form of thin plastic films, bags, etc.) and as insulation for electrical wires and cables.

2. **High Density Polythene.** It is prepared by *coordination polymerization* of ethylene. In this process, ethylene in a solvent is heated to 333–343 K under a pressure of 6–7 atmospheres in the presence of a catalyst consisting of triethylaluminium and titanium tetrachloride called **Zeigler-Natta catalyst.**

$$\underset{\text{Ethylene}}{n(\mathrm{CH_2=CH_2})} \xrightarrow[\text{Traces of oxygen}]{\text{473 K, 1500 atm.}} \underset{\text{Polythene}}{(—\mathrm{CH_2}—\mathrm{CH_2}—)_n}$$

This polythene consists of linear chains of polymer molecules. These polymer molecules pack well and, hence, this polythene has higher density (0.97 g/cm^3) and higher melting point (403 K) than the polymer produced by *free-radical* polymerization. That is, why polythene prepared by coordination polymerization is called high density polythene.

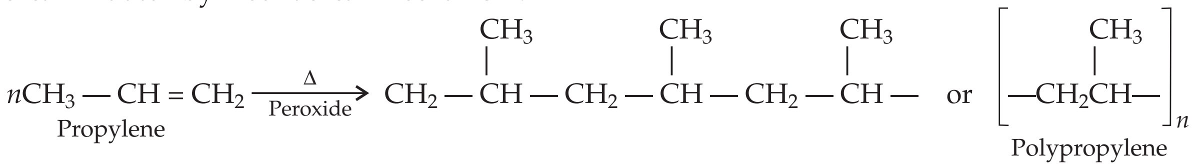
Properties and Uses. High density polythene is a *translucent polymer*. It is also chemically inert but has greater toughness, hardness and tensile strength compared to low density polythene.

It is used in the manufacture of containers, housewares, pipes and bottles.

3. Polypropylene or Polypropene

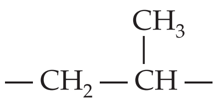
Monomer used: Propylene ($CH_3CH = CH_2$).

Polypropylene is prepared by heating propylene in presence of trace amount of benzoyl peroxide as radical initiator by free-radical mechanism.



$$\underset{\text{Propylene}}{nCH_3-CH=CH_2} \xrightarrow[\text{Peroxide}]{\Delta} CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}- \quad \text{or} \quad \underset{\text{Polypropylene}}{\left[-CH_2\overset{\overset{CH_3}{|}}{CH}-\right]_n}$$

The monomer of polypropylene is $CH_3–CH = CH_2$ and the repeat unit is



$$-CH_2-\overset{\overset{CH_3}{|}}{CH}-$$

Uses. It is harder and stronger than polythene. It is used:

(*i*) in the manufacture of stronger pipes and bottles.

(*ii*) for packing of textiles and foods.

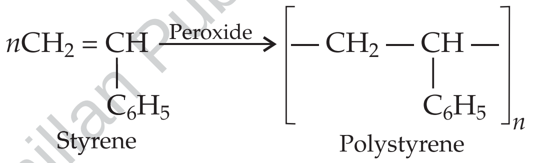
(*iii*) for making liners for bags and heat shrinkable wraps for records.

(*iv*) for making automotive mouldings, seat covers, carpet fibres and ropes.

4. Polystyrene or Styron

Monomer used: Styrene ($C_6H_5CH = CH_2$).

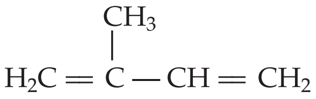
In presence of peroxides, styrene polymerises to form polystyrene.



$$\underset{\text{Styrene}}{nCH_2=\underset{\underset{C_6H_5}{|}}{CH}} \xrightarrow{\text{Peroxide}} \underset{\text{Polystyrene}}{\left[-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-\right]_n}$$

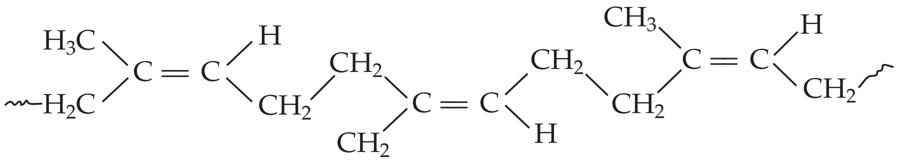
Uses. It is a transparent polymer and is used for making plastic toys, household-wares, radio and television bodies.

5. Natural Rubber. Rubber is a natural polymer and possesses elastic properties. It is put to various uses and is termed as elastomer. It is commercially obtained from rubber latext (from rubber tree) which is a colloidal dispersion of rubber in water. Natural rubber is a linear polymer of isoprene (2-methyl 1, 3-butadiene) and is also known as *cis*-1, 4-polyisoprene.



$$H_2C=\overset{\overset{CH_3}{|}}{C}-CH=CH_2$$

(Isoprene)



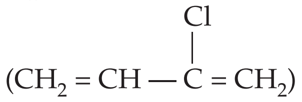
Natural rubber

The *cis*-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure. It can be stretched and exhibit elastic properties. Natural rubber becomes soft at high temperature and becomes brittle at low temperature. It is soluble in non-polar solvents and gets attacked by oxidising agents. To improve its quality vulcanisation of rubber is carried out.

Uses. It is used in making low quality rubber articles.

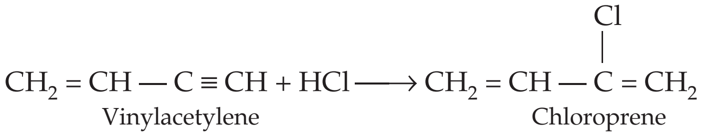
6. **Neoprene (Synthetic rubber).** It is a polymer of chloroprene.

Monomer used: Chloroprene



$$(CH_2=CH-\underset{}{\overset{\overset{\displaystyle Cl}{|}}{C}}=CH_2)$$

Chloroprene is prepared by the Markownikoff's addition of HCl to vinylacetylene at the triple bond.

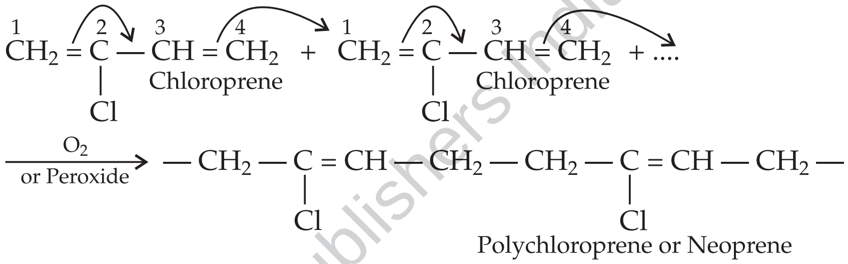


$$\underset{\text{Vinylacetylene}}{CH_2=CH-C\equiv CH}+HCl\longrightarrow \underset{\text{Chloroprene}}{CH_2=CH-\overset{\overset{\displaystyle Cl}{|}}{C}=CH_2}$$

Vinylacetylene needed for the purpose is prepared by dimerization of acetylene as given below.

$$\underset{\text{Acetylene (2 molecules)}}{CH\equiv CH+HC\equiv CH}\longrightarrow \underset{\text{Vinylacetylene}}{CH_2=CH-C\equiv CH}$$

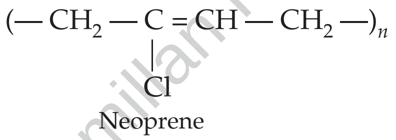
Chloroprene polymerises very fast. No specific catalysts are needed. The polymerization is slower in absence of oxygen. The reaction occurs by 1, 4-addition of one chloroprene molecule to the other as shown below:



$$\underset{\text{Chloroprene}}{\overset{1}{CH_2}=\underset{\underset{\displaystyle Cl}{|}}{\overset{2}{C}}-\overset{3}{CH}=\overset{4}{CH_2}}+\underset{\text{Chloroprene}}{\overset{1}{CH_2}=\underset{\underset{\displaystyle Cl}{|}}{\overset{2}{C}}-\overset{3}{CH}=\overset{4}{CH_2}}+\ldots$$

$$\xrightarrow[\text{or Peroxide}]{O_2}\underset{\text{Polychloroprene or Neoprene}}{-CH_2-\underset{\underset{\displaystyle Cl}{|}}{C}=CH-CH_2-CH_2-\underset{\underset{\displaystyle Cl}{|}}{C}=CH-CH_2-}$$

The polymer may be represented as



$$\underset{\text{Neoprene}}{(-CH_2-\underset{\underset{\displaystyle Cl}{|}}{C}=CH-CH_2-)_n}$$

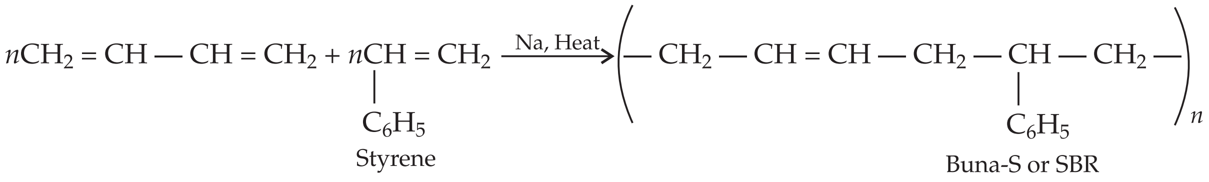
It has excellent rubber like properties.

Uses. Neoprene is inferior to natural rubber in some properties but is quite stable to aerial oxidation and resistant to oils, gasoline and other solvents. It is, therefore, used in the manufacture of hoses, shoe heels, stoppers, etc.

7. **Buna-S (Synthetic rubber).** It is copolymer of 1, 3-butadiene and styrene. **But** stands for 1, 3-butadiene **na** for sodium which is used as the polymerizing agent and **S** stands for styrene. It is also called SBR (Styrene, Butadiene, Rubber).

Monomers used: 1, 3-Butadiene ($CH_2=CH–CH=CH_2$) and styrene ($C_6H_5=CH_2$).

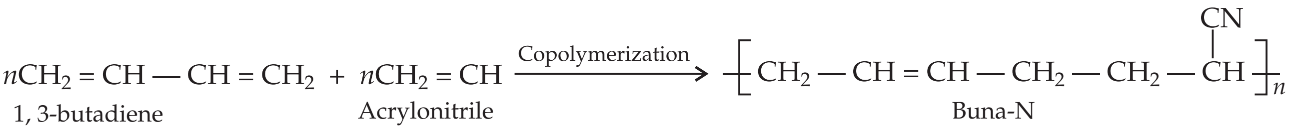
It is obtained by copolymerization of 1, 3-butadiene and styrene in the ratio 3 : 1 in the presence of sodium.



$$nCH_2=CH-CH=CH_2+n\underset{\text{Styrene}}{\underset{\underset{\displaystyle C_6H_5}{|}}{CH}=CH_2}\xrightarrow{\text{Na, Heat}}\underset{\text{Buna-S or SBR}}{\left(-CH_2-CH=CH-CH_2-\underset{\underset{\displaystyle C_6H_5}{|}}{CH}-CH_2-\right)_n}$$

Uses. It is used in the manufacture of tyres, rubber soles, water-proof shoes, etc.

8. **Buna-N (Synthetic rubber):** Buna-N is obtained by copolymerization of 1,3-butadiene and acrylonitrile in the presence of a peroxide catalyst.



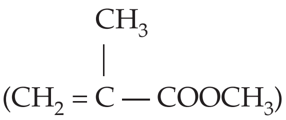
$$\underset{\text{1, 3-butadiene}}{n\mathrm{CH_2=CH-CH=CH_2}} + \underset{\text{Acrylonitrile}}{n\mathrm{CH_2=CH}} \xrightarrow{\text{Copolymerization}} \underset{\text{Buna-N}}{\left[\mathrm{CH_2-CH=CH-CH_2-CH_2-\overset{\overset{CN}{|}}{CH}}\right]_n}$$

It is resistant to the action of petrol, lubricating oils and organic solvents.

Uses: It is used in making oil seals, tank linings, etc.

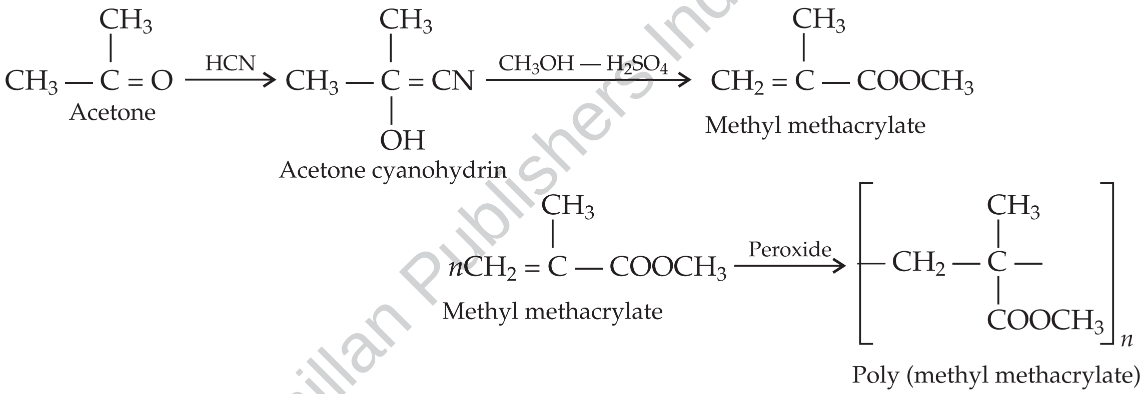
9. **Poly (Methyl methacrylate), PMMA.**

Monomer used: Methyl methacrylate



$$\left(\mathrm{CH_2=\overset{\overset{CH_3}{|}}{C}-COOCH_3}\right)$$

The monomer methyl methacrylate is obtained by treating acetone cyanohydrin with $\mathrm{CH_3OH{-}H_2SO_4}$ which brings about simultaneous hydrolysis, dehydration and esterification. This is polymerized in the presence of a radical initiator to give poly (methyl methacrylate).



$$\underset{\text{Acetone}}{\mathrm{CH_3-\overset{\overset{CH_3}{|}}{C}=O}} \xrightarrow{\text{HCN}} \underset{\text{Acetone cyanohydrin}}{\mathrm{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}=CN}} \xrightarrow{\mathrm{CH_3OH-H_2SO_4}} \underset{\text{Methyl methacrylate}}{\mathrm{CH_2=\overset{\overset{CH_3}{|}}{C}-COOCH_3}}$$

$$\underset{\text{Methyl methacrylate}}{n\mathrm{CH_2=\overset{\overset{CH_3}{|}}{C}-COOCH_3}} \xrightarrow{\text{Peroxide}} \underset{\text{Poly (methyl methacrylate)}}{\left[-\mathrm{CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COOCH_3}{|}}{C}}-}\right]_n}$$

Poly (methyl methacrylate) is a hard and transparent substance.

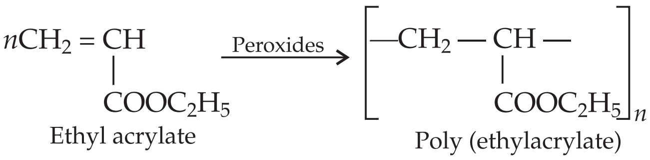
The most important property of poly (methyl methacrylate) is its clearness and excellent light transmission even better than glass.

Uses. It is used in the manufacture of lenses, light covers, light shades, transparent domes and skylights, aircraft windows, dentures and plastic jewellery.

10. **Poly (Ethyl acrylate)**

Monomer used: Ethyl acrylate ($\mathrm{CH_2 = CH - COOC_2H_5}$).

Ethyl acrylate on polymerization in the presence of peroxides gives poly (ethyl acrylate).



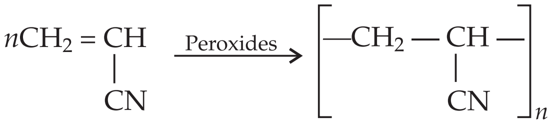
$$\underset{\text{Ethyl acrylate}}{n\mathrm{CH_2=\underset{\underset{COOC_2H_5}{|}}{CH}}} \xrightarrow{\text{Peroxides}} \underset{\text{Poly (ethylacrylate)}}{\left[-\mathrm{CH_2-\underset{\underset{COOC_2H_5}{|}}{CH}-}\right]_n}$$

Poly (ethyl acrylate) is tough but with somewhat rubber-like properties.

11. Polyacrylonitrile (PAN)

Monomer used: Acrylonitrile ($CH_2 = CH–CN$).

Acrylonitrile polymerizes in the presence of peroxides to give polyacrylonitrile.



$$nCH_2 = \underset{\displaystyle CN}{\underset{|}{CH}} \xrightarrow{\text{Peroxides}} \left[-CH_2 - \underset{\displaystyle CN}{\underset{|}{CH}} - \right]_n$$

Acrylonitrile — Polyacrylonitrile

The monomer acrylonitrile is manufactured by either of the following reactions:

$$\underset{\text{Acetylene}}{CH \equiv CH} + HCN \xrightarrow{\text{Peroxides}} \underset{\text{Acrylonitrile}}{CH_2 = CH - CN}$$

$$\underset{\text{Propylene}}{2CH_3CH = CH_2} + \underset{\text{(From air)}}{3O_2} + 2NH_3 \xrightarrow[723\text{ K}]{\text{Oxides of Mo, Co and Al}} \underset{\text{Acrylonitrile}}{2CH_2 = CH - CN} + 6H_2O$$

Uses. Polyacrylonitrile is a hard and high melting material.

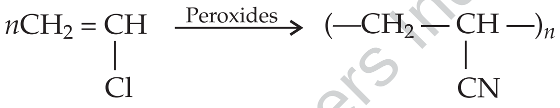
(*i*) It is used in the manufacture of *Orlon* and *Acrilan* fibres used for making clothes, carpets and blankets.

(*ii*) It is blended with other polymers to improve their qualities.

12. Polyvinyl Chloride (PVC)

Monomer used: Vinyl chloride ($CH_2 = CH — Cl$).

Vinyl chloride polymerises in the presence of peroxides to form polyvinyl chloride.



$$nCH_2 = \underset{\displaystyle Cl}{\underset{|}{CH}} \xrightarrow{\text{Peroxides}} (-CH_2 - \underset{\displaystyle CN}{\underset{|}{CH}} -)_n$$

Vinyl chloride — Polyvinyl chloride

The monomer vinyl chloride is itself manufactured by the addition of HCl to acetylene in the presence of mercury salts as catalyst or by dehydrochlorination of ethylene dichloride.

$$\underset{\text{Acetylene}}{CH \equiv CH} + CHl \xrightarrow{Hg^{2+}} \underset{\text{Vinyl chloride}}{CH_2 = CH - Cl}$$

$$CH_2Cl - CH_2Cl \xrightarrow{873\text{-}923\text{ K}} \underset{\text{Vinyl chloride}}{CH_2 = CH - Cl} + HCl$$

Uses

(*i*) It is good electrical insulator and, hence, is used for coating wires and cables.

(*ii*) It is also used in making gramophone records and pipes.

(*iii*) It is used for making raincoats, hand bags, plastic dolls, upholstery, shoe soles and vinyl flooring. Since dibutylphthalate is slightly volatile, it evaporates slowly.

13. Polytetrafluoroethylene (PTFE) or Teflon

Monomer used: Tetrafluoroethylene ($F_2C = CF_2$).

Tetrafluoroethylene polymerises in the presence of oxygen to give polytetrafluoroethylene popularly called **teflon.**

$$\underset{\text{Tetrafluoroethylene}}{nCF_2 = CF_2} \xrightarrow{O_2} \underset{\text{Polytetrafluoroethylene or Teflon}}{(–CF_2 –CF_2 –)_n}$$

Uses. Teflon is unaffected by solvents, boiling acids, aqua-regia and temperature up to 598 K.

(*i*) Because of its great chemical inertness and high thermal stability, teflon is used for making **non-sticks utensils.**

(*ii*) It is also used for making gaskets, pump packing, valves, seals, non-lubricated bearings, etc.

Common articles made of polymers

11.18 ALKYNES

Acyclic (open-chain) unsaturated hydrocarbons containing a carbon-carbon triple bond are called alkynes. Their general formula is C_nH_{2n-2} where n = 2, 3, 4, ..., etc.

11.18.1 Structure of Alkynes

A molecule of ethyne or acetylene (CH ≡ CH) contains two carbon atoms, which are *sp*-hybridized. An *sp*-hybridized carbon atom has two *sp*-hybrid orbitals which are oriented along a straight line while the two unhybridized orbitals (*i.e.*, $2p_y$ and $2p_z$) are perpendicular to each other.

In the formation of acetylene molecule, one of the *sp*-orbitals of one carbon atom overlaps with a similar orbital of the other carbon along the internuclear axis to form one C–C, σ-bond. The second *sp*-orbital of each carbon atom overlaps with 1*s*-orbital of hydrogen atom to form C–H, σ-bond. Since the *sp*-orbitals of each carbon lie along a straight line and overlapping takes place along their internuclear axis, all the four atoms of acetylene lie along the same straight line. Thus, *acetylene is a linear molecule.* There are two unhybridized, $2p_y$ and $2p_z$-orbitals left on each C-atom which are perpendicular to each other and also to the plane of carbon and hydrogen atoms. The two $2p_y$-orbitals, of each carbon atom overlap sideways to form a π-bond. Similarly, $2p_z$-orbitals of each carbon atom overlap resulting in the formation of a second π-bond as shown in Fig. 11.16(*a*).

Electron cloud of a π-bond has two halves. The two halves of one π-bond lie above and below the line joining the two carbon atoms and the two halves of the second π-bond lie in front and at the back of this line. However, the four halves of the electron clouds of two π-bonds merge with one another to form a single electron cloud which has cylindrical symmetry about the internuclear axis [Fig. 11.16(*b*)].

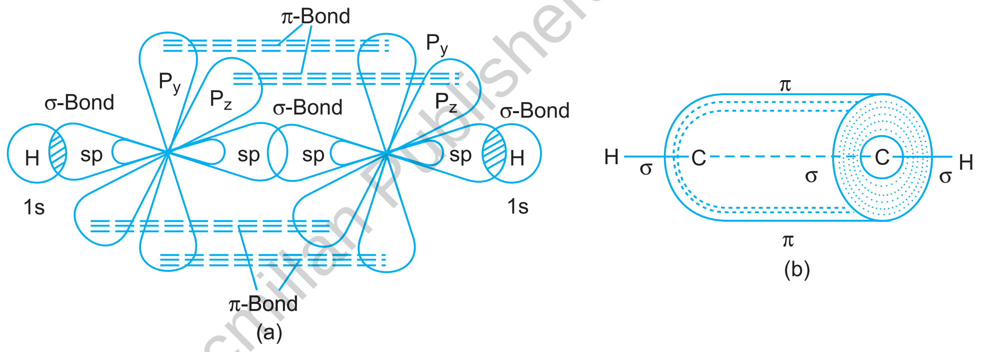
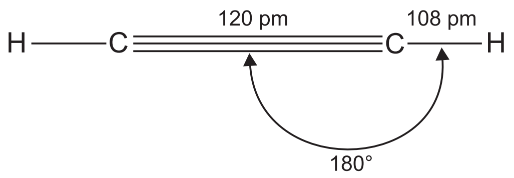


Fig. 11.16: *(a) Orbital picture of acetylene (Ethyne) molecule; (b) Acetylene molecule with its carbon atoms surrounded by a cylindrical π-electron cloud.*

Thus, it follows that a carbon-carbon triple bond is made up of one strong σ-bond and two weak π-bonds. Bond strength of triple bond is 80.3 kJ mol^{-1} as compared to 598 kJ mol^{-1} for carbon-carbon double bond in ethene and 347 kJ mol^{-1} for carbon-carbon single bond in ethane.

Due to the smaller size of *sp*-orbitals (50% *s*-character) and sideways overlapping of unhybridized *p*-orbitals, the carbon-carbon bond distance in acetylene is only 120 pm with H–C–C bond angle of 180º.



Alkynes do not exhibit geometrical isomerism due to their linear structure.

11.19 NOMENCLATURE OF ALKYNES

Nomenclature of some alkynes, according to common system and IUPAC system is given in Table 11.2.

Table 11.2

Compound	Common Name	IUPAC Name
$CH \equiv CH$	Acetylene	Ethyne
$CH_3C \equiv CH$	Methyl acetylene	Propyne
$CH_3CH_2C \equiv CH$	Ethyl acetylene	But-1-yne
$CH_3C \equiv CCH_3$	Dimethyl acetylene	But-2-yne
$CH_3CH_2C \equiv CCH_3$	Ethyl methyl acetylene	Pent-2-yne

The following points may be borne in mind while naming alkynes:

1. The longest carbon chain containing the triple bond forms the parent chain and the alkyne is named accordingly.
2. The positions of the triple bond and other substituents (including double bond) are indicated by Arabic numerals.
3. Numbering of the parent chain is done such that the triple bond gets the lowest number. If the triple bond gets the same number from either side of the parent chain, then, the numbering is done in a manner that the substituents get the lowest numbers.
4. If both the double and triple bonds are present, then the compound is named as derivative of alkyne rather than alkene. The terminal '*e*' from the suffix '*ene*' is dropped while naming.
5. Numbering of the parent chain containing both double and triple bonds is done in such a manner that gives a lower number to the double or the triple bond, i.e. lowest sum rule for multiple bonds is followed. However, preference is given to the *double* bond over the *triple* bond. This is illustrated with the help of the following examples:

$$\overset{5}{HC} \equiv \overset{4}{C} - \overset{3}{CH_2} - \overset{2}{CH} = \overset{1}{CH_2} \qquad\qquad \overset{6}{HC} \equiv \overset{5}{C} - \overset{4}{CH} = \overset{3}{CH} - \overset{2}{CH} = \overset{1}{CH_2}$$

Pent-1-en-4-yne Hexa-1, 3-dien-5-yne

11.20 ISOMERISM IN ALKYNES

Alkynes exhibit the following types of isomerism:

(*i*) **Position Isomerism.** Butyne and higher alkynes exhibit position isomerism due to different possible position of the triple bond on the carbon chain. For example,

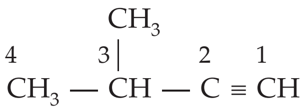
$$CH_3 - CH_2 - C \equiv CH \qquad\qquad CH_3 - C \equiv C - CH_3$$

But-1-yne But-2-yne

(*ii*) **Chain Isomerism.** Alkynes having five or more carbon atoms exhibit chain isomerism due to different structures of the carbon chain. For example,

$$CH_3 - CH_2 - CH_2 - C \equiv CH$$

Pent-1-yne



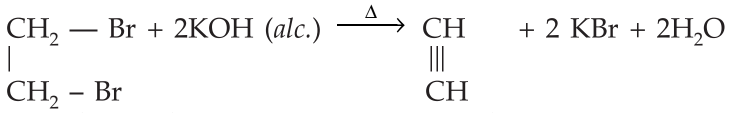
$$\overset{4}{CH_3} - \overset{\overset{CH_3}{|}}{\overset{3}{CH}} - \overset{2}{C} \equiv \overset{1}{CH}$$

3-Methylbut-1-yne

11.21 PREPARATION OF ALKYNES

Methods of preparation of alkynes are discussed as below:

1. **By Dehydrohalogenation of Dihaloalkanes.** Alkynes can be prepared by dehydrohalogenation of *vicinal*-dihaloalkanes by heating them with an alcoholic solution of potassium hydroxide. For example,



$$\begin{array}{l} CH_2 - Br \\ | \\ CH_2 - Br \end{array} + 2KOH\ (alc.) \xrightarrow{\Delta} \begin{array}{c} CH \\ ||| \\ CH \end{array} + 2\ KBr + 2H_2O$$

1, 2-Dibromoethane — Acetylene

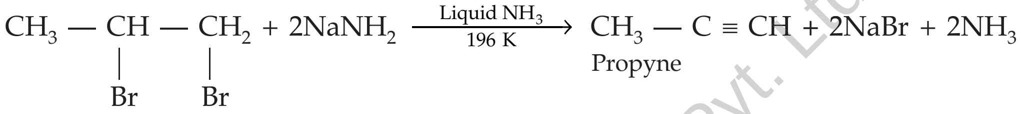
The reaction takes place in two steps. It is possible to isolate the intermediate product vinyl bromide, as shown by the following equations:

$$\underset{\text{Ethylene dibromide}}{BrCH_2 - CH_2Br} + KOH\ (alc.) \xrightarrow{\Delta} \underset{\text{Vinyl bromide}}{CH_2 = CHBr} + KBr + H_2O$$

$$CH_2 = CH - Br + KOH\ (alc.) \xrightarrow{\Delta} \underset{\text{Acetylene}}{CH \equiv CH} + KBr + H_2O$$

Sodamide in liquid ammonia can also bring about this reaction. We get a better yield of the product by this method.

$$\underset{\text{1, 2-Dibromoethane}}{BrCH_2 - CH_2Br} + 2NaNH_2 \xrightarrow[196\ K]{\text{Liquid } NH_3} \underset{\text{Acetylene}}{CH \equiv CH} + 2NaBr + 2NH_3$$



$$CH_3 - \underset{Br}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH_2}} + 2NaNH_2 \xrightarrow[196\ K]{\text{Liquid } NH_3} \underset{\text{Propyne}}{CH_3 - C \equiv CH} + 2NaBr + 2NH_3$$

1, 2-Dibromopropane

Alkynes can also be prepared by the action of alcoholic potassium hydroxide on *gem*-dihalides. For example,

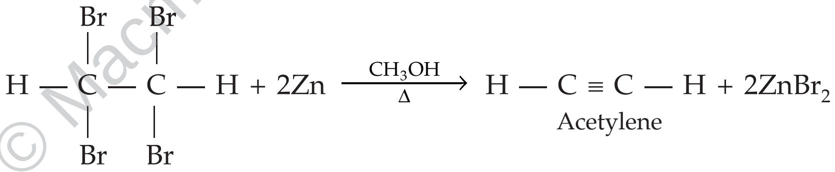
$$\underset{\text{1, 1-Dibromoethane}}{CH_3 - CHBr_2} \xrightarrow[-HBr]{KOH\,(alc.),\ \Delta} \underset{\text{Vinyl bromide}}{CH_2 = CHBr} \xrightarrow[-HBr]{KOH\,(alc.),\ \Delta} \underset{\text{Acetylene}}{CH \equiv CH}$$

2. **From Natural Gas.** Natural gas is mostly methane. Ethyne is prepared by high-temperature cracking of methane. Heat for the cracking operation is developed by partial oxidation of methane with oxygen. The heat evolved cracks the excess methane to ethyne. After rapid quenching with water, ethyne is separated from the gas stream by absorption-desorption in a suitable solvent. The reactions are given below:

$$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O$$

$$2CH_4 \longrightarrow CH \equiv CH + 3H_2,\ \Delta H = +\ 79.8\ \text{kcal}$$

3. **By Dehalogenation of Tetrahalides.** Tetrahaloalkanes on heating with zinc dust in methanol solution undergo dehalogenation to yield alkynes. For example,



$$H - \overset{Br}{\underset{Br}{\overset{|}{\underset{|}{C}}}} - \overset{Br}{\underset{Br}{\overset{|}{\underset{|}{C}}}} - H + 2Zn \xrightarrow[\Delta]{CH_3OH} \underset{\text{Acetylene}}{H - C \equiv C - H} + 2ZnBr_2$$

1, 1, 2, 2-Tetrabromomethane

4. **Synthesis from Carbon and Hydrogen (Berthelot Synthesis).** Acetylene can be obtained by passing hydrogen through an electric arc between carbon electrodes.

$$2C + H_2 \xrightarrow[3270\ K]{\text{Electric arc}} \underset{\text{Acetylene}}{HC \equiv CH}$$

11.21.1 Laboratory Preparation of Acetylene

Ethyne (acetylene) is prepared in the laboratory as well as on commercial scale by the action of water on calcium carbide as shown by the following equation:

$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O \longrightarrow \underset{(\textit{Acetylene})}{\underset{\text{Ethyne}}{HC \equiv CH}} + Ca(OH)_2$$

Calcium carbide needed for the purpose is manufactured by heating limestone (calcium carbonate) with coke in an electric furnace at 2275 K.

$$CaCO_3 \xrightarrow{2275\text{ K}} CaO + CO_2$$

$$CaO + 3C \xrightarrow{2275\text{ K}} CaC_2 + CO$$

Procedure. Set-up of the apparatus for the laboratory preparation of acetylene is shown in Fig. 11.17. Calcium carbide lumps are placed on a layer of sand in a conical flask, fitted with a dropping funnel and a delivery tube. Water is now dropped from the dropping funnel and the acetylene gas thus formed is collected by downward displacement of water.

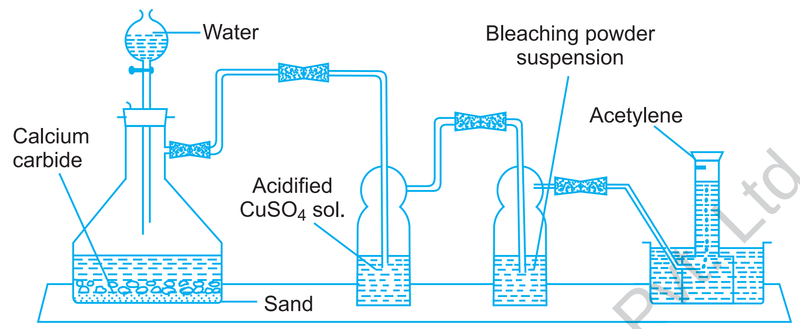


Fig. 11.17: *Laboratory preparation of acetylene*

Acetylene gas prepared by this method contains impurities of hydrogen sulphide and phosphine due to the contaminations of calcium sulphide and calcium phosphide in calcium carbide. Hydrogen sulphide is removed by bubbling the gas through an acidified solution of copper sulphate while phosphine is removed by passing the gas through a suspension of bleaching powder. Pure acetylene is finally collected over water.

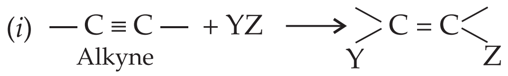
11.22 PHYSICAL PROPERTIES OF ALKYNES

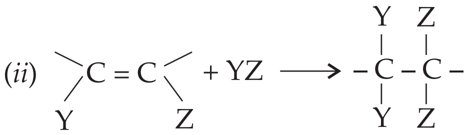
1. Physical state of the first three members ($C_2 - C_4$) are gases, the next eight ($C_5 - C_{11}$) members are liquids while higher members are solids at room temperature.
2. They possess lower density than water.
3. All alkynes are colourless and odourless except acetylene which has characteristic garlic odour due to the presence of impurities of phosphine and arsine.
4. They are insoluble in water, but dissolve in organic solvents of low polarity such as benzene and carbon tetrachloride.
5. They have higher melting points and boiling points than the alkanes and alkenes containing same number of carbon atoms. Their melting and boiling points gradually increase with the increase in their molecular mass. This is due to gradual increase in the magnitude of van der Waals' force of attraction.
6. Like alkanes and alkenes, branched-chain alkynes have lower melting points than straight-chain isomers due to smaller surface area.

11.23 CHEMICAL PROPERTIES OF ALKYNES

Alkynes contain a carbon-carbon triple bond ($C \equiv C$) which is made up of a strong σ-bond and two weak π-bonds. Presence of π-bonds makes alkynes highly reactive and accounts for their tendency to undergo addition reaction.

Alkynes undergo electrophilic addition reactions due to the availability of π-electrons. Against expectation alkynes undergo electrophilic addition reactions less readily than alkenes. The addition reactions in alkynes take place in two stages, the triple bond initially changes to double bond and finally to single bonds as illustrated below:

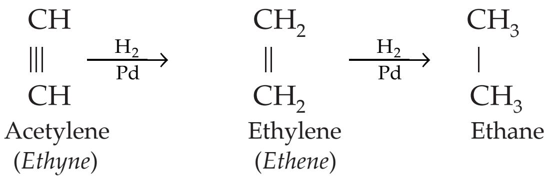




Reactions of alkynes are described as under:

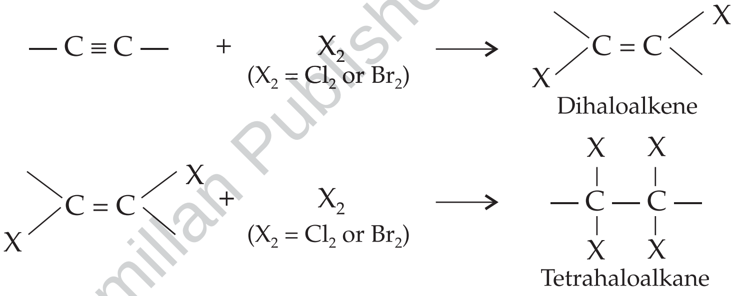
A. ELECTROPHILIC ADDITION REACTIONS

1. **Addition of Hydrogen.** In the presence of catalyst, such as finely-divided Ni, Pd or Pt, acetylene combines with hydrogen to form ethylene and finally ethane (*catalytic hydrogenation*) in two steps as given below:



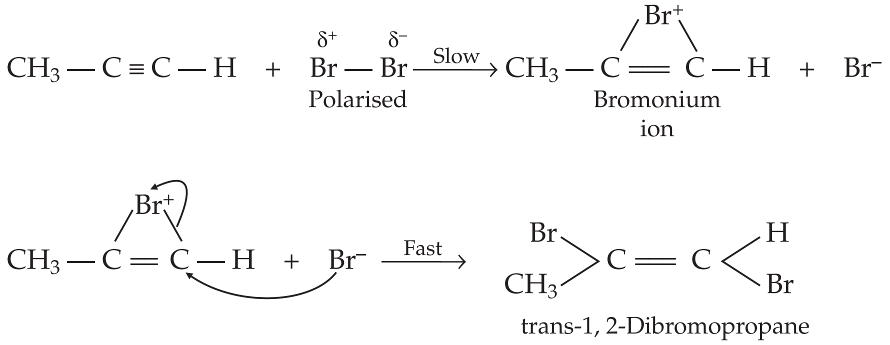
The reaction can be stopped at ethylene stage by using palladium catalyst deposited on barium sulphate poisoned with quinoline or *Lindlar's catalyst* (Pd-$CaCO_3$ catalyst partially poisoned with lead acetate).

2. **Addition of Halogens.** Alkynes add to halogens to form generally *trans* dihaloalkenes and finally tetrahalo alkanes.



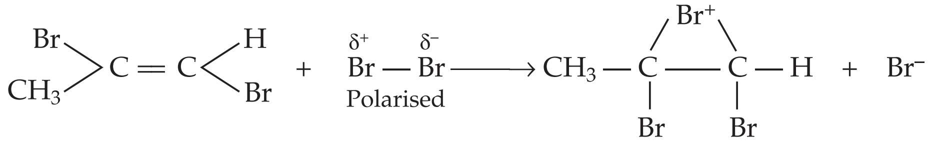
Mechanism. The mechanism of the reaction involves electrophilic addition. It takes place in two steps. This is known as halonium ion mechanism of addition. Bromine (or any halogen) gets polarised under the influence of π-electrons. Bromonium ion (Br^+) adds first forming a bridge bond, followed by the attachment of bromide ion.

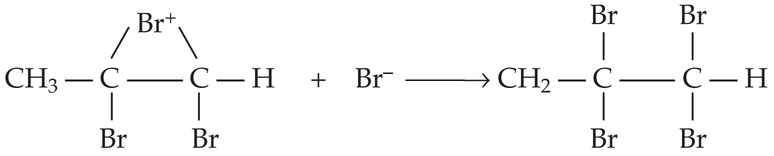
First step.



This sequence is repeated in the addition of another bromine molecule.

Second step.



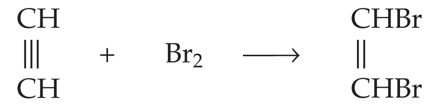


1, 1, 2, 2-Tetrabromopropane

(*i*) With chlorine. Acetylene reacts explosively with *gaseous chlorine* to form carbon and HCl.

$$C_2H_2 + Cl_2 \longrightarrow 2C + 2HCl$$

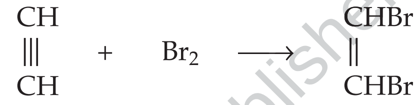
However, controlled reaction can be carried out when acetylene adds on gaseous chlorine in dark to form acetylene di and tetrachloride. Light and metallic halides such as $FeCl_3$ catalyse the reaction.



$$\begin{array}{c}CH\\ |||\\ CH\end{array} + Br_2 \longrightarrow \begin{array}{c}CHBr\\ ||\\ CHBr\end{array}$$

Acetylene (*Ethyne*) + (*aq. sol.*) (Brown) → Acetylene dibromide (White) (1, 2-*Dibromoethene*)

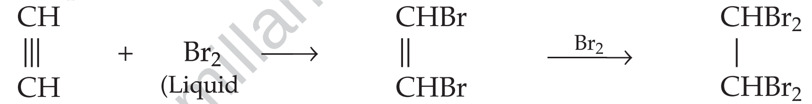
(*ii*) With bromine. Acetylene decolourises dilute bromine water to form acetylene dibromide. *This reaction is used as a test for unsaturation.*



$$\begin{array}{c}CH\\ |||\\ CH\end{array} + Br_2 \longrightarrow \begin{array}{c}CHBr\\ ||\\ CHBr\end{array}$$

Acetylene (*Ethyne*) + (*aq. sol.*) (Brown) → Acetylene dibromide (White) (1, 2-*Dibromoethene*)

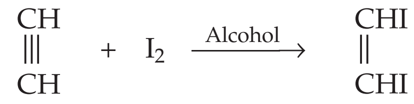
With pure liquid bromide, tetrabromide is obtained.



$$\begin{array}{c}CH\\ |||\\ CH\end{array} + Br_2 \longrightarrow \begin{array}{c}CHBr\\ ||\\ CHBr\end{array} \xrightarrow{Br_2} \begin{array}{c}CHBr_2\\ |\\ CHBr_2\end{array}$$

Acetylene (Ethyne) + (Liquid bromine) → Acetylene dibromide (1, 2-*Dibromoethene*) → Acetylene tetrabromide (1, 1, 2, 2-*Tetrabromoethene*)

(*iii*) With iodine. With iodine, the reaction is slow but in alcoholic solution, acetylene di-iodide is formed.

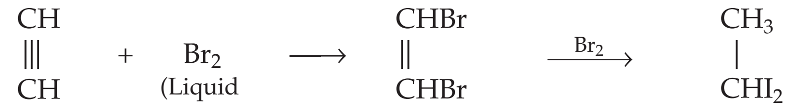


$$\begin{array}{c}CH\\ |||\\ CH\end{array} + I_2 \xrightarrow{\text{Alcohol}} \begin{array}{c}CHI\\ ||\\ CHI\end{array}$$

Acetylene → Acetylene di-iodide

3. Addition of Halogen Acids. Acetylene undergoes addition reactions with halogen acids to give the addition products.

The addition of second molecule of halogen acid takes place in accordance with Markownikoff's rule.



$$\begin{array}{c}CH\\ |||\\ CH\end{array} + Br_2 \longrightarrow \begin{array}{c}CHBr\\ ||\\ CHBr\end{array} \xrightarrow{Br_2} \begin{array}{c}CH_3\\ |\\ CHI_2\end{array}$$

Acetylene (Ethyne) + (Liquid bromine) → Acetylene dibromide (1, 2-*Dibromoethene*) → Ethylidene iodide (1, 1, *Di-iodoethane*)

Decreasing order of reactivity of halogen acid is:

$$HI > HBr > HCl$$

B. ACIDITY OF ALKYNES

(*i*) Hydrogen atoms of acetylene and terminal alkynes are acidic in nature. They produce hydrogen with sodium metal, a reaction characteristic of acids.

$$\underset{\text{Acetylene}}{2HC \equiv CH} + 2Na \xrightarrow{\text{Liq.}NH_3} \underset{\text{Sodium acetylide}}{2HC \equiv \overset{..}{\bar{C}}\overset{+}{N}a} + H_2$$

$$2CH_3 - C \equiv CH + 2Na \rightarrow 2CH_3\ C \equiv CNa + H_2$$

Sodium acetylide is also formed when acetylene is treated with sodamide dissolved in liquid ammonia.

$$\underset{\text{Acetylene}}{HC \equiv CH} + \underset{\text{Sodamide}}{\overset{+}{N}a\overset{-}{N}H_2} \rightarrow \underset{\text{Sodium Acetylide}}{CH \equiv \overset{..}{\bar{C}}\overset{+}{N}a} + NH_3$$

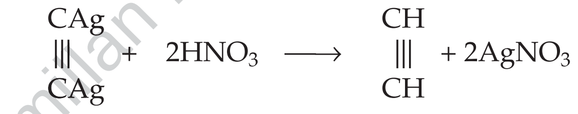
(*ii*) Heavy metal acetylides notably those of copper and silver can be obtained by passing acetylene through ammoniacal solutions of cuprous and silver salts.

$$HC \equiv HC + 2[Cu(NH_3)_2]Cl \longrightarrow \underset{\substack{\text{Cuprous acetylide}\\ \text{(Red ppt.)}}}{CuC \equiv CCu} + 2NH_4Cl + 2NH_3$$

$$HC \equiv CH + 2[Ag(NH_3)_2]NO_3 \longrightarrow \underset{\substack{\text{Silver acetylide}\\ \text{(White ppt.)}}}{AgC \equiv CAg} + 2NH_4NO_3 + 2NH_3$$

The formation of acetylides can be used to distinguish terminal alkynes, *i.e.* alkynes in which the triple bond occurs at the end of a chain, (–C ≡ CH) from other hydrocarbons and also from disubstituted alkynes (RC ≡ C – R). The latter do not undergo this reaction.

The above metallic acetylides are easily decomposed by acids to reproduce acetylene,



$$\underset{\text{Silver acetylene}}{\begin{array}{c}CAg\\|||\\CAg\end{array}} + 2HNO_3 \longrightarrow \underset{\text{Acetylene}}{\begin{array}{c}CH\\|||\\CH\end{array}} + 2AgNO_3$$

This reaction, therefore, can be used for the separation and purification of acetylene from gaseous mixture.

Explanation of acidity of alkynes. The acidic nature of terminal alkynes (1-Alkynes) can be explained as under:

Carbon atoms in alkynes are in a state of *sp-hybridization* and each of the two *sp-hybridized* orbital has 50% *s*-character. On the other hand, *hybridized* orbitals in alkenes and alkanes have 33.3% (sp^2) and 25% (sp^3) *s*-character respectively. Since the *s*-electrons are held, more closely to the nucleus than the *p*-electrons, the *sp-hybridized* carbon atoms of alkynes (having 50% *s*-character) will attract with greater force the bonded pair of electrons of C–H bond. This facilitates the release of hydrogen atom of C–H bond as H^+ ion making alkynes acidic under suitable conditions. In other words, greater electronegativity of the *sp-hybridised* carbon atoms of alkynes due to their 50% *s*-character is responsible for the acidic nature of hydrogen atoms of alkynes.

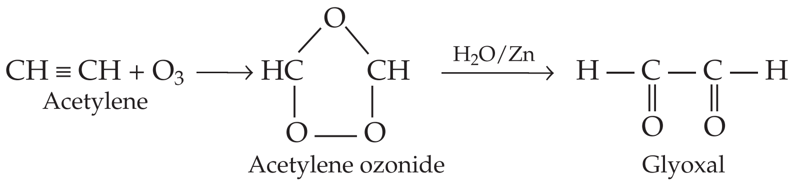
The decreasing order of acidity of various hydrocarbons is given below:

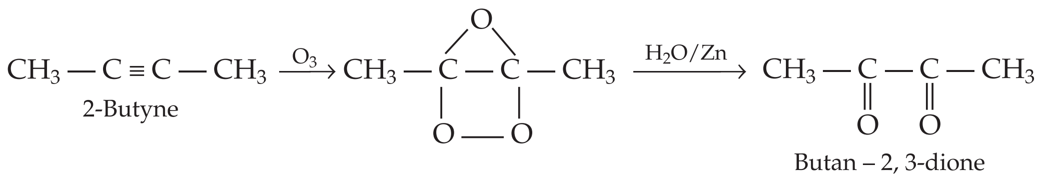
$$\underset{\text{Ethyne}}{HC \equiv CH} > \underset{\text{Ethene}}{H_2C = CH_2} > \underset{\text{Ethane}}{H_3C - CH_3}$$

C. OXIDATION OF ALKYNES

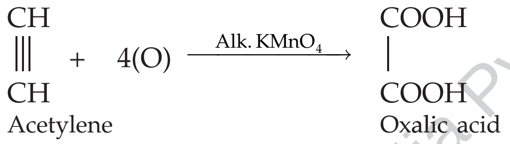
Alkynes form different oxidation products under different conditions as illustrated below:

(*i*) **Ozonolysis.** Alkynes add on ozone to form ozonides which on hydrolysis form dicarbonyl compounds.





(*ii*) **Oxidation with Potassium Permanganate.** With cold dilute alkaline potassium permanganate (Baeyer's reagent), acetylene is oxidized to oxalic acid.



$$\begin{matrix} CH \\ ||| \\ CH \end{matrix} + 4(O) \xrightarrow{\text{Alk. } KMnO_4} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

Acetylene — Oxalic acid

Under drastic conditions (conc. $KMnO_4$ solution in alkaline medium), alkynes get oxidized, as under.

$$\underset{\text{Propyne}}{CH_3C \equiv CH} \xrightarrow[\text{[O], } KMnO_4]{373 - 383 \text{ K}} \underset{\text{Acetic acid}}{CH_3COOH} + CO_2$$

(*iii*) **Combustion.** When burnt freely in air or oxygen, alkynes get completely oxidized to form carbon dioxide and water.

$$2C_2H_2\ (g) + 5O_2\ (g) \longrightarrow 4CO_2\ (g) + 2H_2O\ (g)$$

Oxyacetylene flame gives a very high temperature (More than 3000 K) and is used for welding and cutting of metals.

D. POLYMERIZATION

Alkynes undergo many polymerization reactions as illustrated below:

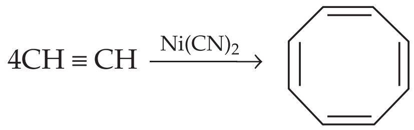
(*i*) When passed through a concentrated solution of cuprous chloride and ammonium chloride in hydrochloric acid, two molecules of acetylene join to give vinyl acetylene which is used in the manufacture of rubber.

$$\underset{\substack{\text{Acetylene} \\ (\textit{Ethyne})}}{2CH \equiv CH} \longrightarrow \underset{\substack{\text{Vinyl acetylene} \\ (\textit{But-1-en-3-yne})}}{\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C} \equiv \overset{4}{C}H}$$

(*ii*) When passed through a *red hot copper tube, three molecules of acetylene join together to form benzene.*

$$\underset{\text{Acetylene}}{2CH \equiv CH} \longrightarrow \underset{\text{Benzene}}{C_6H_6}$$

(*iii*) When a solution of acetylene in tetrahydrofuran is heated in the presence of nickel cyanide, four molecules join together to give cyclo-octatetaene.



11.24 DISTINCTION BETWEEN ALKANE, ALKENE AND ALKYNE

These three types of hydrocarbons can be distinguished by the properties as given in Table 11.3.

Table 11.3

S.No.	Property	Alkane, C_2H_6	Alkene, C_2H_4	Alkyne, C_2H_2
1.	Flame observed on combustion	Non-luminous	Luminous	Smoky (Sooty)
2.	Reaction with cold aqueous or alkaline $KMnO_4$ solution (Baeyer's reagent)	No action	Pink colour is discharged with the formation of a glycol	Pink colour is discharged with the formation of a diketone
3.	Reaction with Br_2/CCl_4 solution	No action	Orange colour is discharged	Orange colour is discharged
4.	Reaction with ammoniacal $AgNO_3$ solution (Tollen's reagent)	No action	No action	White ppt. of silver acetylide (given by terminal alkynes only)
5.	Reaction with ammoniacal cuprous salt solution	No action	No action	Red ppt. of copper acetylide (given by terminal alkynes)

MISCELLANEOUS SOLVED QUESTIONS

1. *What are natural and synthetic polymers? Give two examples of each type.*

Solution. Polymers found in nature, mostly in plants and animals are called natural polymers, e.g., proteins and nucleic acids. Man made polymers are called synthetic polymers, e.g., plastics and synthetic fibres.

2. *Distinguish between the term homopolymers and copolymers and give an example of each.*

Solution. A polymers obtained by identical monomer units is called a homopolymer, e.g., PVC and a polymer obtained from two or more different monomers is called a copolymer, e.g., nylon-66.

3. *In which classes, the polymers are classified on the basis of molecular forces?*

Solution. On the basis of molecular forces present between the chains of various polymers. Polymers are classified as:

(*i*) elastomers (*ii*) fibres (*iii*) thermoplastics and (*iv*) thermosetting polymers.

4. *How can you differentiate between addition and condensation polymerisation?*

Solution. In addition polymerisation monomer units are simply added together to form a macro molecule and in condensation polymerisation monomer units combine together to form a macro molecule by elimination of same simple molecules.

5. *Write two free radical mechanism for polymerisation of an alkene?*

Solution. (*i*) **Initiation:** Initiator are molecules, which decompose to provide radicals easily, e.g., *t*-butyl peroxide.

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{(373-423)\,K} \underset{\dot{In}}{2(CH_3)_3C\dot{O}}$$

$$CH_2=CH_2 \xrightarrow{\dot{In}} In-CH_2-\dot{C}H_2$$

(*ii*) **Propagation:** $In-CH_2-\dot{C}H_2 \xrightarrow{nCH_2=CH_2} In-(CH_2-CH_2-)_nCH_2-\dot{C}H_2$

(*iii*) **Termination:** $In-(CH_2-CH_2)_{n-1}CH_2-\dot{C}H \xrightarrow{In} In-(CH_2-CH_2)_nCH_2-CH_2-CH_2$
$-CH_2-(CH_2-CH_2)_nC_6H_5$

6. *Write structures of monomers used for getting the following polymers?*

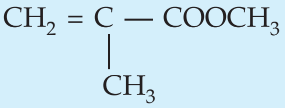
(*i*) *PVC* (*ii*) *Teflon* (*iii*) *PMMA*

Solution.

(*i*) The monomer of PVC is vinyl chloride: $CH_2 = CH.Cl$

(*ii*) Tetrafluoro ethylene: $CF_2 = CF_2$

(*iii*) PMMA : monomer is methyl methacrylate



$$CH_2 = \underset{\substack{| \\ CH_3}}{C} - COOCH_3$$

7. *Write the name and structure of one of the common initiators used in free radical addition polymerisation.*

Solution. *t*-butyl peroxide is a commonly used initiator. It decomposes to form *t*-butoxide radical

$$(CH_3)_3C - O - O - C(CH_3)_3 \xrightarrow{(373-423)\,K} 2(CH_3)_3C - \dot{O}$$

8. *How does the presence of double bonds in rubber molecules influence their structure and reactivity?*

Solution. Natural rubber is a linear cis-1, 4-poly isoprene. In this polymer the double bonds are located between C_2 and C_3 of isoprene units. This is configuration about double bonds to not allow the chains to come closure for effective attraction due to weak intermolecular attractions. Hence the natural rubber has a coiled structure and has elastic property.

9. *How is environmental pollution affected by polymers?*

Solution. Synthetic polymers are frequently used in the form of packing material and throw away bags which are not biodegradable. This stability and durability of plastics poses, a serious waste disposal problem.

10. *Classify the addition polymers on the basis of functional group present in their monomeric unit.*

Solution. The addition polymers are classified into the following four main classes:

(*i*) Polyolefins : polythene, polypropene, polystyrene, etc.

(*ii*) Polydiene: Neoprene, Buna-S, etc.

(*iii*) Polyacrylates: PMMA, PAN, Polyethyl ethacrylate, etc.

(*iv*) Polyhalo-olefins: PVC, teflon, polymonochlorotrifluoro ethene

QUICK SCAN (FOR REVISION)

1. The acyclic saturated hydrocarbons are called alkanes. Their general formula is C_nH_{2n+2} where, $n = 1, 2, 3, ...,$ etc.
2. Cyclic saturated hydrocarbons are called **cycloalkanes**. Their general formula is C_nH_{2n} where, $n = 3, 4, 5, ...,$ etc.
3. Cycloalkanes are isomeric with alkenes.
4. All the bond angles in alkanes are 109º28´.
5. All the carbon atoms in alkanes and cycloalkanes are sp^3-hybridized.
6. Compounds having the same molecular formula but different chemical and physical properties are called isomers. These are of two types: *structural isomers and stereoisomers.*
7. Compounds having the same molecular formula but different structures, *i.e.* different arrangement of atoms within the molecule are called **structural isomers**.
8. Compounds having the same molecular formula but different arrangement of carbon chains are called **chain** or **nuclear isomers**. For example, (*i*) butane and isobutane (*ii*) pentane, isopentane and neopentane are chain isomers.
9. With increase in the number of carbon atoms in alkanes, the number of chain isomers increases.
10. Compounds having the same structure of the carbon chain but differing in position of multiple (double or triple) bonds, functional groups or even the substituents in aromatic compounds are

called **position isomers**. For example, (*i*) but-1-ene and but-2-ene (*ii*) but-1-yne and but-2-yne (*iii*) propan-1-ol and propan-2-ol (*iv*) *o*-, *m*- and *p*-cresols, etc., are position isomers.

11. Compounds having the same molecular formula but possessing open chain and cyclic structure respectively are called **ring chain isomers**. For example, propene and cyclopropane are ring chain isomers.
12. Isomers which have the same structures but differ in the arrangements of atoms or groups in space are called **stereoisomers**. It is of three types, *i.e.* conformational isomerism, optical isomerism and geometrical isomerism.
13. A double bond consists of one strong α-bond and one weak π-bond. A π-bond is formed by sideways or lateral overlap of two *p*-orbitals.
14. The carbon atoms of a double bond are sp^2-hybridized.
15. All the four atoms directly attached to a double bond lie in a plane.
16. **Polymers** are the substances made up of giant molecules of high molecular mass, each molecule of which consists of a very large number of simple molecules joined together through covalent bonds in a regular manner. They are also known as **macromolecules.**
17. Simple molecules from which repeating structural units are derived are called **monomers.**
18. A polymer always consists of a large number of repeating structural units, whereas a macromolecule may or may not. *Thus, all polymers are macromolecules but all macromolecules are not polymers.*
19. Strictly speaking, proteins and nucleic acids are regarded as macromolecules rather than polymers.
20. **Natural polymers** are found in nature, *i.e.* animals and plants. Starch, cellulose, proteins, nucleic acids, natural rubber, etc. are some examples.
21. **Biopolymers** control the various life processes. Polysaccharides (starch and cellulose), proteins and nucleic acids are some examples.
22. Polymers whose repeating structural unit is derived from only one type of monomer units are called **homopolymers.** For example, polythene, polypropylene, PVC, polyisoprene, neoprene, polyacrylonitrile, nylon, etc.
23. **Copolymers** are polymers whose repeating structural units are derived from two or more monomer units. For example, Nylon-66, Buna-S, polyesters, alkyd resins, bakelite, etc.
24. **Linear polymers** consist of long straight chains of polymers. High density polythene, nylon and polyester provide some examples.
25. **Branched-chain polymers** have branches along the main chain. Amylopectin and glycogen are examples of branched chain polymers.
26. **Synthetic polymers** are man-made polymers. Polythene, polypropylene, polystyrene, PVC, teflon, nylon, dacron, bakelite, etc. are some examples.
27. **Cross-linked polymers** consist of a large number of linear polymer chains joined together by at least two cross-links per polymer chain to form three dimensional giant network structure. Bakelite, ureaformaldehyde and melamine-formaldehyde polymers are examples of this class of polymers.
28. **Vulcanization** involves heating of rubber with about 5% sulphur. It introduces sulphur bridges between polymer chains thereby increasing its tensile strength, elasticity and resistance to abrasion.
29. **Elastomers** have the weakest intermolecular attraction between the polymer chains. Natural rubber, vulcanized rubber, Buna-S, etc. are some examples.
30. **Fibres** are polymers with the strongest intermolecular forces of attraction. These intermolecular forces may be either *H-bonding* between N—H and C=O groups or *dipole-dipole interactions* between the polar groups.
31. **Thermoplastics** are polymers in which intermolecular forces are in between those of elastomers and fibres. Polythene, polypropylene, polystyrene, PVC, teflon, polyvinyl acetate, etc., are some examples.
32. **Low density polythene** is obtained by free-radical polymerization of ethylene and has a branched structure.
33. **High density polythene** is obtained by coordination polymerization of ethylene in a hydrocarbon solvent at 333—343 K under a pressure of 5—7 atmosphere in the presence of $(CH_3CH_2)_3Al + TiCl_4$ (Ziegler-Natta catalyst).
34. **Plasticizers.** Substances such as di-*n*-butylphthalates or cresyl phosphates which when added to plastics make them soft and readily workable on heating are called **plasticizers.**
35. **Thermosetting polymers.** Low molecular weight semifluid substances which on heating in a mould undergo change in chemical composition to give a hard, infusible and insoluble mass are called **thermosetting polymers.** For example, Bakelite, urea-formaldehyde, melamine-formaldehyde, etc. Whereas a thermoplastic polymers can be melted again and again without any change. A thermosetting polymer can be heated only once when it permanently sets into a solid which cannot be remelted and reworked.
36. **Poly (methyl methacrylate), PMMA** is an addition polymer obtained by free radical polymerization of methyl methacrylate. It has better light transmission properties than even glass and, hence, is widely

used in transparent domes and skylights and aircraft windows.

37. **Neoprene** is an addition polymer of chloroprene (2-chloro-1, 3-butadiens). It is superior to natural rubber as it is stable to aerial oxidation and resistance to oils, gasoline and solvents.
38. **Teflon** is an addition polymer and is obtained by free-radical polymerization of tetrafluorethylene. It is flexible and inert to solvents and to boiling acids, even to aqua-regia and stable up to 598 K. It is used for preparing non-stick utensils, gaskets, valves, seals, etc.
39. **Polyvinyl Chloride (PVC)** is an addition polymer and is obtained by free radical polymerization of vinyl chloride. It is used as an electrical insulator for coating wire, cables and other electrical goods.
40. Alkynes are also called acetylenes.
41. A triple bond consists of one strong α-bond and two weak π-bonds.
42. The carbon atoms of a triple bond are *sp*-hybridized.
43. Acetylene is a linear molecule with cylindrical electron cloud.
44. Alkynes do not show geometrical isomerism.
45. The four atoms of a triple bond, *i.e.* X, Y and two C-atoms ($X - C \equiv C - Y$) all are linerally arranged.
46. A *sp*-hybridized C-atom is more electronegative than sp^2-hybridized carbon atom. As a result, the dipole moment of 1-butyne is higher than that of 1-butene.
47. The central atom in alkenes ($CH_2 = C = CH_2$) is *sp*-hybridized and the two double bonds are perpendicular to each other.
48. Hydrogenation of alkenes and alkynes in presence of Ni, Pt or Pd as catalyst at 523–573 K gives alkanes. This reaction is used in the manufacture of *Vanaspati Ghee* from edible vegetable oils.
49. **Wurtz reaction.** Alkyl halides react with metallic sodium in presence of dry ether to give symmetrical alkanes, *i.e.* alkanes containing even number of carbon atoms.
50. Reduction of alkyl halides with *nascent hydrogen* (obtained from Zn/HCl, Sn/HCl or Zn-Cu couple/alcohol) or with H_2 gas in presence of Pt or Pd as catalyst gives alkanes.
51. **Grignard reagents** were prepared by Victor Grignard in 1912 by the action of Mg turnings on alkyl halides in presence of dry ether.
52. Substances containing active hydrogen (*i.e.* H_2O, ROH, H_2S, RSH, NH_3, RNH_2, R_2NH) on treatment with Grignard reagents give alkanes corresponding to the alkyl group of the Grignard reagent.

$$R - MgX + H - OH \rightarrow RH + Mg(OH)X$$

53. **Dehydration** of alcohols with conc. H_2SO_4 at 440 K gives alkene. The reaction involves a *carbocation intermediate.* For example, CH_3CH_2OH gives $CH_2 = CH_2$.
54. Reduction of alkyl iodides with HI in presence of a trace of red phosphorus gives alkanes.
55. **Dehydrohalogenation** (*removal of a molecule of a halogen acid*) of alkyl halides with hot alcoholic KOH solution gives **alkenes** while that of 1, 1 and 1, 2-dihaloalkanes gives **alkynes**. For example, ethyl bromide gives ethylene while 1, 1 or 1, 2-dibromoethane gives acetylene.
56. **Decarboxylation** (*removal of a molecule of CO_2*) of sodium salts of fatty acids with soda-lime (NaOH + CaO) at 630 K gives alkanes. For example, decarboxylation of sodium acetate gives methane, that of sodium propionate gives ethane, that of sodium benzoate gives benzene while sodium formate gives only H_2 gas.
57. **Dehalogenation** (removal of a molecule of halogen) of 1, 1 and 1, 2-dibromoethane with Zn dust in boiling methanol or ethanol gives ethylene while that of 1, 1, 2, 2-tetrabromoethane gives acetylene.
58. Dehydration of alcohols, dehydrohalogenation of alkyl halides and dehalogenation of 1, 1 or 1, 2 dihaloalkanes are the examples of **elimination reactions**.
59. Reactivity of various halides towards dehydrohalogenation is in the order:

iodides > bromides > chlorides

60. Elimination follows Saytzeff's rule which states: Hydrogen atom is preferentially removed from that carbon atom which has fewer number of hydrogen atoms.
61. Reaction of monosodium acetylide with alkyl halides gives higher **terminal alkynes** while reaction of disodium acetylide with alkyl halides gives higher **non-terminal alkynes**.
62. Action of water on aluminium carbide gives methane while that on calcium carbide gives acetylene.
63. The melting points of *n*-alkanes with even number of carbon atoms are much higher than those with odd number of carbon atoms – **Alternation effect**.
64. The boiling points of straight chain alkanes increase regularly with the increase in the number of carbon atoms. On an average, the boiling point increases by 20–30 K for addition of each carbon atom to the chain.
65. Amongst isomeric alkanes, boiling point decreases with branching. For example, boiling points decrease in the order:

n-pentane > isopentane > neopentane

66. All hydrocarbons (alkanes, alkenes, alkynes and arenes) are lighter than water.
67. Due to symmetry, the m.p. of neopentane is higher than that of *n*-pentane.

68. **CNG** (*Compressed Natural Gas*) is being used as a fuel for cars in metropolitan cities.

69. **LPG** (*Liquefied Petroleum Gas*) which is chiefly a mixture of butane and isobutane is used for cooking in our kitchens.

70. The order of reactivity of halogens towards the given alkane is: $F_2 > Cl_2 > Br_2 > I_2$.

71. Ease of replacement of various types of hydrogens in a given alkane with the same halogen is in the order:

tertiary > secondary > primary.

72. Ethylene on oxidation with O_2 in presence of Ag at 575 K gives *ethylene oxide*.

73. A cold dilute neutral or alkaline solution of $KMnO_4$ is called **Baeyer's reagent**. Alkenes and alkynes discharge the pink colour of Baeyer's reagent with simultaneous formation of brown ppt. of MnO_2. That is why this reaction is used as a test for unsaturation under the name **Baeyer's test**.

74. Alkenes react with Baeyer's reagent to form 1, 2-diols or 1, 2-glycols. This reaction is called **hydroxylation**. For example, ethylene gives ethylene glycol.

75. With hot $KMnO_4$ solution, cleavage of C = C bond occurs giving a mixture of two acids or one acid and one ketone or two ketones depending upon the structure of the alkene. However, if HCOOH is one of the products of oxidation, it is always further oxidised to $CO_2 + H_2O$.

76. Reductive ozonolysis of alkenes gives a mixture of two aldehydes or one aldehyde and one ketone or two ketones depending upon the structure of alkene. Under similar conditions, alkynes give diketones while acetylene give glyoxal.

77. **Markownikoff's rule** governs the addition of unsymmetrical reagents to unsymmetrical alkenes. During **Markownikoff's additions**, the negative part of the adding molecule goes to that carbon atom of the double bond which has lesser number of H-atoms, *i.e.*

(*i*) $CH_3CH = CH_2 + HBr \rightarrow CH_3 - CHBr - CH_3$

(*ii*) $CH_3CH = CH_2 + H_2SO_4\ (conc.) \rightarrow CH_3 - CH(OSO_3H) - CH_3 \xrightarrow[(-H_2SO_4)]{H_2O,\ boil} CH_3 - CHOH - CH_3$

(*iii*) $CH_3 - CH = CH_2 + HOCl \rightarrow CH_3 - CHOH - CH_2Cl$

(*iv*) $R - C \equiv CH \xrightarrow{HBr} R - CBr = CH_2 \xrightarrow{HBr} R - CBr_2 - CH_3$

78. **Anti-Markownikoff's rule or Peroxide effect or Kharasch effect** states that in presence of peroxides such as benzoyl peroxide, addition of HBr (but not of HCl or HI) to unsymmetrical alkenes occurs contrary to Markownikoff's rule, *e.g.*,

$$CH_3CH = CH_2 + HBr \xrightarrow{Peroxide} CH_3 - CH_2 - CH_2 - Br$$

79. Terminal alkynes on oxidation with Baeyer's reagent give a mixture of CO_2 and a carboxylic acid with one carbon atom less than the starting alkyne, *e.g.*,

$$R - C \equiv CH \xrightarrow[reagent]{Baeyer's} R - COOH + CO_2$$

Acetylene, however, gives oxalic acid.

80. Non-terminal alkynes on oxidation with Baeyer's reagent give, 1, 2-diketones; *e.g.*,

$$R - C \equiv C - R + 2[O] \xrightarrow[reagent]{Baeyer's} \underset{\text{Diketone}}{RCO - COR}$$

81. Oxidation of terminal alkynes with hot $KMnO_4$ solution gives a mixture of $RCOOH + CO_2 + H_2O$ while oxidation of non-terminal alkynes gives a mixture of two carboxylic acids.

82. Alkenes readily undergo polymerization in the presence of catalysts. For example, ethylene gives **polythene**, vinyl chloride gives **PVC**, tetrafluoroethylene gives **teflon**. Because of its great chemical inertness and thermal stability, teflon is used for making non-stick utensils.

83. Reduction of alkynes can be stopped at the alkene stage. With **Lindlar's** catalyst, *i.e.* Pd supported over $CaCO_3$ or $BaSO_4$ and partially poisoned by addition of S or quinoline, *cis*-alkenes are obtained but with Na in liquid NH_3, *trans*-alkenes are formed.

84. Oxidation of alkylbenzenes with hot $KMnO_4$ solution, eventually gives benzoic acid irrespective of the length of the carbon chain.

85. Reductive ozonolysis of benzene gives glyoxal; that of *o*-xylene gives glyoxal, methylglyoxal and dimethyl glyoxal while that of mesitylene gives only methylglyoxal.

86. Oxidation of benzene with O_2 in presence of V_2O_5 at 773 K gives maleic anhydride.

87. Acetylene polymerizes in presence of $Ni(CN)_2$ and high pressure to give cyclooctatetraene.

88. Acetylene when passed through red hot Fe tube gives benzene while propylene gives mesitylene.

89. In presence of $CuCl/NH_4Cl$, acetylene first gives vinylacetylene and then divinylacetylene.

90. With ammoniacal **$AgNO_3$** solution, or Tollen's reagent terminal alkynes give white ppt. of silver alkynides.

91. Due to *sp*-hybridization of acetylenic carbon, *terminal alkynes are acidic* in nature. They react with Na at 475 K or Na in liq. NH_3 at 196 K to form sodium alkynides.

92. With **ammoniacal CuCl solution**, *terminal alkynes give red ppt. of copper alkynides.*

93. The acidic character of ethane, ethene and ethyne follows the order:

$$CH \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$$

EXERCISES

Very Short Answer Type Questions

1. Name the chain isomer of C_5H_{12} which has a tertiary hydrogen atom.
2. An alkyl halide with molecular formula C_4H_9Br is optically active. Draw the structures of its (+) and (–) enantiomers.
3. What is a quaternary carbon atom?
4. What do the prefixes (+), (–), (±) and *dl* before an organic compound mean?
5. Arragne C_2H_6, C_2H_4 and C_2H_2 in the increasing order of C–C bond energies.
6. Give the IUPAC name of the lowest molecular weight alkane that contains a quaternary carbon.
7. Which of the following shows geometrical isomerism?

   (*i*) $CHCL = CHCL$ (*ii*) $CH_2 = CCl_2$

   (*iii*) $CCl_2 = CHCl$

   Give the structures of its *cis* and *trans* forms.
8. Indicate the primary, secondary, tertiary and quaternary carbon atoms in the following:

   (*i*) 3-Ethyl-2-methylhexane

   (*ii*) 2, 2, 4-Trimethylpentane.
9. What is an asymmetric carbon atom?
10. Why is cyclopropane very reactive as compared to cyclohexane?
11. What type of hybridization is involved in (*i*) planar and (*ii*) linear molecules?
12. How many structural and geometrical isomers are possible for a cyclohexane derivative having the molecular formula, C_8H_{16}?
13. What type of isomerism is shown by butane and isobutane?
14. What is the condition to be satisfied for a compound to be chiral?
15. What type of hybridisation is shown by carbon atoms in benzene?
16. Write all the possible isomers for a benzene derivative having the molecular formula C_8H_{10}.
17. A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in propane. What is the number of structural isomers possible?
18. Arrange the following in the increasing order of C–C bond length C_2H_6, C_2H_4, C_2H_2.
19. Name two reagents which can be used to distinguish between ethene and ethyne.
20. Give the structure of an optically active hydrocarbon (C_6H_{12}) which on catalytic hydrogenation gives an optically inactive compound (C_6H_{14}).
21. Name the products formed when an ethereal solution containing ethyl iodide and methyl iodide is heated with sodium metal.
22. Write the structure of the alkene which on reductive ozonolysis gives butanone and ethanal.
23. Out of ethylene and acetylene which is more acidic and why?
24. How will you detect the presence of unsaturation in an organic compound?
25. How can ethylene be converted into ethane?
26. Give the structure of the alkene (C_4H_8) which adds on HBr in the presence and in the absence of peroxide to give the same product, C_4H_9Br.
27. Give the structure of an alkene (C_4H_8) which when treated with H_2O/H_2SO_4 gives $C_4H_{10}O$ which cannot be resolved into optical isomers.
28. Give the name of the polymer which is used for making non-stick utensils.
29. Write the monomer of teflon. Give its uses.
30. Name a natural elastomer.
31. Name monomer units of nylon-66.
32. Give the common and the IUPAC names of the monomer of natural rubber.
33. What does PVC stand for?
34. Give chemical name of teflon.
35. What are thermosetting polymers?
36. What does PMMA stand for?
37. What is copolymer?

Short Answer Type Questions

1. What are alkanes? Why are they called paraffins?
2. What is structural isomerism? Draw all the structural isomers of the hydrocarbon having the molecular formula, C_5H_{12}. Also give their IUPAC names.
3. Although 1, 2-dimethylcyclohexane does not contain a double bond yet it shows geometrical isomerism. Explain.
4. Which of the following alkenes will show geometrical isomerism?

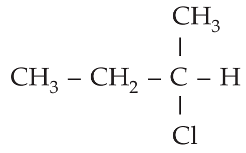
   (*i*) propene (*ii*) but-2-ene

   (*iii*) but-1-ene (*iv*) 2, 3-dimethylbut-2-ene.

   [**Ans.** (*ii*) but-2-ene only]
5. Draw the structure of 2, 2, 4-trimethylhexane and indicate how many each of the 1°, 2°, 3° and 4° carbons does it contain.
6. An alkane has a molecular mass of 72. Give all the possible structural isomers along with their IUPAC names.

7. Classify the following hydrocarbons into alkanes, alkenes, alkynes and arenes:
   (*i*) $(CH_3)_4C$ (*ii*) $CH_3CH = CH_2$
   (*iii*) $CH_3CH_2C \equiv CH$ (*iv*) $C_6H_5CH_3$
   [**Ans.** (*i*) alkane (*ii*) alkene (*iii*) alkyne (*iv*) arene]
8. Enlist the various characteristics of enantiomers.
9. A hydrocarbon has the molecular mass 70. Write all the possible structural isomers and give their IUPAC names.
   [**Ans.** The hydrocarbon having molecular mass of 70 is C_5H_{10}. It exists in the following four structural isomers:
   (*i*) $CH_3CH_2CH_2CH = CH_2$ (pent-1-ene)
   (*ii*) $(CH_3)_2CH - CH = CH_2$ (3-methylbut-1-ene)
   (*iii*) $CH_3CH_2CH = CHCH_3$ (pent-2-ene)
   (*iv*) $(CH_3)_2C = CHCH_3$ (2-methylbut-2-ene)]
10. Alkynes contain two π-bonds but still do not show geometrical isomerism whereas alkenes contain only one π-bond but show geometrical isomerism. Comment.
11. Discuss the orbital diagram of acetylene indicating the hybridization involved and the nature of the bonds formed.
12. What is the origin of geometrical isomerism in alkenes?
13. Explain: (*i*) position isomerism (*ii*) functional isomerism giving one example in each case.
14. Describe the orbital diagram of ethylene indicating the hybridization involved and the nature of the bonds formed.
15. Identify the type of isomerism exhibited by the following compounds:

(*a*)



$$CH_3 - CH_2 - \underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}} - H$$

   (*b*) $CH_3 - CH = CH - CH_2CH_3$
   (*c*) $CH_3CH_2CH_2CH_3$
   (*d*) C_5H_{12}
16. How will you account for the tetravalency of carbon while its configuration suggests it to be divalent?
17. A hydrocarbon has the molecular mass 70. Write all the possible structural isomers and give their IUPAC names.
18. Ethylene dibromide (a vicinal dihalide) is treated with zinc dust. Suggest another reaction by which hydrocarbon obtained in the above reaction can be prepared.
19. What are polymers? How are they classified?
20. Give the classification of polymers based upon their methods of synthesis?
21. What are polymers? Why are they called macromolecules?
22. What is the difference between monomers and polymers? Identity the monomer units in the polythene.
23. Explain addition polymers giving one example in each case.
24. How are polymers classified on the basis of intermolecular forces of attraction?
25. Define the following terms:
   (*i*) Elastomers
   (*ii*) Fibres
   (*iii*) Thermoplastic polymers
   (*iv*) Thermosetting plastics.
26. What are elastomers? Give one example of a natural elastomer.
27. Define the following terms:
   (*i*) Thermoplastic and
   (*ii*) Elastomer.
28. Give one example each of the following:
   (*i*) Thermoplastic
   (*ii*) Natural polymer
29. What is vulcanization? How does vulcanization improve the quality of natural rubber?
30. What are polyolefins and polydienes?
31. How are low density and high density polyethylene manufactured? Why do they differ in their densities?
32. What are synthetic rubbers? Give one example.
33. Write names and structures of the monomer units of the following polymers:
   (*i*) Polystyrene and
   (*ii*) Neoprene.
34. What is teflon? What are its uses?
35. Give the information for the following polymers:
   PVC: Monomer unit.
   Synthetic rubber: Monomer unit
36. Write the monomers of teflon. Give one use of it.
37. What are the starting materials used for preparing the PVC? Write two uses of it.
38. Write chemical equations for the synthesis of:
   (*i*) Teflon (*ii*) Polyvinyl chloride.
39. Describe the reaction of hexamethylenediamine with adipic acid to give nylon.
40. What is teflon? How is it synthesized?
41. Briefly describe the following terms giving one example of each:
   (*i*) Polyolefines (*ii*) Polyamides
42. What are elastomers? Give the chemical equation for the preparation of Buna-S.

43. Write the names and structures of the monomers of each of the following polymers:
    (*i*) Natural rubber (*ii*) Buna-2.
44. What are A, B and C in the following equations?
    (*i*) $A + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$
    (*ii*) $C_2H_5OH \xrightarrow{H_2SO_4} H_2O + B$
    (*iii*) $C + H_2O \xrightarrow{433\ K} CH \equiv CH + Ca(OH)_2$
45. What happens when ethyl bromide is treated with alcoholic caustic potash? Give another reaction by which the hydrocarbon obtained in the above reaction can be prepared?
46. What happens when water is added to calcium carbide? Give chemical equation for the reaction.
47. How can iodoethane be converted into ethane and butane respectively?
48. Write equations for two methods for the preparation of propene in the laboratory.
49. What is the function of iodic acid in the iodination of alkanes? Can we use any other substance in its place?
50. What is the dipole moment of C_6H_6? How is it different from that of C_6H_5Cl?
51. How will you convert:
    (*i*) 2-Butene to *n*-butane,
    (*ii*) Propyl chloride to propene?
52. What happens when:
    (*a*) ethylene is passed through alkaline potassium permanganate solution.
    (*b*) acetylene is hydrated in presence of mercuric sulphate and dilute sulphuric acid?
53. Methyl bromide is heated with magnesium in presence of dry ether and the product so obtained is boiled with water to give a gas 'A'. Name the gas evolved and also give the reactions involved.
54. Give reasons for the following in one or two sentences.
    Propene reacts with HBr to give isopropyl bromide but does not give *n*-propyl bromide.
55. Explain the term 'Polymerisation' with two examples.
56. How will you distinguish between cyclohexane and cyclohexene?
57. Describe a method to distinguish between ethane, ethene and ethyne.
58. (*i*) Write a note on iodination of methane.
    (*ii*) Write the reaction of $KMnO_4$ with 2-methylpropene.
59. How will you convert acetylene into the following compounds? Give reaction conditions.
    (*i*) Acetaldehyde (*ii*) Vinyl chloride
    (*iii*) Ethane.
60. What happens when ethyl alcohol is heated with conc. sulphuric acid?
61. How does ethylene react with:
    (*i*) Bromine (*ii*) Alk. $KMnO_4$
    (*iii*) Ozone (*iv*) Hydrogen?
62. Why does the hydration of propyne give acetone but that of propene gives isopropyl alcohol?
63. Explain Markownikoff's rule for addition reactions of alkenes.

Long Answer Type Questions

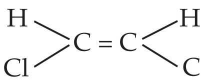
1. Which of the acyclic hydrocarbon series is represented by C_nH_{2n}? What type of hybridisation is involved in this series? Write the structural formulae and IUPAC names of all hydrocarbons of this type having four carbons per molecule.
2. What is meant by chain isomerism? Discuss the isomerism of alkanes up to pentanes.
3. Explain the following terms with suitable examples:
    (*i*) Polyesters (*ii*) Polyamides
4. Write the names and structures of the monomers of the following polymers:
    (*i*) Neoprene (*ii*) Natural rubber.
5. Classify polymers on the basis of:
    (*i*) synthesis (*ii*) molecular force.
    Give examples of each kind.
6. Write equations for the synthesis of:
    (*i*) Poly (methylmethacrylate)
    (*ii*) Teflon
    (*iii*) Polyacrylonitrile.
7. What are alkynes? What is the molecular orbital structure of acetylene? Do alkynes exhibit geometrical isomerism? Give suitable reasons for your answer.
8. What is the cause of geometrical isomerism? Why do alkanes and alkynes not show this type of isomerism?
9. Explain the terms substitution reactions and addition reactions. "Methane gives substitution reactions while ethylene readily gives addition reactions". Justify the statement giving example.
10. Give reasons for the following:
    (*a*) The boiling points of hydrocarbons decrease with increase in branching.
    (*b*) Unsaturated compounds undergo addition reactions.
11. What happens when:
    (*i*) 2-Butene is treated with ozone followed by zinc dust and water?
    (*ii*) Ethene is treated with a cold dilute alkaline potassium permanganate solution?

12. How would you distinguish between:
    - (*a*) Propane and propene,
    - (*b*) Propane and propyne,
    - (*c*) Propene and propyne,
    - (*d*) 1-Butyne and 2-Butyne?
13. Write short notes on:
    - (*a*) Additional reactions.
    - (*b*) Markownikoff's rule.
14. How will you carry out the following conversions?
    - (*i*) Ethyne to ethanal
    - (*ii*) Methane to tetrachloromethane
    - (*iii*) Propene to 2-bromopropane
    - (*iv*) Acetylene to 1, 1-dichloroethane
15. How can the following reactions be used to prepare alkanes?
    - (*i*) Sabatier and Sanderen's reaction
    - (*ii*) Ethylene is passed through ammoniacal silver nitrate solution.
16. Define oxidation, addition, substitution reactions giving examples of each.

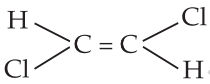
ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. 2-Methylbutane, $(CH_3)_2CH - CH_2 - CH_3$
2. 2-bromobutane (CH_3 – CHBr – CH_2CH_3). For enantiomeric structures, refer to the text.
3. A quaternary carbon atom is directly linked to form other carbon atoms.
4. Dextro, laevo and racemic.
5. $C_2H_6 < C_2H_4 < C_2H_2$
6. 2, 2-Dimethylpropane
7. (*i*) *i.e.,* ClCH = CHCl

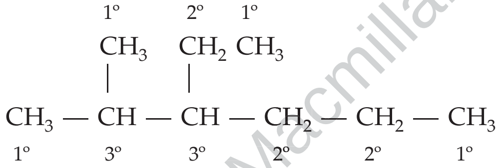


cis-1, 2-Dichloroethene



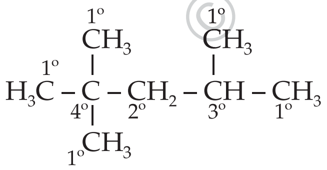
trans-1, 2-Dichloroethene

8. (*i*)



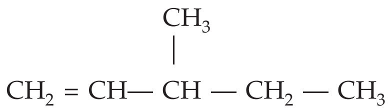
$$\underset{1^\circ}{CH_3} - \underset{3^\circ}{\overset{\overset{1^\circ}{CH_3}}{\overset{|}{CH}}} - \underset{3^\circ}{\overset{\overset{2^\circ\;\;\;1^\circ}{CH_2\,CH_3}}{\overset{|}{CH}}} - \underset{2^\circ}{CH_2} - \underset{2^\circ}{CH_2} - \underset{1^\circ}{CH_3}$$

(ii)



$$\overset{1^\circ}{H_3C} - \underset{\underset{1^\circ CH_3}{|}}{\overset{\overset{1^\circ}{CH_3}}{\overset{|}{\underset{4^\circ}{C}}}} - \underset{2^\circ}{CH_2} - \overset{\overset{1^\circ}{CH_3}}{\overset{|}{\underset{3^\circ}{CH}}} - \underset{1^\circ}{CH_3}$$

9. A carbon atom attached to four different atoms or groups. Even isotopes (H, D, T) are considered as different atoms.
10. In cyclopropane, the ring is quite strained since the C–C–C bond angles are only 60° as compared to 109°28´ in cyclohexane.
11. (*i*) sp^2 and (*ii*) *sp*.
12. Five structural isomers: ethylcyclohexane, 1 : 1; 1 : 2; 1, 3-and 1, 4-dimethyl-cyclohexanes. Six geometrical isomers since each of 1, 2; 1, 3- and 1,4-dimethylcyclohexanes has two geometrical (*cis* and *trans*) isomers.
13. Chain or nuclear isomerism.
14. Its mirror image should be non-superimposable.
15. sp^2
16. Four isomers; ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene. For structures refer to the text.
17. Four : 1, 1-dichloropropane ($CH_3CH_2CHCl_2$),
    2, 2-dichloropropane ($CH_3CCl_2CH_3$),
    1, 2-dichloropropane ($CH_3CHClCH_2Cl$) and
    1, 3-dichloropropane ($ClCH_2CH_2\,CH_2Cl$).
18. $C_2H_2 < C_2H_4 < C_2H_6$
19. Tollen's reagent and ammoniacal CuCl solution.
20. 3-Methylpent-1-ene



$$CH_2 = CH - \overset{\overset{CH_3}{|}}{CH} - CH_2 - CH_3$$

3-Methylpent-1-ene

(*Optically active*)

21. A mixture of ethane, propane and butane is formed.
22. $CH_3CH_2C(CH_3) = CHCH_3$ (3-methyl-2-hexene)
23. Acetylene, due to greater electronegativity of the *sp*-hybridized carbon.
24. Either by Baeyer's reagent or by Br_2 in CCl_4.
25. By catalytic reduction with H_2 in presence of Raney nickel at 523–573 K.
26. 2-Butene (being symmetrical gives the same product, *i.e.* 2-bromobutane)
27. 2-Methylpropene or isobutylene on hydration gives *t*-butyl alcohol which is optically inactive. The other two butenes, *i.e.* 1-butene and 2-butene will give 2-butanol which can be resolved.

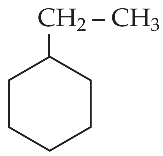
28. Teflon.
29. Tetrafluoroethylene.
30. Natural rubber.
31. Adipic acid and hexamethylenediamine.
32. Isoprene, 2-methyl-1, 3-butadiene.
33. Polyvinyl chloride.
34. Poly (tetrafluoroethylene).
35. Refer to the text.
36. Poly (methyl methacrylate).
37. A polymer formed by polymerization of two or more different monomers is called a copolymer.

COMPETITION FILE

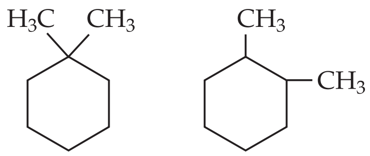
SUBJECTIVE PROBLEMS

Problem 1. *How many structural and geometrical isomers are possible for a cyclohexane derivative having molecular formula C_8H_{16}?*

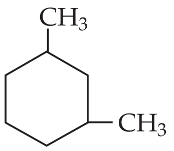
Solution. The following five structural isomers are possible:



Ethylcyclohexane

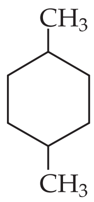


1 : 1, 1 : 2 dimethyl cyclohexane



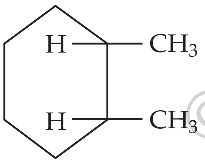
1 : 3

and

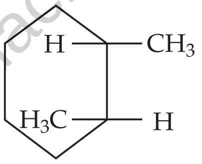


1 : 4 dimethyl cyclohexane

There are six geometrical isomers. The free rotation of each of the six C atoms in the ring is not possible, consequently each of 1, 2; 1, 3 and 1, 4 dimethylcyclohexanes has two geometrical (*cis* and *trans*) isomers. For instance, the *cis-trans* isomers of 1 : 2-Dimethylcyclohexane are given below:



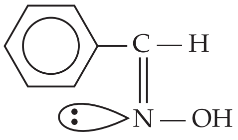
Cis



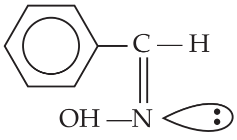
Trans

Problem 2. *Give some examples of compounds showing geometrical isomerism besides alkenes.*

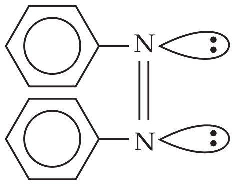
Solution. Besides alkenes, compounds containing C = N and N = N double bond also show geometrical isomerism. However, in these cases the term *syn* and *anti* are used instead of *cis* and *trans*. For example,



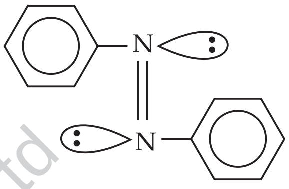
Syn-Benzaldoxime



Anti-Benzaldoxime

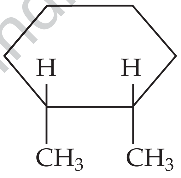


Syn-Azobenzene

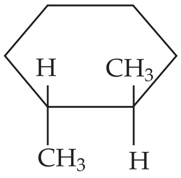


Anti-Azobenzene

Besides alkenes, disubstituted cycloalkanes also show geometrical isomerism. For example, 1, 2- dimethylcyclohexane exists in the following two geometrical forms.



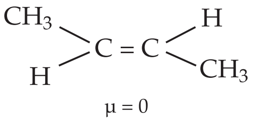
cis-1, 2-Dimethyl cyclohexane

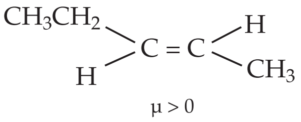


trans-1, 2-Dimethyl cyclohexane

Problem 3. *Trans pent-2-ene is polar while trans-but-2-ene is nonpolar. Explain.*

Solution. In *trans*-but-2-ene, the dipole moments of the two C–CH_3 bonds are equal and opposite and hence they exactly cancel out each other. Thus, *trans*-but-2-ene is non-polar.

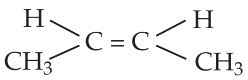




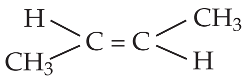
However, in *trans*-pent-2-ene, the dipole moments of C–CH_3 and C–CH_2CH_3 bonds are unequal. Although these two dipoles oppose each other, yet they do not exactly cancel out each other and hence *trans*-pent-2-ene has a small but finite dipole moment and thus is polar.

Problem 4. *Write the maximum numbers of isomers with molecular formula C_4H_8.*

Solution.

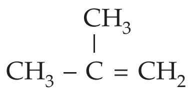


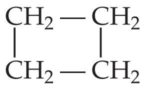
cis-But-2-ene
(*i*)

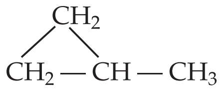


trans-But-2-ene
(*ii*)

$CH_3CH_2CH = CH_2$
(iii)


$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2$$
2-Methylpropene
(iv)


Cyclobutane
(v)

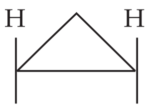

Methylcyclopropane
(vi)

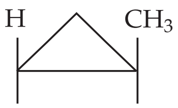
Isomers (*i*) and (*ii*) are configurational isomers; (*iii*) and (*iv*) are chain isomers. Isomers (*v*) and (*vi*) are ring-chain isomers.

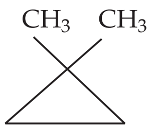
Thus, structures (*iii*), (*iv*), (*v*), (*vi*) and but-2-ene (5 structures) are the structural isomers with the molecular formula C_4H_8.

Problem 5. *Write the isomers of dimethylcyclopropane.*

Solution. Three isomers are possible. These are:


cis-1, 2-dimethyl-cyclopropane

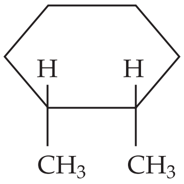

trans-1, 2-dimethyl-cyclopropane

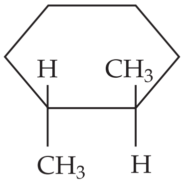

1, 1-dimethyl-cyclopropane

Two of these are geometrical isomers, as shown above. The third namely 1, 1-dimethylcyclopropane does not show geometrical isomers.

Problem 6. *Although 1, 2-dimethylcyclohexane does not contain a double bond yet it shows geometrical isomerism. Explain.*

Solution. It is a ring compound in which each C atom is bound to two more C atoms of the ring, *i.e.* each atom is bonded to two others forming a ring. The free rotation around the C-atoms is, therefore, not possible. So, the positions of two different groups/atoms attached to such C atoms are fixed in space. Thus, 1, 2-dimethylcyclohexane exists as:


cis-form


trans-form

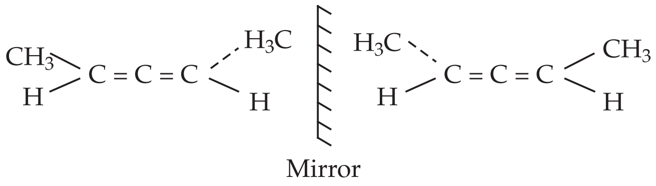
Problem 7. *Which of the following are optically active and why?*

(a) n-Butanol (b) 4-Hydroxyheptane (c) 3-Chlorohexane

(d) 2-Hydroxypropanoic acid

(e) 2, 3-Pentadiene.

Solution. (*a*) and (*b*) are optically inactive due to the absence of asymmertic carbon atom, while (*c*), (*d*) and (*e*) are optically active due to the presence of dissymmetry in them. Structures (*c*) and (*d*) have one asymmetric C atom each and are, therefore, dissymmetric molecules. The structure (*e*) does not have asymmetric carbon atom, yet it is a dissymmetric (chiral) molecule. The object and its mirror image are not superimposable as shown below:



Problem 8. *Give the structures and IUPAC names of all the possible isomers of chlorobutane.*

Solution.

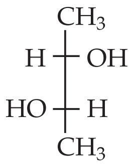
(*i*) $CH_3CH_2CH_2CH_2Cl$ 1-Chlorobutane

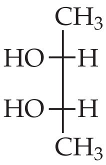
(*ii*) $CH_3CH_2CHClCH_3$ 2-Chlorobutane

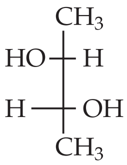
(*iii*) $(CH_3)_2CHCH_2Cl$ 1-chloro-2-methylpropane

(*iv*) $(CH_3)_3CCl$ 2-chloro-2-methylpropane

Problem 9. *Identify the pairs of enantiomers and diastereomers from the following compounds, I, II and III.*


(I)


(II)


(III)

Solution. Enantiomers are the isomers which are mirror images of each other. Diastereomers are the isomers which are not mirror images of each other.

Thus, structures I and III are enantiomers.

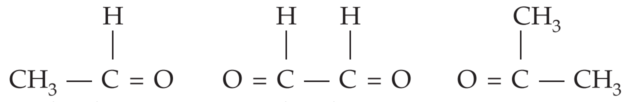
And structures I, II and III are diastereomers.

Problem 10. *Methane does not react with Cl_2 in dark. Explain giving reason.*

Solution. Chlorination of methane is a free radical substitution. To convert Cl_2 molecules into chlorine free radicals (*i.e.* atoms), energy is required which is not available in dark. Thus methane does not react with Cl_2 in dark due to the absence of free radicals to initiate the reaction.

Problem 11. *A hydrocarbon containing two double bonds on reductive ozonolysis gave glyoxal, ethanal and propanone. Give the structure of the hydrocarbon along with its IUPAC name.*

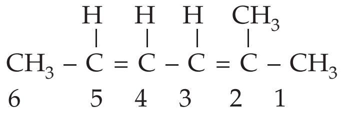
Solution. Write the structure of the products of ozonolysis with their carbonyl groups side by side.



$$CH_3-\overset{\overset{H}{|}}{C}=O \qquad O=\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}=O \qquad O=\overset{\overset{CH_3}{|}}{C}-CH_3$$

Ethanal Glyoxal Propanone

Remove oxygen atoms from each of the three carbonyl compounds and connect them by double bonds. This is how we can obtain the structure of the alkene



$$\underset{6}{CH_3}-\underset{5}{\overset{\overset{H}{|}}{C}}=\underset{4}{\overset{\overset{H}{|}}{C}}-\underset{3}{\overset{\overset{H}{|}}{C}}=\underset{2}{\overset{\overset{CH_3}{|}}{C}}-\underset{1}{CH_3}$$

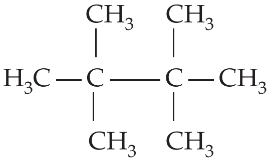
2-Methylhexa-2, 4-diene

Thus, the compound is 2-methylhexa-2, 4-diene.

Problem 12. *Which out of the following has higher octane number? Explain.*

(i) 2, 2, 3-trimethylbutane (ii) 2, 2 4-trimethyl-pentane and (iii) 2, 2, 3, 3 tetramethylbutane.

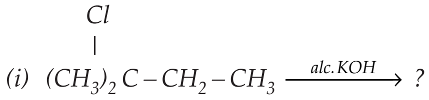
Solution. The hydrocarbon 2, 2, 3, 3-tetramethyl-butane



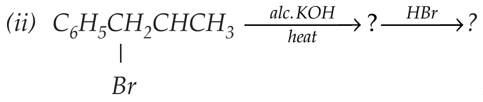
$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

has the highest number of branches (four) as compared to the other hydrocarbons. Hence, this has the highest octane number.

Problem 13. *Complete the following:*



$$(i)\ (CH_3)_2\overset{\overset{Cl}{|}}{C}-CH_2-CH_3 \xrightarrow{alc. KOH} ?$$



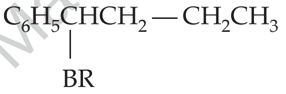
$$(ii)\ C_6H_5CH_2\underset{\underset{Br}{|}}{C}HCH_3 \xrightarrow[heat]{alc. KOH} ? \xrightarrow{HBr} ?$$

$$(iii)\ MeCH_2C\equiv CH \xrightarrow{Na/NH_3} [A] \xrightarrow{EtBr} [B]$$

Solution.

(*i*) $(H_3C)_2CHCH=CH_2$

(*ii*) $C_6H_5CH=CHCH_3$,



$$C_6H_5\underset{\underset{BR}{|}}{C}HCH_2-CH_2CH_3$$

$C_6H_5CH_2\bar{C}HCH_3$ and $C_6H_5\overset{\oplus}{C}HCH_2CH_3$ carbocations are formed on addition of HBr on $C_6H_5CH=CHCH_3$, the latter is stabilised due to resonance and hence Br^- adds on it forming $C_6H_5CHBrCH_2CH_3$ as the final product.

(*iii*) A = $MeCH_2C\equiv CNa$, B = $MeCH_2C\equiv CEt$.

Problem 14. *Why are alkanes chemically inert?*

Solution. Alkanes have no such characteristics as shared pair of electrons, a polar bond, an electron deficient atom or an atom with an expandable octet. Hence, it is chemically unreactive.

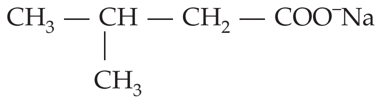
Problem 15. *Why the unsaturated hydrocarbons and the aromatic compounds burn with more sooty flame than the saturated hydrocarbons?*

Solution. Unsaturated hydrocarbons and aromatic hydrocarbons have greater percentage of carbon than saturated hydrocarbons. Hence, they burn with more sooty flame.

Problem 16. *How will you prepare (i) isobutane and (ii) CH_3CH_2D?*

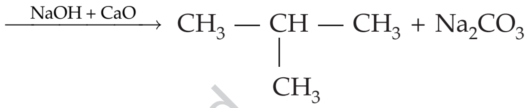
Solution.

(*i*) Isobutane can be prepared by decarboxylation of 3-methylbutanoic acid with sodalime.



$$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2-COO^-Na$$

Sodium, 3-Methylbutanoate



$$\xrightarrow{NaOH + CaO} CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_3 + Na_2CO_3$$

Isobutane

(*ii*) The compound CH_3CH_2D can be obtained by the action of heavy water on CH_3CH_2MgBr.

$$\underset{\text{Grignard reagent}}{CH_3CH_2MgBr} + D_2O \rightarrow \underset{\text{Dueteroethane}}{H_3CCH_2D} + Mg(OD)Br$$

Problem 17. *A hydrocarbon B, adds one mole of hydrogen in presence of platinum catalyst to form hexane. B, on vigorous oxidation with $KMnO_4$ gives a single carboxylic acid containing three carbon atoms. Give the structure and name of B.*

Solution.

(*i*) Since the hydrocarbon B adds one molecule of H_2 in presence of Pt to form hexane, B must be hexene.

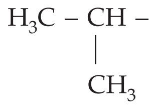
(*ii*) Since B on vigorous oxidation with $KMnO_4$ gives a single carboxylic acid containing three carbon atoms, therefore, B *must be a symmetrical hexene, i.e. hex-3-ene.*

$$\underset{\text{Hex-3-ene (B)}}{CH_3CH_2CH=CHCH_2CH_3} \xrightarrow[KMnO_4]{(O)} \underset{\text{Propionic acid}}{2CH_3CH_2COOH}$$

Thus, the given hydrocarbon B is hex-3-ene.

Problem 18. *Prepare 3-Methylbut-1-yne from Ethyne.*

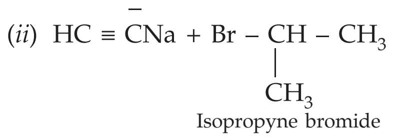
Solution. 3-Methylbut-1-yne is



$$H_3C-\underset{\underset{CH_3}{|}}{C}H-C\equiv CH.$$

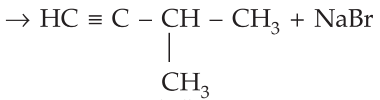
It can be prepared in the following steps:

$$(i)\ HC\equiv CH \xrightarrow[\text{Sodamide}]{NaNH_2} \underset{\text{Sodium acetylide}}{HC\equiv \overset{-}{C}\overset{+}{Na}}$$



$$(ii)\ HC\equiv \bar{C}Na + Br-\underset{\underset{CH_3}{|}}{C}H-CH_3$$

Isopropyne bromide



$$\rightarrow HC\equiv C-\underset{\underset{CH_3}{|}}{C}H-CH_3 + NaBr$$

3-Methylbut-1-yne

Problem 19. *Acetylene is acidic but it does not react with NaOH or KOH. Why?*

Solution. Acetylene is a very weak acid ($K_a = 10^{-25}$) and so it reacts only with extremely strong bases such as $NaNH_2$ and not with NaOH or KOH.

Problem 20. *Propene on heating (at 500°C) with Cl_2 undergoes substitution reaction instead of addition reaction. Why?*

Solution. At high temperature, homolytic cleavage of Cl_2 produces Cl free radicals which result in the formation of allyl carbonium ion due to high energy content during the course of reaction to show free radical substitution.

Problem 21. *Addition of HCl to 3-3-dimethyl but-1-ene gives two isomers. Explain.*

Solution. Branching in alkanes causes decrease in surface area and thereby a decrease in the van der Waals' forces among molecules. This results in lower b.p., *iso*-pentane thus possesses low b.p. *Neo*-pentane being more symmetric possesses a more stable crystal structure than *n*-pentane and thus shows higher melting point.

Problem 22. *A regular copolymer of ethylene and vinyl chloride contains alternate monomers of each type. What is the weight percent of ethylene in this copolymer?*

Solution. 31.28%

Problem 23. *Mention the basic unit in each of the following:*

(i) *Polythene* *(ii)* *Synthetic rubber*

(iii) *Natural rubber.*

Solution.

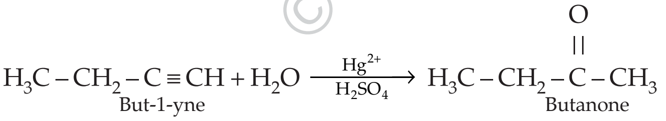
(*i*) Ethene.

(*ii*) 2-Chloro-1, 3-butadiene or Chloroprene or neoprene.

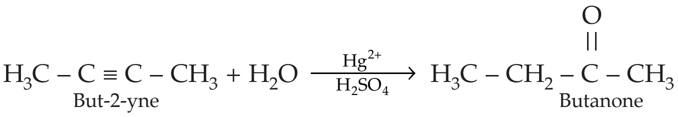
(*iii*) 2-Methyl-1, 3-butadiene or Isoprene.

Problem 24. *When an alkyne is passed through a dilute solution of H_2SO_4 in presence of mercuric sulphate, butanone is formed. Write possible structure of the alkyne.*

Solution. Butanone is ketone with four carbon atoms. It can be obtained by the hydration of butyne, which exists in two forms,



$$\underset{\text{But-1-yne}}{H_3C-CH_2-C\equiv CH} + H_2O \xrightarrow[H_2SO_4]{Hg^{2+}} \underset{\text{Butanone}}{H_3C-CH_2-\overset{\overset{O}{||}}{C}-CH_3}$$

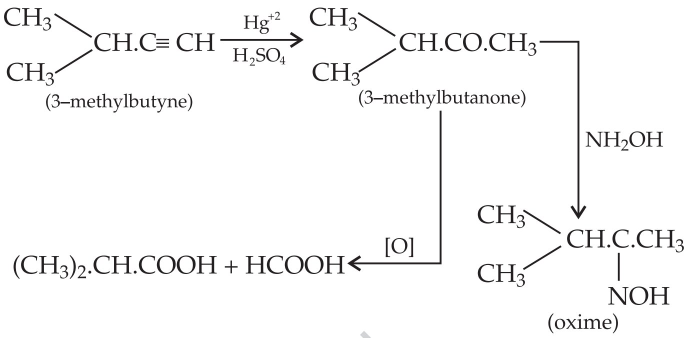


$$\underset{\text{But-2-yne}}{H_3C-C\equiv C-CH_3} + H_2O \xrightarrow[H_2SO_4]{Hg^{2+}} \underset{\text{Butanone}}{H_3C-CH_2-\overset{\overset{O}{||}}{C}-CH_3}$$

The unsaturated alcohol formed in both the cases undergoes tautomerism to form the product.

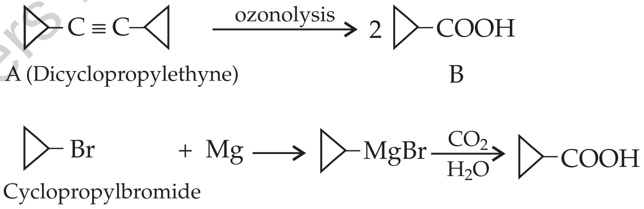
Problem 25. *An alkyne with 5 carbon atoms per molecule when passed through dilute sulphuric acid containing mercuric sulphate gives a compound which forms an oxime, but has no effect on Fehling's Solution. The compound on oxidation gives dimethyl acetic acid. It reacts with sodalime to form a hydrocarbon. What is the structure of the alkyne?*

Solution.



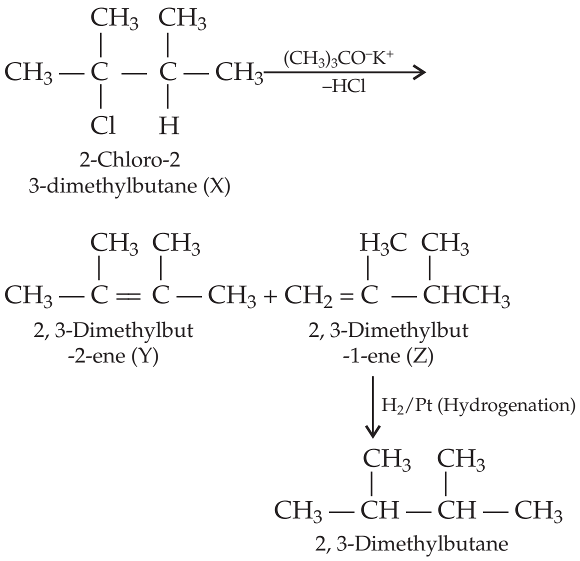
Problem 26. *A hydrocarbon (A) of the formula C_8H_{10} on ozonolysis gives compound (B) ($C_4H_6O_2$) only. The compound (B) can also be obtained from the alkyl bromide (C) (C_3H_5Br) upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify (A), (B) and (C) and also give equations for the reactions.*

Solution. The reactions can be represented as under:



Problem 27. *An alkyl halide, X, of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z.*

Solution.



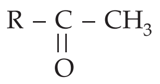
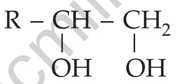
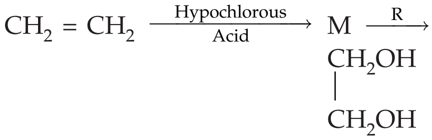
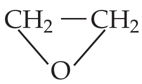
Problem 28. *Explain very briefly why alkynes are generally less reactive than alkenes towards electrophilic reagents such as H^+.*

Solution. Alkynes are less reactive than alkenes towards addition reactions even though they contain two π bonds. This is due to (*i*) greater electronegativity of *sp* hybridised carbon of alkynes, than sp^2 hybridised carbon atoms of alkenes, which hold the π electrons of alkynes more tightly and (*ii*) greater delocalisation of electrons (because of cylindrical nature of their π electrons cloud) than in alkenes. As a result, π electrons of alkynes are less easily available for addition reactions than those of alkenes. Consequently, alkynes are less reactive than alkenes towards addition reactions.

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. The reactive species of nitration of benzene is
   (*a*) NO_2^+ (*b*) HNO_3
   (*c*) NO_3 (*d*) NO_2^-
2. In the free radical chlorination of methane, the chain initiating step involves the formation of
   (*a*) Chlorine atom
   (*b*) Hydrogen chloride
   (*c*) Methyl radical
   (*d*) Chloromethyl radical
3. Alkene $RCH = CH_2$ reacts readily with B_2H_6 and the product on oxidation with alkaline hydrogen peroxides produces
   (*a*) $R - CH_2 - CHO$ (*b*) RCH_2CH_2OH
   (*c*)  $R - \underset{\underset{O}{||}}{C} - CH_3$
   (*d*)  $R - \underset{\underset{OH}{|}}{CH} - \underset{\underset{OH}{|}}{CH_2}$
4. When 3, 3-dimethyl-2-butanol is heated with H_2SO_4, the major product obtained is
   (*a*) *cis* and *trans* isomers of product named under (*c*)
   (*b*) 3, 3 dimethyl-1 butene
   (*c*) 2, 3 dimethyl-2 butene
   (*d*) 2, 3 dimethyl-1 butene
5. Select the major product formed from the reaction of 2-bromobutane and alc. KOH.
   (*a*) $CH_2 = CHCH_2CH_3$
   (*b*) *cis* $CH_3CH = CHCH_3$
   (*c*) *trans* $CH_3CH = CHCH_3$
   (*d*) $CH_2 = CHCH_3$
6. Anti-Markownikoff's addition of HBr is not observed in
   (*a*) propene (*b*) butene-1
   (*c*) but-2-ene (*d*) Pent-2-ene
7. Consider the following compounds:
   $CH_3CH_2CHClCH_3$
   $CH_2 = CHCH_2CH_2Cl$
   $CH_3CH_2CH_2CH_2Cl$
   These compounds are dehydrohalogenated in treatment with a strong base under identical condition. The correct sequence of increasing order of reactivity of these compounds in the given reaction.
   (*a*) 1, 2, 3 (*b*) 2, 1, 3
   (*c*) 3, 1, 2 (*d*) 3, 2, 1
8. Consider the following compounds:
   1. $CH_3CH_2CH_2CH_2OH$
   2. $CH_3CH_2CH(OH)CH_3$
   3. $(CH_3)_3COH$
   These compounds are dehydrated by treatment with sulphuric acid. The correct sequence of increasing order of the reactivity of three compounds toward dehydration is
   (*a*) 3, 1, 2 (*b*) 2, 1, 3
   (*c*) 1, 2, 3 (*d*) 1, 3, 2
9. $(CH_3)_3CMgCl$ on reaction with D_2O produces
   (*a*) $(CH_3)_3CD$ (*b*) $(CH_3)_3OD$
   (*c*) $(CD_3)_3CD$ (*d*) $(CD_3)_3OD$
10. Which one of the following reaction is expected to readily give a hydrocarbon product in good yields?
    (*a*) $RCOOK \xrightarrow[\text{Oxidation}]{\text{Electrolytic}}$ (*b*) $RCOOAg \xrightarrow[CCl_4]{Br_2}$
    (*c*) $CH_3CH_3 \xrightarrow[hv]{Cl_2}$ (*d*) $(CH_3)_3CCl \xrightarrow{C_2H_5OH}$
11. In a reaction,
    
    $CH_2 = CH_2 \xrightarrow[\text{Acid}]{\text{Hypochlorous}} M \xrightarrow{R} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array}$
    M = molecule
    R = reagent
    M and R are
    (*a*) CH_3CH_2Cl and NaOH
    (*b*) CH_2ClCH_2OH and aq. $NaHCO_3$
    (*c*) CH_3CH_2OH and HCl
    (*d*)  and HCl

12. The intermediate during the addition of HCl to propene in the presence of peroxide is
    (*a*) $CH_3\bar{C}HCH_2Cl$ (*b*) $CH_3\bar{C}HCH_3$
    (*c*) $CH_3CH_2\overset{+}{C}H_2$ (*d*) $\overset{+}{C}H_2CH_2CH_2Cl$
13. Which of the following reaction cannot produce RCOAr?
    (*a*) $RCOCl + H - Ar \xrightarrow{AlCl_3}$
    (*b*) $ArCOCl + RMgX \longrightarrow$

(*c*) $Ar - R + CrO_3 \longrightarrow$

(*d*) None of these

14. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane is

(*a*) 3 (*b*) 2

(*c*) 4 (*d*) 1

15. The alkene that exhibits geometrical isomerism is

(*a*) propene (*b*) 2–methylpropene

(*c*) 2-butene (*d*) 2-methyl-2-butene

16. One mole of a symmetical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 *u*. The alkene is

(*a*) ethene (*b*) propene

(*c*) 1–butene (*d*) 2–butene

17. Which one of the following is used to make non-stick cookwares?

(*a*) Polystyrene.

(*b*) Polyethylene terephthalate.

(*c*) Polytetrafluoroethylene.

(*d*) Poly vinyl chloride.

18. Orlon is a polymer of

(*a*) Tetrafluoroethylene (*b*) Acrylonitrile

(*c*) Acetic acid (*d*) Benzene.

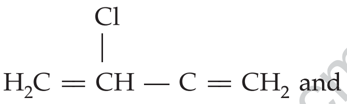
19. $\left[NH(CH_2)NHCO(CH_2)_4CO \right]$ is a

(*a*) homopolymer (*b*) copolymer

(*c*) addition polymer

(*d*) thermosetting polymer

20. Buna-N synthetic rubber is a copolymer of

(*a*) 
$H_2C = CH - \overset{\overset{Cl}{|}}{C} = CH_2$ and

$H_2C = CH - CH = CH_2$

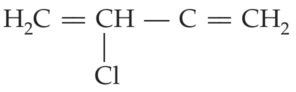
(*b*) $H_2C = CH - CH = CH_2$ and

$H_5C_6 - CH = CH_2$

(*c*) $H_2C = CH - CN$ and

$H_2C = CH - CH = CH_2$

(*d*) $H_2C = CH - CN$ and

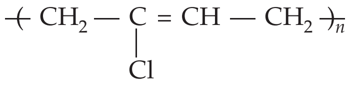

$H_2C = CH - \underset{\underset{Cl}{|}}{C} = CH_2$

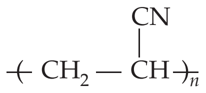
21. Among cellulose, polyvinyl chloride, nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is

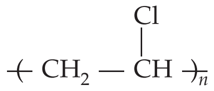
(*a*) nylon (*b*) polyvinyl chloride

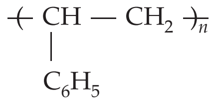
(*c*) cellulose (*d*) natural rubber.

22. Which of the following structures represents neoprene polymer?

(*a*) 
$\left(CH_2 - \underset{\underset{Cl}{|}}{C} = CH - CH_2 \right)_n$

(*b*) 
$\left(CH_2 - \overset{\overset{CN}{|}}{CH} \right)_n$

(*c*) 
$\left(CH_2 - \overset{\overset{Cl}{|}}{CH} \right)_n$

(*d*) 
$\left(\underset{\underset{C_6H_5}{|}}{CH} - CH_2 \right)_n$

(B) Fill in the Blanks

Fill in the blank spaces:

1. Chain isomerism arises due to different arrangements of ________.
2. Ethane molecule has ________ geometry.
3. Pentane has ________ chain isomers.
4. Open chain compounds are also called ________ compounds.
5. Cyclopropane is an ________ while benzene is ________.
6. In methane, carbon exhibits ________ hybridisation and the hybrid orbitals are inclined at an angle of ________.
7. The valence atomic orbitals of C in silver acetylide are ________ hybridised.
8. An alkyl group is formed by removing________ from the parent alkane.
9. Restricted rotation about carbon-carbon double bond gives rise to________ isomerism.
10. The organic compounds containing carbon and hydrogen atoms only are called ________.
11. Bond angles in methane are ________ each.
12. C = C bonds is ________ than C – C bond.
13. Buna-S is obtained by copolymerization of ________ with ________.
14. Polythene is a ________ while bakelite is a ________ polymer.
15. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with ________.
16. Natural rubber is a polymer of ________.
17. ___________ is used for making eye lenses.
18. Gutta-percha is ___________ .
19. The process of vulcanization was introduced by ___________ .
20. Polymerization of styrene in the presence of KNH_2 is an example of ___________ addition polymerization.

(C) True/False Statements

Write T for true and F for false the statements:

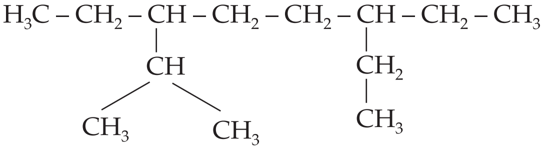
1. Acetylene is more acidic than ethylene.
2. Photobromination of 2-methylbutane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methyl propane in the ratio of 9 : 1.
3. Organic compounds contain ionic linkages.
4. The chair form of cyclohexane is less stable than its boat form.
5. Achiral objects are those which are superimposable on their mirror images.
6. The IUPAC names of various classes of organic compounds are derived from alkenes.
7. 2, 2-Dimethylbutane and 2-methylbutane are chain isomers of hexane.
8. The large number of organic compounds is due to catenation.
9. Isomerism is phenomenon when different compounds have the same molecular formula.
10. Acetylene is a tetrahedral molecule.
11. Neoprene is a biopolymer.
12. Vulcanization introduces sulphur bridges between polymer chains.
13. Polyacrylonitrile is a polymer of acrolein.
14. Intermolecular forces of attraction in nylons are dipole-dipole interactions.
15. Natural rubber is all *cis*-polyisoprene.
16. Tetrafluorethylene is the monomer of the polymer teflon.

SOME ADDITIONAL QUESTIONS

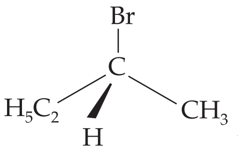
I. Multiple Choice Questions

With one or more than one correct answer(s):

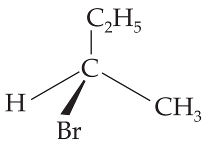
1. Arrange the following in decreasing order of their boiling points.
   (A) *n*-butane (B) 2-methylbutane
   (C) *n*-pentane (D) 2,2-dimethylpropane
   (*a*) A > B > C > D (*b*) B > C > D > A
   (*c*) D > C > B > A (*d*) C > B > D > A
2. Arrange the halogens F_2, $C1_2$, Br_2, I_2, in order of their increasing reactivity with alkanes.
   (*a*) $I_2 < Br_2 < Cl_2 < F_2$ (*b*) $Br_2 < Cl_2 < F_2 < I_2$
   (*c*) $F_2 < Cl_2 < Br_2 < I_2$ (*d*) $Br_2 < l_2 < Cl_2 < F_2$
3. The increasing order of reduction of alkyl halides with zinc and dilute HCl is
   (*a*) R–C1 < R–I < R–Br (*b*) R–C1 < R–Br < R–I
   (*c*) R–I < R–Br < R–Cl (*d*) R–Br < R–I < R–Cl
4. The correct IUPAC name of the following alkane is



   (*a*) 3, 6 – Diethyl – 2 – methyloctane
   (*b*) 5 – Isopropyl – 3 – ethyloctane
   (*c*) 3 – Ethyl – 5 – isopropyloctane
   (*d*) 3 – Isopropyl – 6 – ethyloctane
5. The addition of HBr to 1-butene gives a mixture of products A, B and C



(A)



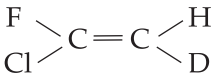
(B)

$CH_3 — CH_2 — CH_2 — Br$

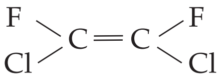
(C)

   The mixture consists of
   (*a*) A and B as major and C as minor products
   (*b*) B as major, A and C as minor products
   (*c*) B as minor, A and C as major products
   (*d*) A and B as minor and C as major products
6. Which of the following will not show geometrical isomerism?

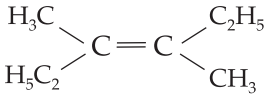
(*a*)



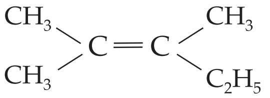
(*b*)



(*c*)

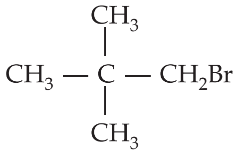


(*d*)



7. Arrange the following hydrogen halides in order of their decreasing reactivity with propene.
   (*a*) HCl > HBr > HI (*b*) HBr > HI > HCl
   (*c*) HI > HBr > HCl (*d*) HCl > HI > HBr
8. Arrange the following carbanions in order of their decreasing stability.
   (A) $H_3C — C \equiv C^-$ (B) $H — C \equiv C^-$
   (C) $H_3C — CH_2^-$
   (*a*) A > B > C (*b*) B > A > C
   (*c*) C > B > A (*d*) C > A > B

9. Arrange the following alkyl halides in decreasing order of the rate of β-elimination reaction with alcoholic KOH.

(A) 

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Br$

(B) $CH_3 - CH_2 - Br$

(C) $CH_3 - CH_2 - CH_2 - CH_2 - Br$

(*a*) A > B > C (*b*) C > B > A

(*c*) B > C > A (*d*) A > C > B

10. Which of the following reactions of methane is incomplete combustion?

(*a*) $2CH_4 + O_2 \xrightarrow{Cu/523\,K/100\,atm} 2CH_3OH$

(*b*) $CH_4 + O_2 \xrightarrow{MO_2O_3} HCHO + H_2O$

(*c*) $CH_4 + O_2 \longrightarrow C(s) + 2H_2O\ (l)$

(*d*) $CH_4 + 2O_2 \longrightarrow CO_2(g) + 2H_2O(l)$

11. The commercial name of polyacrylonitrile is ________.

(*a*) Dacron (*b*) Orlon (acrilan)

(*c*) PVC (*d*) Bakelite

12. Which of the following polymers are thermoplastic?

(*a*) Teflon (*b*) Natural rubber

(*c*) Neoprene (*d*) Polystyrene

13. Which of the following are addition polymers?

(*a*) Nylon

(*b*) Melamine formaldehyde resin

(*c*) Orlon

(*d*) Polystyrene

II. Short Answer Type Questions

1. Alkynes on reduction with sodium in liquid ammonia form trans alkenes. Will the butene thus formed on reduction of 2-butyne show the geometrical isomerism?
2. Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.
3. Draw Newman and Sawhorse projections for the eclipsed and staggered conformations of ethane. Which of these conformations is more stable and why?
4. The relative reactivity of 1°, 2°, 3° hydrogen's towards chlorination is 1 : 3.8 : 5. Calculate the percentages of all monochlorinated products obtained from 2-methylbutane.
5. Write the structures and names of products obtained in the reactions of sodium with a mixture of l-iodo-2-methylpropane and 2-iodopropane.
6. Write the hydrocarbon radicals that can be formed as intermediates during monochlorination of 2-methylpropane. Which of them is more stable? Give reasons.
7. An alkane C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide.

III. Assertion-Reason Type Questions

In the following questions a statement of assertion (A) followed by a statement of reason (R) is given. Choose the correct option out of the choices given below in each question.

1. ***Assertion*** **(A):** The compound cyclooctane has the following structural formula:

It is cyclic and has conjugated 8π-electron system but it is not an aromatic compound.

***Reason* (R):** (4*n* + 2) π electrons rule does not hold good and ring is not planar.

(*i*) Both A and R are correct and R is the correct explanation of A.

(*ii*) Both A and R are correct but R is not the correct explanation of A.

(*iii*) Both A and R are not correct.

(*iv*) A is not correct but R is correct.

2. ***Assertion (A):*** Toluene on Friedal-Crafts methylation gives *o*-and *p*-xylene.

Reason (R): CH_3-group bonded to benzene ring increases electron density at *o*-and *p*-position.

(*i*) Both A and R are correct and R is the correct explanation of A.

(*ii*) Both A and R are correct but R is not the correct explanation of A.

(*iii*) Both A and R are not correct.

(*iv*) A is not correct but R is correct.

3. ***Assertion (A):*** Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.

Reason (R): The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2^+

(*i*) Both A and R are correct and R is the correct explanation of A.

(*ii*) Both A and R are correct but R is not the correct explanation of A.

(*iii*) Both A and R are not correct.

(*iv*) A is not correct but R is correct.

4. ***Assertion (A):*** Among isomeric pentanes, 2, 2-dimethylpentane has highest boiling point.

   Reason (R): Branching does not affect the boiling point.

   (*i*) Both A and R are correct and R is the correct explanation of A.
   (*ii*) Both A and R are correct but R is not the correct explanation of A.
   (*iii*) Both A and R are not correct.
   (*iv*) A is not correct but R is correct.

IV. Long Answer Type Questions

1. An alkyl halide $C_5H_{11}Br$ (A) reacts with ethanolic KOH to give an alkene 'B', which reacts with Br_2 to give a compound 'C', which on dehydrobromination gives an alkyne 'D'. On treatment with sodium metal in liquid ammonia one mole of 'D' gives one mole of the sodium salt of 'D' and half a mole of hydrogen gas. Complete hydrogenation of 'D' yields a straight chain alkane. Identify A, B, C and D. Give the reactions involved.
2. An unsaturated hydrocarbon 'A' adds two molecules of H_2 and on reductive ozonolysis gives butane-1,4-dial, ethanal and propanone. Give the structure of 'A', write its IUPAC name and explain the reactions involved.
3. In the presence of peroxide addition of HBr to propene takes place according to anti Markovnikov's rule but peroxide effect is not seen in the case of HCl and HI. Explain.

ANSWERS

(A) Multiple Choice Questions

1. (*a*) 2. (*a*) 3. (*b*) 4. (*c*) 5. (*c*) 6. (*c*) 7. (*c*) 8. (*c*)
9. (*a*) 10. (*a*) 11. (*b*) 12. (*b*) 13. (*c*) 14. (*b*) 15. (*c*) 16. (*d*)
17. (*c*) 18. (*b*) 19. (*b*) 20. (*c*) 21. (*d*) 22. (*a*)

(B) Fill in the Blanks

1. carbon chain 2. Tetrahedral 3. Three 4. staggered, eclipsed
5. aliphatic 6. alicyclic, aromatic 7. sp^3, 109° 28′ 8. *sp*
9. one hydrogen atom 10. geometrical 11. hydrocarbons 12. 109° 28′
13. shorter 14. 1, 3-butadiene, styrene 15. Thermoplastic, Thermosetting
16. acetylene 17. Isoprene 18. Poly (methyl methacrylate)
19. All *trans* polyisoprene 20. Charles' Goodyear

(C) True/False Statements

1. True 2. False 3. False 4. False 5. True 6. False 7. False 8. True
9. True 10. False 11. False 12. True 13. False 14. False, H-bonding
15. True 16. True

Some Additional Questions

I. Multiple Choice Questions

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

III. Assertion-Reason Type Questions

1. (*i*) 2. (*i*) 3. (*i*) 4. (*iii*)

12

CHAPTER

Haloalkanes

LEARNING OBJECTIVES

- Structure and isomersim
  - Apply the IUPAC rules to the nomenclature of simple halogenoalkanes.
  - Classify halogenoalkanes as primary halogenoalkane, secondary halogenoalkane and tertiary halogenoalkane and name them accordingly.
- Substitution reactions of halogenoalkanes
  - Describe the reactions of halogenoalkanes with OH^-, CN^- and NH_3.
  - Explain the mechanism of nucleophilic substitution reactions for the halogenoalkanes with OH, CN^- and NH_3.
  - Outline the importance of the reactions with CN^- in organic synthesis as a means to add a carbon atom to an organic compound.
  - Explain the rates of hydrolysis of halogenoalkanes in terms of the relative bond enthalpies of carbon-halogen bonds (e.g. C–F, C–Cl, C–Br, C–I).
- Elimination reactions of halogenoalkanes
  - Explain how simultaneous elimination and displacement occur in the reaction of a halogenoalkanes (e.g. 2-bromopropane with potassium hydroxide) and the role of reagent as a base and a nucleophile (including mechanisms).

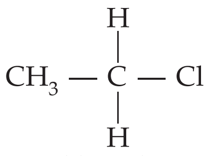
12.1 HALOALKANES

Alkyl halides or haloalkanes are the compounds in which a halogen is attached to an aliphatic carbon. They have the general formula RX (where R is the alkyl group, and X is the halogen atom). These are obtained from an alkane by replacement of one hydrogen atom by a halogen atom.

$$\mathrm{RH} \xrightarrow[-\mathrm{H}]{+\mathrm{H}} \mathrm{RX}$$

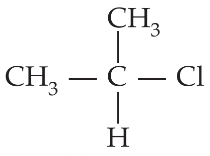
For example, $$\underset{\text{Methane}}{\mathrm{CH_4}} \xrightarrow[-\mathrm{H}]{+\mathrm{Cl}} \underset{\text{Chloromethane}}{\mathrm{CH_3Cl}}$$

Alkyl halides are classified as primary, secondary and tertiary alkyl halides depending on whether the halogen atom is attached to a primary, secondary or tertiary carbon atom respectively. Example of each is given below:



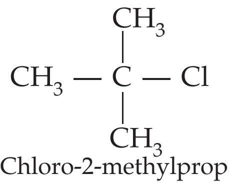
$$\mathrm{CH_3-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-Cl}$$

Chloroethane
(*Primary*) (1°)



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-Cl}$$

2-Chloropropane
(*Secondary*) (2°)



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl}$$

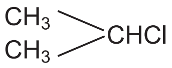
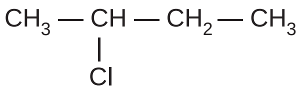
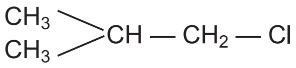
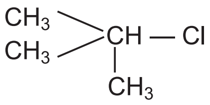
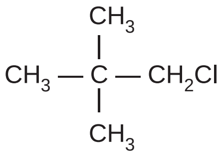
2-Chloro-2-methylpropane
(*Tertiary*) (3°)

A primary carbon is one which is further attached to one carbon (in some cases no carbon). A secondary carbon is one which is further attached to two carbon atoms. A tertiary carbon is one which is further attached to three carbon atoms.

12.2 NOMENCLATURE OF HALOALKANES

In the common system, aliphatic halogen derivatives are named as *alkyl halides*. The words, *n-*, *sec-*, *ter-*, *iso-* and *neo-* are usually employed in writing the common names. In IUPAC system, they are named as derivatives of corresponding alkanes. The common and IUPAC names of some of the compounds are given below in Table 12.1.

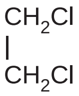
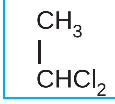
Table 12.1

Formula name	Common name	IUPAC
CH_3Cl	Methyl chloride	Chloromethane
CH_3CH_2Cl	Ethyl chloride	Chloroethane
$CH_3CH_2CH_2Cl$	*n*-Propyl chloride	1-Chloropropane
	*iso*-Propyl chloride	2-Chloropropane
$CH_3CH_2CH_2CH_2Cl$	*n*-Butyl chloride	1-Chlorobutane
 $CH_3-\underset{\underset{\displaystyle Cl}{\vert}}{CH}-CH_2-CH_3$	*sec*-Butyl chloride	2-Chlorobutane
	*iso*-Butylchloride	1-Chloro-2-methylpropane
	*tert*-Butyl chloride	2-Chloro-2-methylpropane
$CH_3CH_2CH_2CH_2CH_2Cl$	*n*-Pentyl chloride or *n*-Amyl chloride (amyl stands for 5 carbon atoms)	1-Chloropentane
 $CH_3-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\displaystyle CH_3}{\vert}}{C}}-CH_2Cl$	*neo*-Pentyl chloride or *neo*-Amyl chloride	1-Chloro-2, 2-dimethyl-propane

12.2.1 Dihalogen Compounds

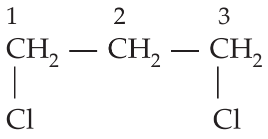
There could be two halogens in one molecule of a compound. Common and IUPAC names of a few dihalides are also given below in Table 12.2.

Table 12.2

Formula	Common name	IUPAC name
CH_2Cl_2	Methylene chloride	Dichloromethane
 $\underset{\underset{\displaystyle CH_2Cl}{\vert}}{CH_2Cl}$	Ethylene chloride or Ethylene dichloride **(vic. dihalide)**	1, 2-Dichloroethane
 $\underset{\underset{\displaystyle CHCl_2}{\vert}}{CH_3}$	Ethylidene chloride or Ethylidene dichloride **(gem. dihalide)**	1, 1-Dichloroethane

Vic is the abbreviated form of *vicinal* and ***gem*** is the abbreviated form of *geminal*. A **vicinal dihalide** has two halogen atoms on adjacent carbon atoms while **geminal dihalide** has two halogen atoms on the same carbon atom.

If the two carbons carrying halogens are separated by one or more carbons then numbering is done to name the compound.



$\underset{\underset{Cl}{|}}{\overset{1}{CH_2}} — \overset{2}{CH_2} — \underset{\underset{Cl}{|}}{\overset{3}{CH_2}}$ 1, 3-Dichloropropane

PROBLEMS FOR PRACTICE

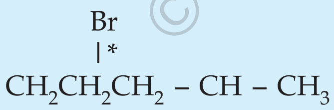
1. Write all the possible structures for the molecular formula $C_5H_{11}Br$. Give their IUPAC names and point out if any one is optically active.
2. Write structural formula of:
   - (*i*) 3-Bromohexane
   - (*ii*) *Neo*-pentyl iodide
   - (*iii*) Ethylene dibromide
   - (*iv*) 2-Chloro-3, 3-dimethyl butane.
3. Give common names of the following compounds:
   - (*i*) $(CH_3)_3C(CH_2)_2CH_2Br$
   - (*ii*) $(CH_2)_3Cl_2$
4. Give structural formula and IUPAC names of:
   - (*i*) *n*-amyl chloride
   - (*ii*) *sec*-butyl iodide
   - (*iii*) *iso*-pentyl chloride.

ANSWERS

1. There are eight compounds (isomers) possible with this formula. These are:

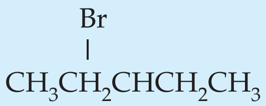
(*i*) $CH_3CH_2CH_2CH_2CH_2Br$

1-Bromopentane



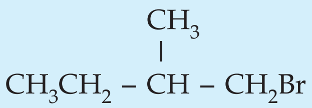
(*ii*) $CH_3CH_2CH_2-\overset{\overset{Br}{|^*}}{CH}-CH_3$

2-Bromopentane



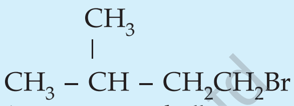
(*iii*) $CH_3CH_2\overset{\overset{Br}{|}}{CH}CH_2CH_3$

3-Bromopentane



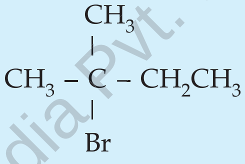
(*iv*) $CH_3CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2Br$

1-Bromo-2-methylbutane



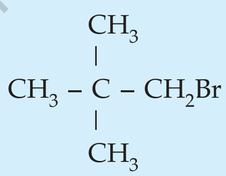
(*v*) $CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2CH_2Br$

1-Bromo-3-methylbutane



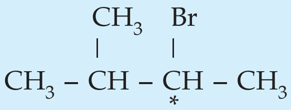
(*vi*) $CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$

2-Bromo-2-methylbutane



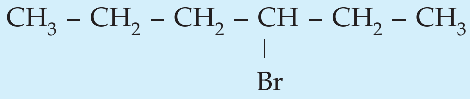
(*vii*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Br$

1-Bromo-2, 2-dimethylpropane

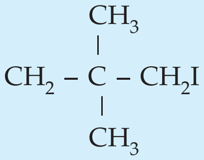


(*viii*) $CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{*}{\overset{\overset{Br}{|}}{CH}}-CH_3$

2-Bromo-3-methylbutane

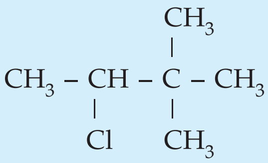
2. 

(*i*) $CH_3-CH_2-CH_2-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3$



(*ii*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2I$

(*iii*) CH_2BrCH_2Br

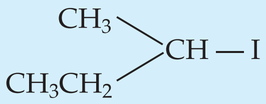


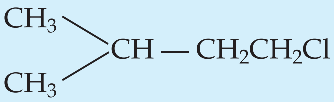
(*iv*) $CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

3. (*i*) *Neo*-heptyl bromide

(*ii*) Trimethylene dichloride or Cyclopropane dichloride

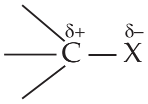
4. (*i*) $CH_3CH_2CH_2CH_2CH_2Cl$
1-Chloropentane

(*ii*)

2-Iodobutane

(*iii*)

1-Chloro-3-methylbutane

12.3 NATURE OF C–X BOND

Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



Since the size of halogen atom increases as we go down the group in the periodic table, fluorine atom is the smallest and iodine atom, is the largest, consequently the carbon-halogen bond length also increases from C—F to C—I. Some typical bond lengths, bond enthalpies and dipole moments are given in Table 12.3.

Table 12.3: Carbon-Halogen (C–X) Bond Lengths, Bond Enthalpies and Dipole Moments

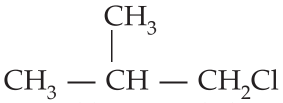
Bond	Bond length/pm	C–X Bond enthalpy/kJmol^{-1}	Dipole moment/Debye
CH_3-F	139	452	1.847
CH_3-Cl	178	351	1.860
CH_3-Br	193	293	1.830
CH_3-I	214	234	1.636

12.4 ISOMERISM IN HALOALKANES

Compounds having the same molecular formula but different structures are called *isomers* and this phenomenon is called *isomerism*.

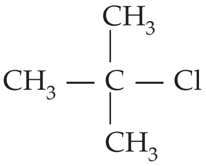
1. **Chain isomerism.** The haloalkanes with four or more carbon exhibit this kind of isomerism.

$CH_3CH_2CH_2CH_2Cl$
1-Chlorobutane



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2Cl$$

1-Chloro-2-methylpropane

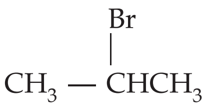


$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-Cl$$

2-Chloro-2-methylpropane

2. **Position isomerism.** The haloalkanes with three or more carbon atoms show this kind of isomerism. For example, C_3H_7Br has two isomers.

$CH_3CH_2CH_2Br$
1-Bromopropane

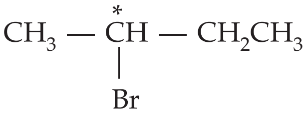


$$CH_3-\overset{\displaystyle Br}{\overset{|}{C}}HCH_3$$

2-Bromopropane

The number of chain and position isomers will increase with the increase in number of carbon atoms.

3. **Optical isomerism.** Haloalkanes having one asymmetric carbon give optical isomers. For example, sec-butyl bromide has one asymmetric carbon (marked with *) and it exists in two optically active forms which are mirror images of each other.



$$CH_3 - \overset{*}{C}H - CH_2CH_3 \quad (\text{Br on } \overset{*}{C})$$

4. **Conformational isomerism.** Haloalkanes can also form conformational isomers due to free rotation around C — C bond.

Before we move to preparation and properties of halogen compounds, we shall take up some points that are relevant to the mechanisms involved in the reactions.

Inductive Effect

When a covalent bond involves two atoms of different electronegativities, the shared pair of electrons is displaced towards the more electronegative element. As a result, the more electronegative atom gets a small negative charge and the other atom gets a small equal positive charge. For example, consider a chain of carbon atoms joined to a chlorine atom

$$- C_3 - C_2 - C_1 - Cl$$

Chlorine has a greater electronegativity than carbon, therefore, the electron pair forming the covalent bond between the chlorine atom and C_1 will be displaced towards chlorine atom. This causes the chlorine atom to acquire a small negative charge represented by –δ and the carbon atom to acquire a small positive charge +δ as shown below.

$$- C_3 - C_2 - \overset{+\delta}{C_1} - \overset{-\delta}{Cl}$$

Since C_1 is slightly positivity charged, it will attract towards itself the electron pair forming the covalent bond between C_1 and C_2. This will cause C_2 to acquire a small positive charge but this charge will be smaller than that on C_1 because the effect of chlorine atom has been passed from C_1 to C_2.

$$- C_3 - \overset{+\delta}{C_2} - C_1 - \overset{-\delta}{Cl}$$

This type of electron shift or displacement along a carbon chain is known as *inductive effect*. Inductive effect is permanent and decreases rapidly as the distance from the source (Cl) increases. The inductive effect is shown by a line marked with arrow head (→) pointing towards the electron attracting atoms or groups.

If the atom or group of atoms attached to a carbon atom is such that it attracts the shared pair of electrons towards itself, it is said to exert negative or –I effect. The decreasing order of –I effect of some of the atoms or groups is:

$$NO_2 > CN > COOH > F > Cl > Br > I > OCH_3 > C_6H_5$$

If the atom or group of atoms attached to a carbon atom is such that it pushes the electrons away from it, it is said to exert positive or +I effect. The decreasing order of +I effect of some groups is:

$$(CH_3)_3\,C > (CH_3)_2CH > CH_3CH_2 > CH_3$$

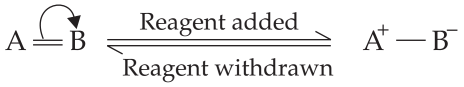
For comparison of inductive effect, hydrogen (H) is chosen as the standard. Atoms or groups with –I effect are more electron-withdrawing than H while those with +I effect are less electron-withdrawing than H or, in other words, they are more electron-releasing than H.

Electromeric Effect

It is a temporary effect which involves a complete and instantaneous transfer of a shared pair of electrons to one or the other atom joined by multiple bond at the requirement of an attacking reagent.

The electromeric effect is represented by a curved arrow beginning from the position of the electron pair and ending where the pair has migrated. Let us consider a molecule AB having a double bond between atoms

A and B. In the presence of the attacking reagent, one of the shared pair of electrons is completely transferred to one of the atoms (say B) as shown below:

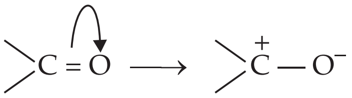


$$A{=}B \underset{\text{Reagent withdrawn}}{\overset{\text{Reagent added}}{\rightleftharpoons}} \overset{+}{A}-\overset{-}{B}$$

Thus A becomes positively charged while B becomes negatively charged. The removal of the attacking reagent causes the charged molecule to revert to its original condition.

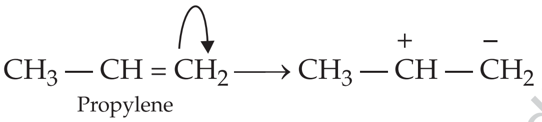
Electronegativity plays an important role in knowing the direction of transfer of shared pair of electrons to one of the atoms. For example,

(*i*) In a carbonyl group present in aldehydes or ketones, the displacement is towards the oxygen atom. This is due to greater electronegativity of oxygen than carbon.



(–E-effect)

(*ii*) In propylene, the displacement of shared electron pair is towards the carbon atom which is away from methyl group. This is due to the inductive effect of methyl group which is electron repelling.



$$\underset{\text{Propylene}}{CH_3-CH=CH_2} \longrightarrow CH_3-\overset{+}{CH}-\overset{-}{CH_2}$$

(+E-effect)

Thus, the electromeric effect is of two types. When the electron displacement is away from the group, it is denoted by +E and when the displacement is towards the group, it is denoted by –E.

Resonance or Mesomerism

Sometimes it is found that a single structural formula cannot satisfactorily explain all the properties of a given compound. In such a case the compound is represented by two or more structural formulae which differ only in the arrangement of electrons. None of the structural formula alone can explain all the observed properties of the compound. The compound is then said to show resonance. The various structures are called resonating structures or canonical structures. The true structure of the molecule is not represented by any of the resonating structures but is considered to be a resonance hybrid (intermediate) of the various resonating structures.

For example, the most frequently used Lewis structure for carbon dioxide molecule is

$$:\ddot{O}::O::\ddot{O}: \quad \text{or} \quad \underset{\text{I}}{O=C=O}$$

On the basis of this structure, the heat of formation of carbon dioxide from its elements should have been 1463 kJ/mole and C = O bond length should have been 1.21 Å. But the experimental values for the heat of formation of CO_2 is 1588 kJ/mole and C = O bond length is 1.15 Å. Thus, structure I for CO_2 cannot explain its properties completely. Structures II and III contain triple bonds which have shorter bond lengths. But they have shorter bond lengths than 1.15 Å. Thus, structures II and III also fail to account for all the observed properties of carbon dioxide.

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{O}}:C:::\overset{\cdot\cdot\,+}{O}: \quad \text{or} \quad \underset{\text{II}}{\overset{-}{O}-C\equiv\overset{+}{O}}$$

and

$$:\underset{\cdot\cdot}{\overset{+}{O}}:::C:\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{O}} \quad \text{or} \quad \underset{\text{III}}{\overset{+}{O}\equiv C-\overset{-}{O}}$$

In the light of the above concept, CO_2 is regarded as a resonance hybrid of the structures I, II and III, *i.e.*,

$$\underset{\text{I}}{O=C=O} \longleftrightarrow \underset{\text{II}}{\overset{-}{O}-C\equiv\overset{+}{O}} \longleftrightarrow \underset{\text{III}}{\overset{+}{O}\equiv C-\overset{-}{O}}$$

Conditions for Resonance

Main conditions for resonance are:

(*i*) The positions of the nuclei (of each atom) in each structure must be the same.

(*ii*) The number of unpaired electrons in each structure must be the same.

(*iii*) Each structure must have about the same internal energy.

(*iv*) The contributing structures, which involve separation of positive and negative charges are of high energy and, hence, contribute less towards the resonance hybrid.

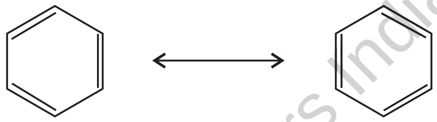
(*v*) The larger the number of bonds in the contributing structure, the greater is its stability.

(*vi*) The greater the number of contributing structures, the greater will be the stability of the molecule.

Consequences of Resonance

(*i*) Bond length. The bond length in actual molecule is different from that of any of the contributing structures.

Let us consider the example of benzene molecule. Had I or II been the structure of benzene then it should have shown two bond lengths, *i.e.,* three C=C double bonds should have been 1.34 Å long and three C — C single bonds should have been 1.54 Å long. But the X-ray analysis of benzene shows that all the carbon-carbon bond lengths are identical and equal to 1.39 Å. This can be explained if we consider benzene to be a resonance hybrid of two Kekule's structures I and II.



In other words, the real structure of benzene is neither represented by Kekule's structure I nor by II but is somewhat in between these two structures. This means that any two adjacent carbon atoms of the benzene molecule are joined neither by a pure single bond nor by a pure double bond. As a result, all the carbon-carbon bond lengths should not only be equal but should also lie in between C=C bond length of 1.34 Å and C — C bond length of 1.54 Å. This is an excellent agreement with the experimental value of 1.39 Å.

(*ii*) Stability. A resonance hybrid is always more stable than any of its canonical (resonating) structures. For example, the observed heat of formation of carbon dioxide is 125 kJ/mole more than the value calculated on the basis of structure O = C = O. This implies that the internal energy of CO_2 is less than the calculated value by 125 kJ/mole. In other words, the real molecule of CO_2 is 125 kJ/mole more stable than the Lewis structure O = C = O.

The magnitude of stability conferred on a molecule as a result of resonance is expressed in terms of **resonance energy of delocalization energy**. It is defined as the difference between the actual energy of the molecule capable of exhibiting resonance and the energy calculated for the resonating structures.

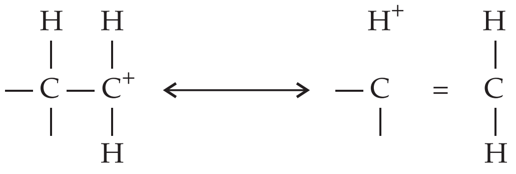
Low reactivity of halogen in vinyl chloride can be explained on account of the phenomenon of resonance or mesomerism.

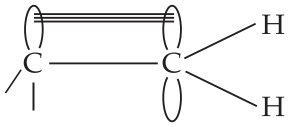
$$CH_2 = CH - \underset{\cdot\cdot}{\overset{\cdot\cdot}{Br}}: \longleftrightarrow \overset{-}{C}H_2 - CH - \underset{\cdot\cdot}{\overset{+}{BR}}:$$

Halogen compounds generally give nucleophilic substitution reactions in which the halogen is removed as halide ion.

But in the case of vinyl bromide, resonance takes place as illustrated above. This creates a double bond between carbon and bromine. Removal of bromine, thus, becomes difficult. Moreover, bromine acquires a positive charge and, hence, cannot be substituted by a nucleophile. That is, why vinyl bromide shows low reactivity.

Hyperconjugation (No-Bond Resonance): It is a special type of resonance which involves the overlapping of a σ-orbital with a π-orbital or *p*-orbital. Hyperconjugation takes place in the following carbonium ion as depicted.


(I) (II)



Since in structure (II), there is no bond between H^+ and C, hyperconjugation is also referred to as no-bond resonance.

Homolytic and Heterolytic Fission: Consider a covalent bond between atoms A and B.

$$A:B \quad \text{or} \quad A—B$$

The cleavage (or breaking) of this bond can take place in three possible ways depending upon the relative electronegativities of A and B.

(*i*) $A:B \longrightarrow A\cdot + B\cdot$ (A and B of equal electronegativity)

(*ii*) $A:B \longrightarrow \bar{A}: + \overset{+}{B}$ (A more electronegative than B)

(*iii*) $A:B \longrightarrow \overset{+}{A} + :\bar{B}$ (B more electronegative than A)

The first type of cleavage is called **homolytic fission** or homolysis and leads to the formation of very reactive species called **free-radicals** (atoms or group of atoms containing odd or unpaired electrons).

In homolytic fission, the covalent bond breaks in such a way that each fragment carries one unpaired electron.

The second and third types of cleavage is called **heterolytic fission** and leads to the formation of ionic species. These ionic species are also very reactive and carry charges on carbon. Cationic species carrying positive charge on a carbon atom are called **carbonium ions** or **carbocations.** Anionic species carrying negative charge on carbon atom are called **carbanions.**

In heterolytic fission, the covalent bond breaks in such a way that the pair of electrons stays on the more electronegative atom.

For nucleophiles and electrophiles, refer to Chapter 10.

12.5 GENERAL METHODS OF PREPARATION OF HALOALKANES

Methods of preparation of haloalkanes are described as under:

1. From Alcohols

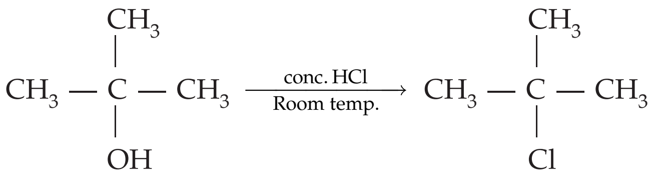
(*a*) By reaction with halogen acids. Alcohols can be converted into haloalkanes by treatment with halogen acids. The reaction, in general, can be represented as

$$\underset{\text{Alcohol}}{R-OH} + HX \rightarrow \underset{\text{Alkyl halide}}{R-X} + H_2O$$

(*i*) Chloroalkanes are obtained by treating alcohols with HCl in the presence of anhydrous zinc chloride **(Groove's Process)**. *The anhydrous $ZnCl_2$ acts as a dehydrating agent. The mixture of HCl and anhydrous $ZnCl_2$ is known as Lucas reagent.*

$$CH_3CH_2OH + HCl \xrightarrow{\text{anhyd. } ZnCl_2} CH_3CH_2Cl + H_2O$$

Tertiary alcohols readily react with conc. HCl even in the absence of $ZnCl_2$.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3 \xrightarrow[\text{Room temp.}]{\text{conc. HCl}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-CH_3$$

tert-Butyl alcohol *tert*-Butyl chloride

(*ii*) **Bromoalkanes** can be obtained by heating alcohols with HBr. *HBr is generated in situ by reaction of KBr with conc.* H_2SO_4.

$$KBr + H_2SO_4 \rightarrow KHSO_4 + HBr$$
$$C_2H_5OH + HBr \rightarrow C_2H_5Br + H_2O$$

(*iii*) **Iodoalkanes** are obtained by heating alcohols with HI, hydriodic acid.

$$C_2H_5OH + HI \rightarrow C_2H_5I + H_2O$$

Reactivity of halogen acids towards this reaction is **HI > HBr > HCl**.

It is because the bond dissociation energy of HI is less than that of HBr which, in turn, is less than that of HCl. More easily the bond between hydrogen and halogen is broken, greater will be the reactivity of the acid.

Reactivity of alcohols towards this reaction is **Tertiary > Secondary > Primary**. *It is because greater the number of electron releasing groups on* α*-carbon atom of alcohol, greater is the polarity of C–OH bond. Consequently, greater is the ease with which C–O bond will break.*

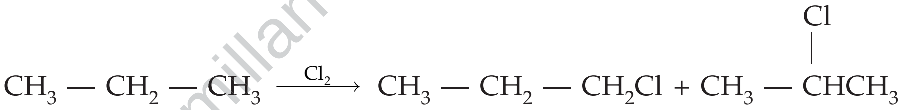
2. From Alkanes

Alkanes on treatment with halogens such as chlorine or bromine in the presence of light or catalysts, give a mixture of mono- and poly- substituted products.

$$CH_4 \xrightarrow[-HCl]{Cl_2} CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{Cl_2} CHCl_3 \xrightarrow[-HCl]{Cl_2} CCl_4$$

We obtain a mixture of *mono, di, tri* and *tetra* halogen compounds. It is possible to some extent to obtain monosubstitution product by controlling the ratio of halogen to alkane.

In case of higher alkanes, different isomeric products are formed.



$$CH_3-CH_2-CH_3 \xrightarrow{Cl_2} CH_3-CH_2-CH_2Cl + CH_3-\overset{\overset{\displaystyle Cl}{|}}{C}HCH_3$$

Propane 1-Chloropropane (45%) 2-Chloropropane (55%)

In general, the ease of substitution in such cases is: tertiary H-atom > sec. H-atom > primary H-atom. The *iodination* of alkanes is carried out by heating with iodine in the presence of oxidising agents such as conc. HNO_3, HIO_4 or HIO_3. *The function of using such agents is to oxidize HI formed during the reaction to iodine, and to shift the equilibrium in the forward direction.*

$$\underset{\text{Methane}}{CH_4} + I_2 \rightleftharpoons \underset{\text{Iodomethane}}{CH_3I} + HI \qquad 5HI + \underset{\text{Iodic acid}}{HIO_3} \rightarrow 3I_2 + 3H_2O$$

Fluorine has a great affinity for hydrogen. It abstracts all the hydrogens present in the hydrocarbon. Hence, it is almost impossible to prepare fluoroalkanes by fluorination.

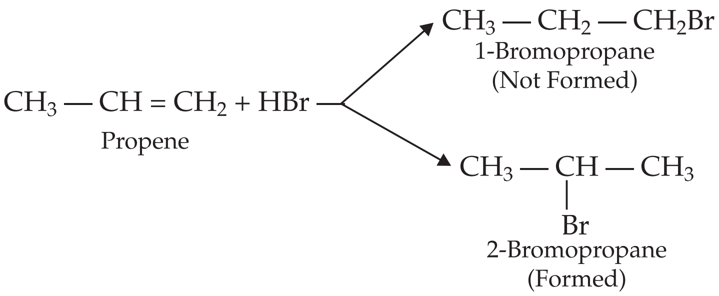
$$CH_4 + 2F_2 \rightarrow 4HF + C$$

3. From Alkenes

Haloalkanes can be prepared from alkenes by the addition of halogen acids.

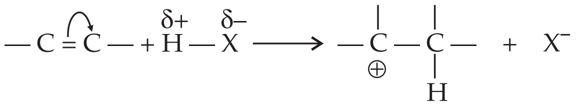
$$\underset{\text{Ethene}}{CH_2=CH_2} + HI \rightarrow \underset{\text{Iodoethane}}{CH_3CH_2I}$$

In unsymmetrical alkenes, the addition of halogen acids takes place according to the **Markownikoff's rule**. ***According to this, negative part of the addendum molecule attaches itself to the carbon atom carrying smaller number of hydrogen atoms.***



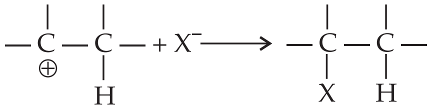
Mechanism of Markownikoff's addition. The electrophilic addition of hydrogen halides follows the mechanism as given below:

(*i*)



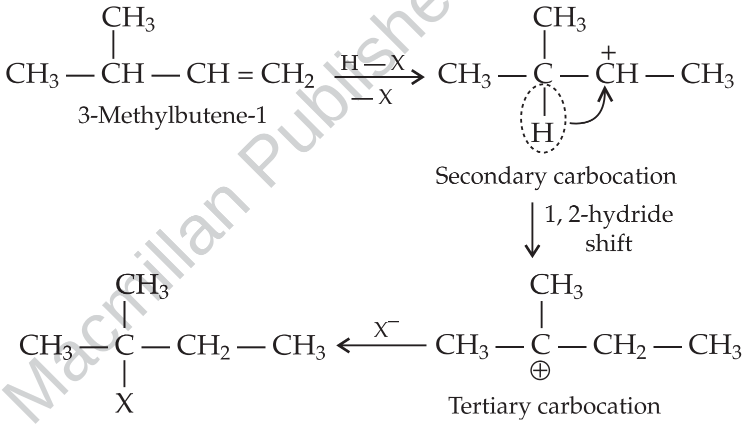
$$-C=C- + \overset{\delta+}{H}-\overset{\delta-}{X} \longrightarrow -\underset{\oplus}{C}-\underset{H}{C}- + X^-$$

(*ii*)



$$-\underset{\oplus}{C}-\underset{H}{C}- + X^- \longrightarrow -\underset{X}{C}-\underset{H}{C}-$$

In certain cases, the intermediate carbocation may undergo rearrangement through **1, 2-methyl shift** or **1, 2-hydride shift** to form a more stable carbocation.



In the above reaction, hydride shift has occurred to give a more stable tertiary carbocation.

In the presence of organic peroxide such as *benzoyl peroxide* ($C_6H_5CO - O - O - COC_6H_5$), HBr reacts with alkyl halides to give the product in defiance of Markownikoff's rule.

$$\underset{\text{Propene}}{CH_3 - CH = CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}$$

This is called **peroxide effect** or **Kharasch effect**.

It may be noted that the Kharasch effect occurs in the addition of HBr only and not in the addition of HI or HCl. It can be explained as follows:

It does not occur in the case of HCl because of high dissociation energy.

HI has a low bond dissociation energy, but iodine radicals produced combine with each other to form iodine molecules instead of reacting with the alkene.

PROBLEMS FOR PRACTICE

1. The product formed by treatment of isobutylene with HBr is ....

[**Ans.** *tert*-butyl bromide]

2. Haloalkanes can be prepared from alkenes by the addition of ....

[**Ans.** halogen acids]

3. On chlorination of ethane, two isomeric dihalides are formed along with C_2H_5Cl. Give their structures.

[**Ans.** (*i*) CH_3CHCl_2 (1, 1-dichloroethane); (*ii*) CH_2ClCH_2Cl (1, 2-dichloroethane)]

12.6 PHYSICAL PROPERTIES OF HALOALKANES

(*i*) Boiling points

(*a*) The boiling points of haloalkanes follow the order: RCl < RBr < RI. *It is because with the increase in size and mass of the halogen atom, the magnitude of van der Waals' forces of attraction increases which is responsible for higher boiling point.*

(*b*) Among isomeric alkyl halides, the boiling point decreases with the increase in branching in the alkyl group. This is because with increase in branching, the molecule tends to gain spherical shape with less surface area. As a result intermolecular forces become weaker, resulting in lower boiling point.

Thus, among isomeric butyl chlorides, the straight chain isomer, *n*-butyl chloride has the highest boiling point whereas *tert*-butyl chloride has the lowest boiling point. *n*-butyl chloride has the largest and *tert*-butyl chloride has the small surface area respectively.

(*c*) For same halogen, the boiling point increases with the increase in molecular mass of the halogen compound. Thus, haloethane boils at a higher temperature than halomethane. Halopropane boils at a higher temperature than haloethane and so on.

(*d*) Haloalkanes have higher boiling points as compared to those of corresponding alkanes. This is due to their polarity and strong dipole-dipole attractive interactions between haloalkane molecules.

(*ii*) Solubility in water. Alkyl halides are insoluble in water *because they are not able to form hydrogen bonds with water molecules*. However, they are soluble in organic solvents such as alcohols, ether and benzene.

(*iii*) Density. Alkyl chlorides are generally lighter than water whereas bromides and iodides are heavier. Their densities are in the order R–I > R – Br > R – Cl. Polychlorides are, however, heavier than water.

12.7 CHEMICAL PROPERTIES OF HALOALKANES

Haloalkanes are highly reactive class of aliphatic compounds due to the presence of *polar carbon-halogen bond* in their molecules. In general, for a given alkyl group, the order of reactivity follows the order:

Iodides > Bromides > Chlorides

The above order is based on the fact that most of the reactions of alkyl halides involve the cleavage of C–X bond. Higher the bond dissociation energy of C–X bond, smaller is the reactivity. The bond dissociation energy decreases with the increase in the size of halogen atom. Hence, the reactivity increases from alkyl chlorides to bromides and from bromides to iodides. Bond dissociation energy data is given in Table 12.4.

Table 12.4

Bond	Bond dissociation energy (kJ mol^{-1})
C–Cl	328
C–Br	275.6
C–I	240

The chemical reactions of haloalkanes can be divided into the following:

(*i*) *Nucleophilic substitution reactions*

(*ii*) *Dehydrohalogenation*

(*iii*) *Reactions with metals*

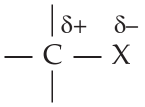
(*iv*) *Reduction*

(*v*) *Halogenation*

(*vi*) *Isomerisation*

I. Nucleophilic Substitution Reactions

In haloalkanes, the halogen atom is attached to the carbon atom. As the halogen atom is more electronegative than carbon, the bond between carbon and halogen is polar in character.



$$-\overset{|}{\underset{|}{\overset{\delta+}{C}}}-\overset{\delta-}{X}$$

Due to the presence of partial positive charge on the carbon atom, the nucleophiles can attack on electron deficient carbon thereby displacing weaker nucleophile, the halide ion. Thus, typical reactions of alkyl halides are **nucleophilic substitution reactions**.

$$\underset{}{R:X} + \underset{\text{Nucleophile}}{:Z^-} \rightarrow R:Z + \underset{\text{Halide ion}}{X^-}$$

It must be noted that halide ion is substituted only if the attacking nucleophile is stronger than it. Since halide ion itself is very weak nucleophile the attacking nucleophile is generally stronger than it.

Mechanism of nucleophilic substitution reaction

Nucleophilic substitution reaction may take place in two different ways:

(*i*) **SN^1 Mechanism** (*nucleophilic substitution of first order*): Here, the rate of reaction is dependent only on the concentration of alkyl halide, *i.e.*

$$\text{Rate} = k\,[RX]$$

The tertiary alkyl halides react by SN^1 mechanism via formation of carbocation as an intermediate.

Step I $R - X \xrightarrow{\text{Slow}} R^+ + X^-$ (Rate determining step)

Step II $R^+ + Z^- \xrightarrow{\text{Slow}} R - Z$

The order of reactivity of various alkyl halides following SN^1 mechanism is: 3° > 2° > 1°. The 3° alkyl halides are most reactive because the intermediate carbocation (tertiary carbocation) formed in their cases is the most stable.

(*ii*) **SN^2 Mechanism** (*nucleophilic substitution of second order*): Here the rate of reaction is dependent on the concentration of alkyl halide as well as nucleophile, *i.e.*

$$\text{Rate} = k\,[RX]\,[Z^-]$$

Primary alkyl halides react by SN^2 mechanism via formation of a transition state as given below:

$$R - X + Z^- \xrightarrow{\text{Slow}} \left[\overset{\delta-}{Z}\ldots\ldots R\ldots\ldots\overset{\delta-}{X}\right] \xrightarrow{\text{Fast}} Z - R + X^-$$

Some of the nucleophilic reactions of haloalkanes are described as under:

1. **Replacement by hydroxyl group** *(Formation of alcohols)*. When treated with aqueous solution of KOH or moist silver oxide (Ag_2O/H_2O) haloalkanes give *alcohols*.

$$\underset{\text{Haloalkane}}{R - Z} + :OH^- \rightarrow \underset{\text{Alcohol}}{R - OH} + :Z^-$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + KOH\,(aq) \rightarrow \underset{\text{Ethanol}}{C_2H_5OH} + KBr$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + AgOH \xrightarrow{\text{Moist silver oxide}} C_2H_5OH + AgBr$$

The ease of substitution of alkyl halides follows the order:

$$RI > RBr > RCl > RF$$

This can be explained in terms of relative bond enthalpies of carbon-halogen bond (*e.g.*, C—F, C—Cl, C—Br, C—I).

Bond enthalpies of C—H, C—F, C—Cl, C—Br, C—I are given below (in kJ $mole^{-1}$).

C — H : 413
C — F : 467
C — Cl : 346
C — Br : 290
C — I : 228

It may be noted that in the substitution reactions of haloalkanes, carbon–halogen bond has to be broken. Only after that the attachment of —OH group will take place. Greater the ease with which carbon–halogen bond can be broken, greater will be the possibility of formation of the product. From the bond enthalpy data given above, we can say that ease of fission of carbon–halogen bond follows the order: C—I > C—Br > C—Cl > C—F. Hence the formation of alcohol from a haloalkane follows the same order. In fact fluoroalkanes do not react with alkali at all. This is because C—F bond enthalpy is higher even than that of C—H bond. Thus, there is a greater possibility that C—H bond may get ruptured instead of C—F bond.

2. **Replacement by alkoxy group** *(Formation of ethers)* or **(Williamson Synthesis)**. Haloalkanes on treatment with alcoholic sodium or potassium alkoxide form *ethers.*

$$\underset{\text{Haloalkane}}{R - X} + \underset{\text{Alkoxide ion}}{:OR'} \rightarrow \underset{\text{Ether}}{R - O - R'} + :X^-$$

$$\underset{\text{Iodoethane}}{C_2H_5I} + \underset{\text{Sodium ethoxide}}{NaOC_2H_5} \rightarrow \underset{\text{Ethoxyethane}}{C_2H_5OC_2H_5} + NaI$$

Ethers can also be prepared by heating alkyl halides with dry silver oxide, Ag_2O.

$$\underset{\text{Bromoethane}}{2C_2H_5Br} + Ag_2O \xrightarrow{\text{heat}} \underset{\text{Ethoxyethane}}{C_2H_5 - O - C_2H_5} + 2AgBr$$

3. **Replacement by cyano group.** On treatment with alcoholic KCN solution, haloalkanes give *alkanenitriles* or *alkyl cyanides* as the major product and small amount of alkyl isocyanide.

$$\underset{\text{Haloalkane}}{R - X} + :CN^- \rightarrow \underset{\text{Alkane nitrile}}{R - C \equiv N} + :X^-$$

$$\underset{\text{Iodoethane}}{CH_3 - CH_2 - I} + KCN \rightarrow \underset{\text{Propane nitrile}}{CH_3 - CH_2 - C \equiv N} + KI$$

The alkyl cyanides so obtained have synthetic value and can be used as starting materials for the preparation of a number of other compounds.

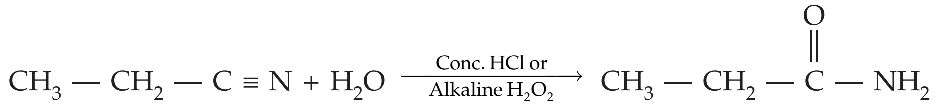
(*i*) Alkyl cyanides on reduction with Na/ethyl alcohol give primary amines (**Mendius reaction**). The reduction can also be achieved catalytically using H_2/Ni.

$$CH_3-CH_2-C\equiv N\xrightarrow[\text{Na / Alcohol}]{\text{H}_2\text{ / Ni or}}\underset{\text{Propan-1-amine}}{CH_3-CH_2-CH_2-NH_2}$$

(*ii*) Alkyl cyanides can also be reduced with $SnCl_2$ and HCl to produce aldehydes (**Stephen's reaction**).

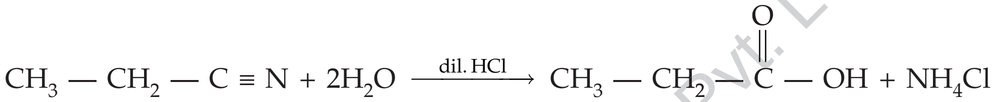
$$\underset{\text{Propane nitrile}}{CH_3-CH_2-C\equiv N}\xrightarrow[\text{HCl}]{\text{SnCl}_2}CH_3CH_2CH=NH.HCl\xrightarrow[-\text{NH}_4\text{Cl}]{\text{H}_2\text{O/H}^+}\underset{\text{Propanal}}{CH_3CH_2CHO}$$

(*iii*) Alkyl cyanides on **partial hydrolysis** with conc. HCl or alkaline solution of H_2O_2 give amides.



$$\underset{\text{Propane nitrile}}{CH_3-CH_2-C\equiv N+H_2O}\xrightarrow[\text{Alkaline H}_2\text{O}_2]{\text{Conc. HCl or}}\underset{\text{Propanamide}}{CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2}$$

(*iv*) Alkyl cyanides on **complete hydrolysis** with dil. HCl, give carboxylic acids.



$$\underset{\text{Propane nitrile}}{CH_3-CH_2-C\equiv N+2H_2O}\xrightarrow{\text{dil. HCl}}\underset{\text{Propanoic acid}}{CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH}+NH_4Cl$$

The reaction of alkyl with KCN provides us an important method for increasing the length of carbon chain by the one carbon atom, *i.e.* **ascending of series**.

4. Replacement by isocyanide *(Formation of isocyanides).* On treatment with alcoholic silver cyanide solution, haloalkanes give *alkyl carbylamines* or *alkyl isocyanides* as the major product along with a small amount of alkyl isocyanide

$$R-X+\text{alc. }AgCN\rightarrow\underset{\text{Isocyanide}}{R-NC}+AgX$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br}\quad+\quad\text{alc. }AgCN\quad\rightarrow\quad\underset{\text{Ethyl isocyanide}}{C_2H_5NC}\quad+\quad AgBr$$

5. Replacement by amino group *(Formation of amines).* Haloalkane on heating with alcoholic ammonia solution in a sealed tube at 383 K, form *primary amine.*

$$\underset{\text{Haloalkanes}}{R\text{–}X}\quad+\quad NH_3\text{ (alc.)}\rightarrow\underset{\text{Primary amine}}{R\text{–}NH_2}\quad+\quad HX$$

$$\underset{\text{Bromoethane}}{C_2H_5\text{–}Br}+NH_3\text{ (alc.)}\rightarrow\underset{\text{Ethanamine}}{C_2H_5NH_2}+HBr$$

In case haloalkane is in excess, the reaction continues and other two hydrogen atoms of amino group are also replaced by alkyl groups leading to the formation of *secondary* and *tertiary amines, step by step.*

$$\underset{\text{Bromoethane}}{C_2H_5Br}\quad+\quad\underset{\text{Ethyl amine}}{HNHC_2H_5}\quad\rightarrow\quad\underset{\substack{\text{Diethyl amine}\\\text{(N-Ethylethanamine)}}}{(C_2H_5)_2NH}\quad+\quad HBr$$

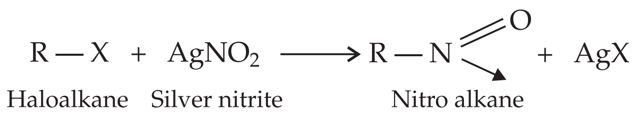
$$\underset{\text{Diethylamine}}{(C_2H_5)_2NH}\quad+\quad\underset{\text{Bromoethane}}{Br-C_2H_5}\quad\rightarrow\quad\underset{\substack{\text{Triethyl amine}\\\text{(N, N-Diethylethanamine)}}}{(C_2H_5)_3N}\quad+\quad HBr$$

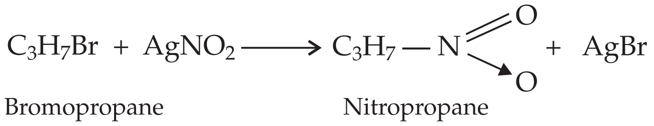
The reaction does not stop here and tertiary amine so formed can further combine with another molecule of alkyl halide to give *quaternary ammonium salt.*

$$C_2H_5Br\quad+\quad\underset{\text{Triethyl amine}}{(C_2H_5)_3N}\quad\rightarrow\quad\underset{\substack{\text{Tetraethyl ammonium}\\\text{bromide (Quaternary salt)}}}{[(C_2H_5)_4N]^+\,Br^-}$$

This reaction is known as **Hofmann ammonolysis** of alkyl halides.

6. **Replacement by nitro group** *(Formation of nitroalkane).* On treating ethanolic solution of haloalkanes with silver nitrite ($AgNO_2$), *nitroalkane* is obtained.





7. **Replacement by nitrite group** *(Formation of alkyl nitrites).* On treating haloalkanes with sodium nitrite, *alkyl nitrite* is formed.

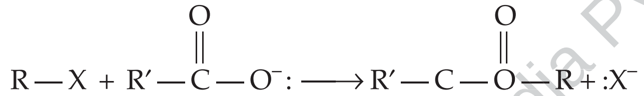
$R - X + NaNO_2 \rightarrow R - O - N = O + NaX$

Haloalkane Alkyl nitrite

$C_2H_5Br + NaNO_2 \rightarrow C_2H_5 - O - N = O + NaBr$

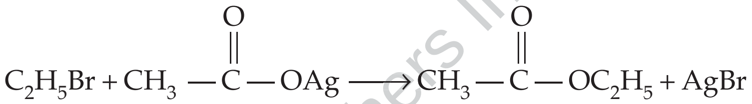
Bromoethane Ethyl nitrite

8. **Replacement by carboxylate group** *(Formation of esters).* Haloalkanes on treatment with silver salt of carboxylic acid in ethanol, give esters.



$$R - X + R' - \overset{\overset{\large O}{\|}}{C} - O^{-}: \longrightarrow R' - \overset{\overset{\large O}{\|}}{C} - O - R + :X^{-}$$

Haloalkanes Ether



$$C_2H_5Br + CH_3 - \overset{\overset{\large O}{\|}}{C} - OAg \longrightarrow CH_3 - \overset{\overset{\large O}{\|}}{C} - OC_2H_5 + AgBr$$

Silver acetate Ethyl acetate

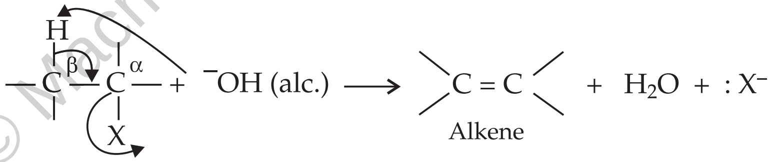
II. Dehydrohalogenation Reactions

On heating with alcoholic KOH, haloalkanes undergo dehydrohalogenation to form *alkenes*. Hydrogen atom present at β^{-} position of the haloalkane is removed.

$$CH_3 - CH_2 - Br + KOH\ (alc.) \longrightarrow H_2C = CH_2 + KBr + H_2O$$

Bromoethane Ethene

Mechanism of the reaction is as follows:

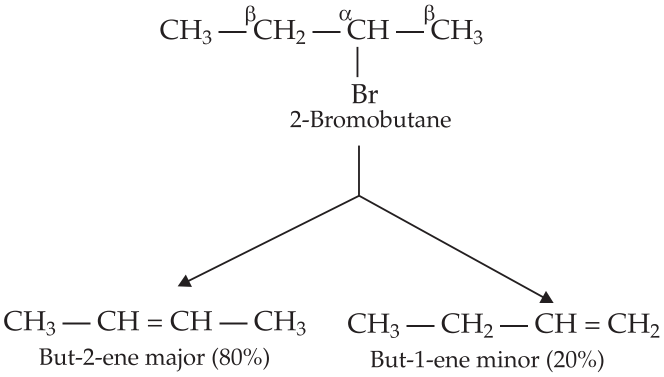


The **reactivity** of haloalkanes towards elimination reaction follows the order:

Tertiary > Secondary > Primary

This can be explained in terms of the stability of the alkene formed after dehydrohalogenation. Tertiary alkyl halides on dehydrohalogenation give most substituted alkenes, which being more stable are formed at faster rate. In contrast primary alkyl halides yield least substituted alkenes, which being less stable are formed at slower rate. Secondary alkyl halides show intermediate reactivity.

Saytzeff Rule. *In case the haloalkanes can eliminate hydrogen halide in two different ways, the preferred alkene is the one which has maximum alkylation, i.e., which carries maximum number of alkyl groups attached to the doubly bonded carbon atoms.* This is known as **Saytzeff Rule**. For example, 2-Bromobutane on treatment with alc. KOH can give two possible products.



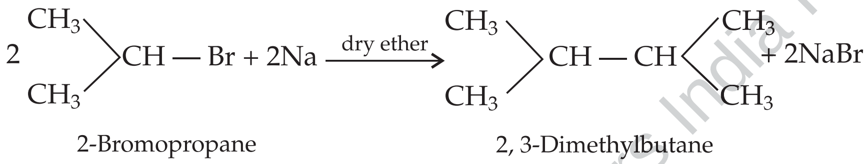
Butene-2 is the major product because it has greater alkylation (two alkyl groups) around the double bond.

III. Reactions with Metals

WURTZ

1. **Reaction with sodium (Wurtz Reaction).** Haloalkanes react with sodium in presence of ether to form *alkanes*.

$$2RX + 2Na \xrightarrow{\text{ether}} R-R + 2NaX$$



This reaction is known as **Wurtz reaction**. This reaction is employed to prepare symmetrical alkanes with greater number of carbon atoms (*ascending of series*). The tertiary halides do not undergo this reaction.

2. **Reaction with magnesium.** Haloalkanes react with magnesium in presence of dry ether to form alkyl magnesium halides (**Grignard reagents**).

$$RX + Mg \rightarrow RMgX$$

$$CH_3Br + Mg \rightarrow \underset{\text{Methyl magnesium bromide}}{CH_3MgBr}$$

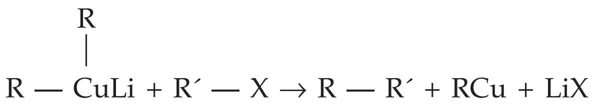
3. **Reaction with lithium.** Haloalkanes react with lithium in presence of dry ether to form *alkyl lithium.* These salts serve as strong bases and also have synthetic value.

$$CH_3CH_2Br + 2Li \rightarrow \underset{\text{Ethyl lithium}}{CH_3CH_2Li} + LiBr$$

4. **Reaction with lead-sodium alloy.** Ethyl bromide reacts with lead sodium alloy in presence of dry ether to form *tetraethyl lead* (TEL). This compound prevents knocking in internal combustion engines.

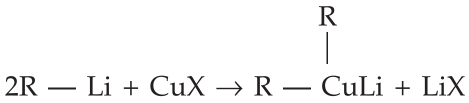
$$4CH_3CH_2Br + 4Pb(Na) \rightarrow (CH_3CH_2)_4Pb + 4NaBr + 3Pb$$

Coupling of Alkyl halides with Organometallic Compounds (Corey-House Reaction). This reaction is used to prepare alkanes with higher number of carbon atoms. In this method, lithium dialkyl copper R_2CuLi is treated with an alkyl halide. A general reaction is represented as follows:



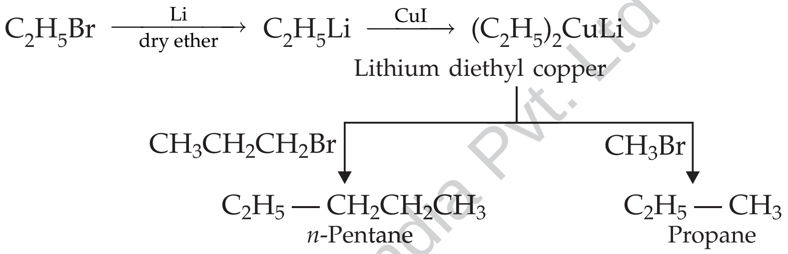
$$\underset{\substack{\text{Lithium}\\ \text{dialkyl copper}}}{R_2CuLi} + R'-X \rightarrow \underset{\text{Alkane}}{R-R'} + RCu + LiX$$

Lithium dialkyl copper needed for the reaction is prepared by the reaction of alkyl lithium with cuprous halide, CuX.



$$2R-Li + CuX \rightarrow R_2CuLi + LiX$$

To obtain good yield, the alkyl halide should preferrably be primary while the alkyl group in R_2CuLi may be primary, secondary or tertiary. Propane and *n*-pentane can be obtained as given below:



IV. Reduction

Haloalkanes can be reduced to alkanes by the following methods:

1. **Reaction with H_2/Ni.** Haloalkanes on reaction with hydrogen in the presence of nickel or palladium as catalyst give *alkanes*.

$$R-X + H_2 \xrightarrow[525\text{ K}]{\text{Ni}} R-H + HX$$

$$\underset{\substack{\text{Ethyl}\\ \text{bromide}}}{C_2H_5Br} + H_2 \xrightarrow[525\text{ K}]{\text{Ni}} \underset{\text{Ethane}}{C_2H_6} + HBr$$

2. Zn/HCl, Zn/NaOH, Na/C_2H_5OH and Sn/HCl at 430 K can also reduce *haloalkanes to alkanes*.

$$CH_3CH_2CH_2I + 2[HI] \xrightarrow[\text{Na / Alcohol}]{\text{Zn / HCl}} CH_3CH_2CH_3 + HI$$

V. Halogenation

Alkyl halides on treatment with halogens give *di*, *tri* and *tetra* halogen substituted products.

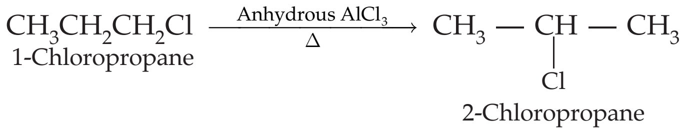
$$\underset{\text{Chloromethane}}{CH_3Cl} + Cl_2 \xrightarrow[520-670\text{ K}]{h\nu} \underset{\substack{\text{Dichloromethane}\\ \text{(Methylene dichloride)}}}{CH_2Cl_2} + HCl$$

$$\underset{\text{Dichloromethane}}{CH_2Cl_2} + Cl_2 \xrightarrow[520-670\text{ K}]{h\nu} \underset{\substack{\text{Trichloromethane}\\ \text{(Chloroform)}}}{CHCl_3} + HCl$$

$$\underset{\text{Chloroform}}{CHCl_3} + Cl_2 \xrightarrow[520-670\text{ K}]{h\nu} \underset{\substack{\text{Tetrachloromethane}\\\text{(Carbon tetrachloride)}}}{CCl_4} + HCl$$

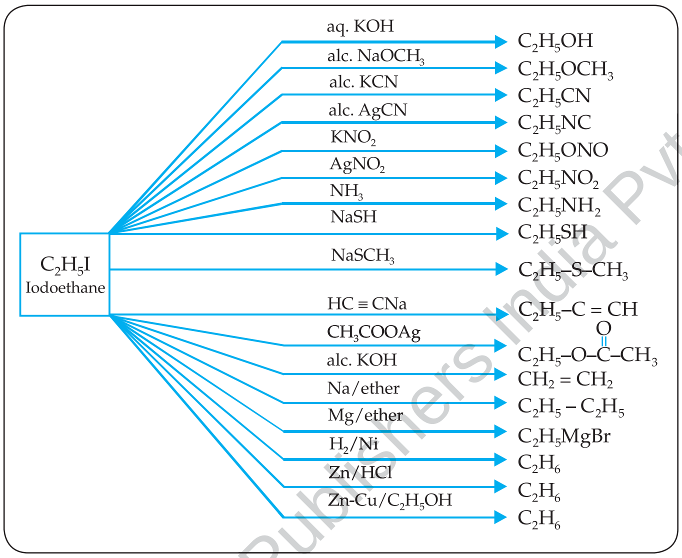
VI. Isomerisation

Alkanes on heating in the presence of a Lewis acid like anhydrous aluminium chloride undergo rearrangement to form *isomeric alkanes.* For example,



$$\underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} \xrightarrow[\Delta]{\text{Anhydrous }AlCl_3} \underset{\text{2-Chloropropane}}{CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3}$$

Taking the example of iodoethane, different reactions of alkyl halides are summarized below:



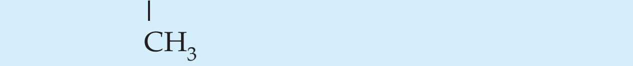
PROBLEMS FOR PRACTICE

1. Which metal and solvent are used in the preparation of Grignard's reagent from alkyl halides?

[**Ans.** Magnesium in dry ether.]

2. Name the following reactions:

(*i*) $C_2H_5I + NaOC_2H_5 \longrightarrow C_2H_5OC_2H_5 + NaI$



(*ii*) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CuLi}} + R'X \rightarrow CH_3R' + CH_3Cu + LiX$

(*iii*) $C_2H_5Br + (C_2H_5)_3N \longrightarrow [(C_2H_5)_4N] + Br^-$

[**Ans.** (*i*) Williamson synthesis; (*ii*) Corey House reaction; (*iii*) Hofmann ammonolysis]

3. Which isomer of C_4H_9Cl will have the lowest boiling point?

[**Ans.** $(CH_3)_3CCl$]

4. Which reagent is known as lucas reagent?

[**Ans.** HCl + anhy. $ZnCl_2$]

5. Arrange the following in order of increasing reactivity towards nucleophilic substitution (SN^1).
(*i*) $(CH_3)_2CHBr$ (*ii*) $(CH_3)_2CHI$ (*iii*) $(CH_3)_2CHCl$
[**Ans.** (*ii*) < (*i*) < (*iii*)]

6. Which product will be formed when optically active halide with formula C_4H_9Br is subjected to dehydrohalogenation? [**Ans.** But-2-ene]

7. Name the reagents used to convert:
(*i*) Haloalkanes to alkyl nitrite (*ii*) Ethyl chloride to ethoxy ethane
(*iii*) Bromoethane to ethanamine (*iv*) Bromopropane to nitropropane
[**Ans.** (*i*) $NaNO_2$; (*ii*) Sodium ethoxide; (*iii*) NH_3(alc.); (*iv*) $AgNO_2$]

8. Which isomer of C_4H_9Cl will have the lowest reactivity towards substitution reactions?
[**Ans.** $CH_3CH_2CH_2CH_2Cl$]

12.8 STEREOCHEMICAL ASPECT OF NUCLEOPHILIC SUBSTITUTION REACTIONS

Optical Isomerism: Ordinary light consists of waves of different wavelengths vibrating in all possible directions. Monochromatic light consists of a fixed wavelength vibrating in all possible directions. When a monochromatic light passes through a special type of prism called Nicol prism, vibrations are cut in one plane. Such a light is called *plane polarised light*.

Some substances have the ability to rotate the plane of polarised light either to right or to the left. These substances are called *optically active* and the property is called *optical activity*. The apparatus which measures the extent of rotation of polarised light is called *polarimeter* (Fig. 12.1).

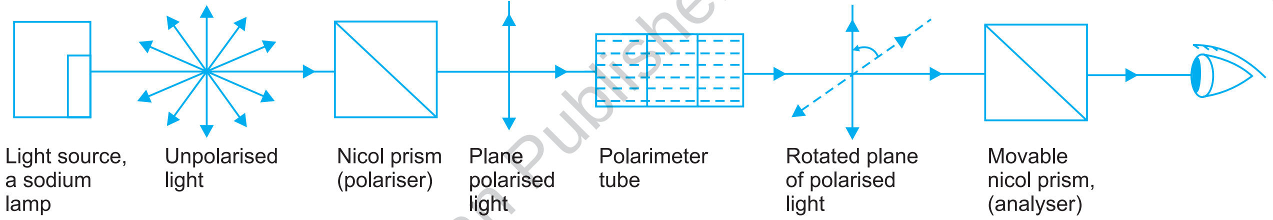


Fig. 12.1: *Demonstration of optical activity by a polarimeter*

If the substance rotates light to the right, *i.e.*, in the clockwise direction, it is called *dextrorotatory* and is represented by '*d*' or (+). If the light is rotated towards left, *i.e.*, in the anticlockwise direction the substance is said to be *laevorotatory* and is represented by '*l*' or (–) sign.

12.9 MOLECULAR ASYMMETRY, CHIRALITY AND ENANTIOMERS

The phenomenon of optical activity was discovered by Louis Pasteur in 1848. He observed that crystals with mirror images exist. He demonstrated that when a concentrated solution of sodium ammonium tartrate was allowed to crystallise, two types of crystals separate out. Each type of crystal when dissolved in water was found to rotate the plane of polarised light to the same extent but in the opposite direction. Later on, millions of molecules have been discovered which rotate the plane of polarised light.

In 1874, Van't Hoff and LeBel proposed that all the four valencies of carbon are directed towards the four corners of a regular tetrahedron, and if all the four substituents are different the resulting molecule will have no symmetry. Such a molecule is referred to as *asymmetric molecule* and asymmetry of the molecule is responsible for optical activity in such organic compounds.

A plane which divides an object into two symmetrical halves is said to be plane of symmetry. An object lacking a plane of symmetry is called *dissymmetric or chiral* (Fig. 12.2). A symmetric object is referred to as *achiral*. A dissymmetric or chiral object can be defined as one that is not superimposable on its mirror image. For example, a ball is an achiral object while human hand is a chiral object.

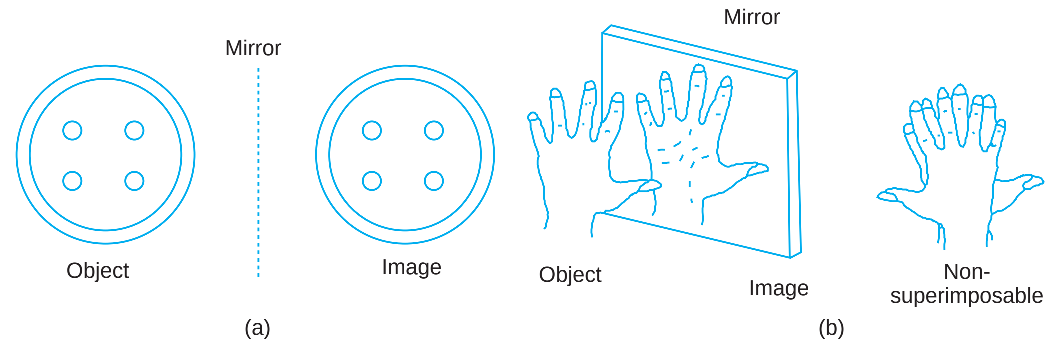
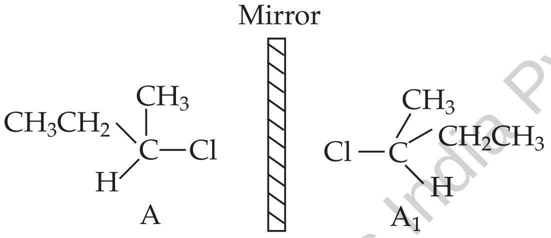
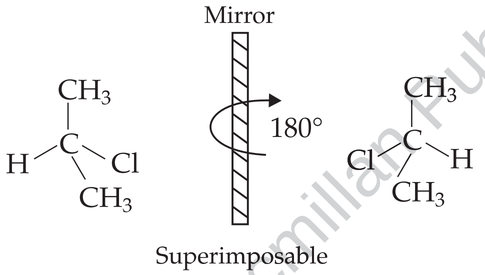


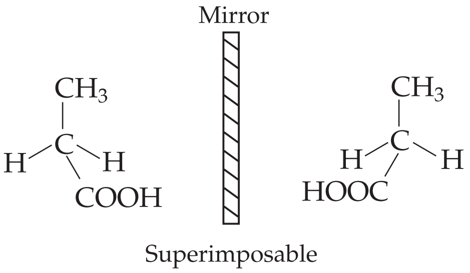
Fig. 12.2: *(a) Superimposable image of achiral object, (b) Non-superimposable image of chiral object*

Let us consider a simple molecule *i.e.* 2-chloro butane and its mirror image.



The object 2-chloro butane (A) and its mirror image A_1 are not superimposable. Lactic acid, $CH_3CH(OH)COOH$ is another example of chiral or dissymmetric molecule. On the other hand, 2-chloro propane and propanoic acid are the examples of achiral or symmetric molecules.

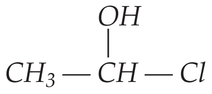




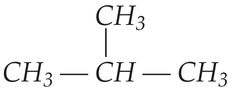
The necessary condition for a molecule to be chiral is not just the presence of an asymmetric carbon atom but the asymmetry of the molecule as a whole.

The stereoisomers related to each other as non-superimposable mirror images are called *enantiomers*. Enantiomers possess identical physical properties but they differ with respect to specific rotation. If one is dextrorotatory the other one will be laevorotatory. A 50 - 50% mixture of dextro and leavo rotation enantiomer will have no optical rotation. Such a mixture is called *racemic mixture* or *racemic modification*, represented by (*dl*) or (±). The process of conversion of an enantiomer into a racemic mixture is called *racemisation*.

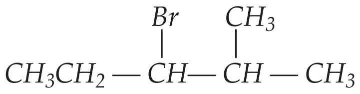
Example 1. *Which of the following will exhibit optical isomerism?*

(*a*) 

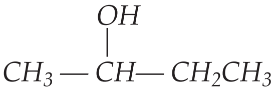
$$CH_3-\overset{\displaystyle OH}{\overset{|}{CH}}-Cl$$

(*b*) 

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

(*c*) 

$$CH_3CH_2-\overset{\displaystyle Br}{\overset{|}{CH}}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

(*d*) 

$$CH_3-\overset{\displaystyle OH}{\overset{|}{CH}}-CH_2CH_3$$

Solution. Compounds (*a*), (*c*) and (*d*) will show optical rotation as they contain asymmetric carbon atom or atoms and do not superimpose on their mirror images.

Compound (*b*) will not show optical isomerism as it can be superimposed on its mirror image.

Example 2. *Which of the following contain asymmetric carbon?*

(a) 2-Amino butane *(b) 3-Bromo pentane* *(c) 2-Methyl butane* *(d) sec-butyl chloride*

Solution. 3-Bromo pentane, sec- butyl chloride

Example 3. *Name the hydrocarbon with lowest possible molecular mass to show chirality.*

Solution. Penta – 2, 3 – diene

12.10 OPTICALLY ACTIVE MOLECULE

There are two ways to decide whether a given molecule is optically active or not. First, if a non-superimposable mirror image can be built, then it is optically active. The second way is to look at element of symmetry. There are two such elements:

1. ***Plane of Symmetry:*** The plane of symmetry, is a plane which divides an object in such a way that the part of it on one side of the plane is mirror image of that on the other side of the plane. For example, a ball has plane of symmetry which has two equal halves and human hand which has two unequal halves as shown in Fig. 12.3.
2. ***Centre of Symmetry:*** It is a point in the molecule through which if a line is drawn and extended to equal distance in the opposite direction it meets identical atoms or groups at its either end. For example, ethane has a centre of symmetry.

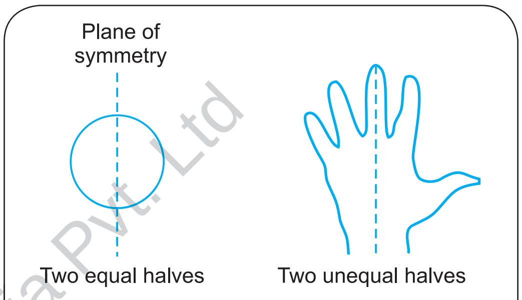
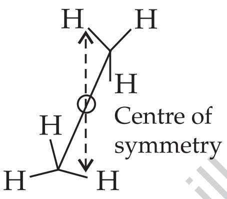
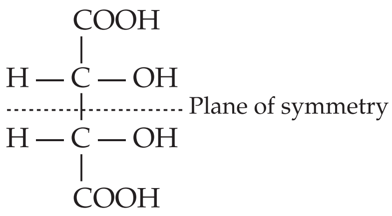


Fig. 12.3: *(a) The plane of symmetry of an achiral object, i.e., sphere. (b) Chirality of human hand since it is asymmetric.*





$$\begin{array}{c} \text{COOH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{COOH} \end{array}$$

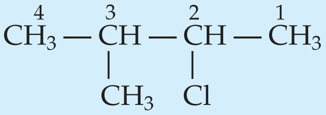
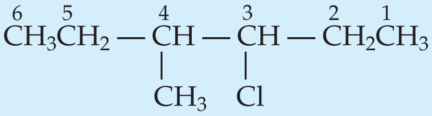
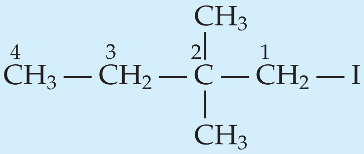
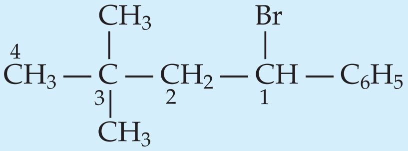
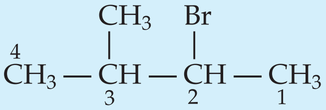
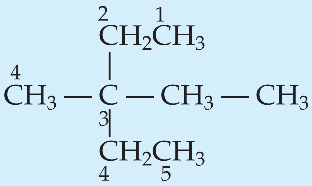
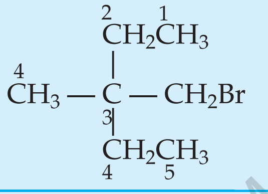
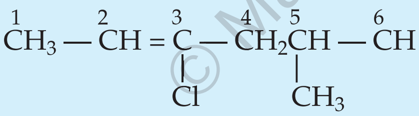
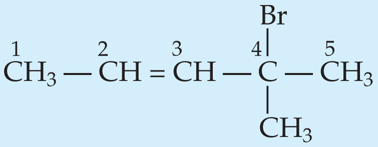
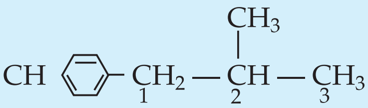
Plane of symmetry

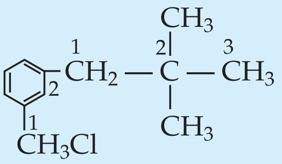
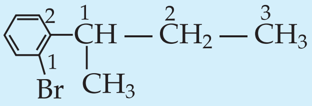
MISCELLANEOUS SOLVED QUESTIONS

1. *Name the following halides according to the IUPAC system and classify them as alkyl, allylic, benzylic (primary, secondary, tertiary) vinylic or aryl halides:*

(i)	$(CH_3)_2CHCH(Cl_3)_2CH_3$	*(ii)*	$CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$
(iii)	$CH_3CH_2C.(CH_3)_2CH_2I$	*(iv)*	$(CH_3)_3C.CH_2CH(Br)C_6H_5$
(v)	$CH_3CH(CH_3)CH(Br)CH_3$	*(vi)*	$CH_3C(Cl)(C_2H_5)CH_2CH_3$
(vii)	$CH_3C(C_2H_5)_2CH_2Br$	*(viii)*	$CH_3CH = C(Cl)CH_2CH(CH_3)_2$
(ix)	$CH_3CH = CHC(Br)(CH_3)_2$	*(x)*	$p\text{-}ClC_6H_4CH_2CH(CH_3)_2$
(xi)	$m\text{-}ClCH_2C_6H_4CH_2C(CH_3)_3$	*(xii)*	$o\text{-}BrC_6H_4CH(CH_3)CH_2CH_3$

Ans.

	Structure of the compounds	*Class*	*IUPAC name*
(*i*)	 $\overset{4}{CH_3}-\underset{CH_3}{\overset{3}{CH}}-\underset{Cl}{\overset{2}{CH}}-\overset{1}{CH_3}$	Alkyl halide (1°)	2-chloro-3-methylbutane
(*ii*)	 $\overset{6}{CH_3}\overset{5}{CH_2}-\underset{CH_3}{\overset{4}{CH}}-\underset{Cl}{\overset{3}{CH}}-\overset{2}{CH_2}\overset{1}{CH_3}$	Alkyl halide (2°)	3-chloro-4-methylhexane
(*iii*)	 $\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{1}{CH_2}-I$	Alkyl halide (1°)	1-iodo-2,2-dimethylbutane
(*iv*)	 $\overset{4}{CH_3}-\underset{\underset{CH_3}{3}}{\overset{CH_3}{C}}-\underset{2}{CH_2}-\underset{1}{\overset{Br}{CH}}-C_6H_5$	Benzylic halide (1°)	1-bromo-3,3-dimethyl-1-phenyl butane
(*v*)	 $\overset{4}{CH_3}-\underset{3}{\overset{CH_3}{CH}}-\underset{2}{\overset{Br}{CH}}-\underset{1}{CH_3}$	Alkyl halide (2°)	2-bromo-3-methylbutane
(*vi*)	 $\overset{4}{CH_3}-\underset{\underset{\underset{4\ \ 5}{CH_2CH_3}}{3}}{\overset{\overset{2\ \ 1}{CH_2CH_3}}{C}}-CH_3-CH_3$	Alkyl halide (3°)	3-chloro-3-methylpentane
(*vii*)	 $\overset{4}{CH_3}-\underset{\underset{\underset{4\ \ 5}{CH_2CH_3}}{3}}{\overset{\overset{2\ \ 1}{CH_2CH_3}}{C}}-CH_2Br$	Alkyl halide (1°)	3-bromomethyl-3-methylpentane
(*viii*)	 $\overset{1}{CH_3}-\overset{2}{CH}=\underset{Cl}{\overset{3}{C}}-\overset{4}{CH_2}\underset{CH_3}{\overset{5}{CH}}-\overset{6}{CH}$	Vinylic halide	3-chloro-5-methyl hex-2-ene
(*ix*)	 $\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\underset{CH_3}{\overset{Br}{\overset{4}{C}}}-\overset{5}{CH_3}$	Allylic halide (3°)	4-bromo-4-methyl pent-2-ene
(*x*)		Aryl halide	1-(4-chloro phenyl)-2-methylpropane

(*xi*)		Benzylic halide (1°)	1-chloromethyl-3-(2,2-dimethyl propyl) benzene
(*xii*)		Aryl halide	1-bromo-2-(1′-methyl propyl) benzene

2. *Write the structure of the following organic halogen compounds:*

(*i*) *2-chloro-3-methyl pentane*

(*ii*) *p-bromochloro benzene*

(*iii*) *1-chloro-4-ethyl cyclohexane*

(*iv*) *2-(2 chlorophenyl)-1-iodo octane*

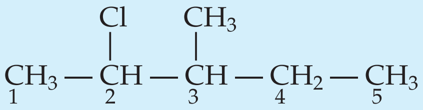
(*v*) *Perflurobenzene*

(*vi*) *4-tert-butyl-3-iodo heptane*

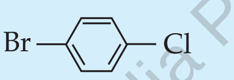
(*vii*) *1-bromo-4-sec butyl-2-methyl benzene*

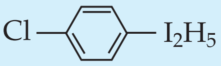
(*viii*) *1, 4-dibromobut-2-ene*

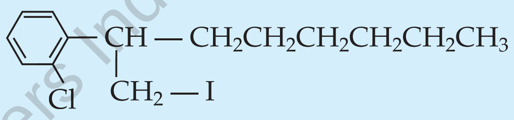
Ans.

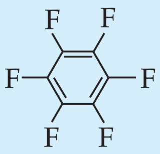
(*i*) 

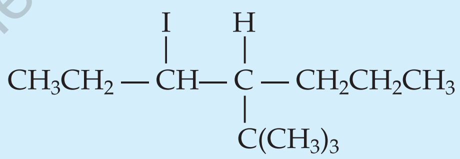
$$\underset{1}{CH_3}-\underset{2}{\overset{Cl}{CH}}-\underset{3}{\overset{CH_3}{CH}}-\underset{4}{CH_2}-\underset{5}{CH_3}$$

(*ii*) 

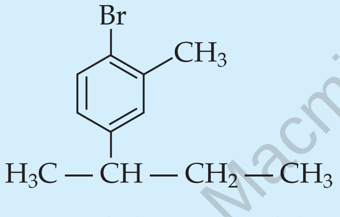
(*iii*) 

(*iv*) 

(*v*) 

(*vi*) 

$$CH_3CH_2-\overset{I}{CH}-\underset{C(CH_3)_3}{\overset{H}{C}}-CH_2CH_2CH_3$$

(*vii*) 

(*viii*) Br.CH_2 – CH = CH.CH_2Br

3. *What are ambident nucleophiles? Explain with example.*

Ans. Nucleophiles that can get attached from two sites are called ambident nucleophiles.

For example, :C ≡ N:

$$RX + KCN \longrightarrow RCN + KX$$
$$RX + AgCN \longrightarrow RNC + AgX$$

4. *Which compound in each of the following pairs will react faster in S_N2 reaction with OH^-?*

(*i*) *CH_3Br or CH_3I*

(*ii*) *$(CH_3)_3C.Cl$ or CH_3Cl*

(*iii*) *$CH_2 = CHBr$ or $CH_2 = CH.CH_2Br$*

Ans.

(*i*) CH_3I will react faster as bond dissociation energy of C – I bond is less than C – Br bond.

(*ii*) CH_3 – Cl will react faster as $(CH_3)_3C.Cl$ is highly sterically hindered.

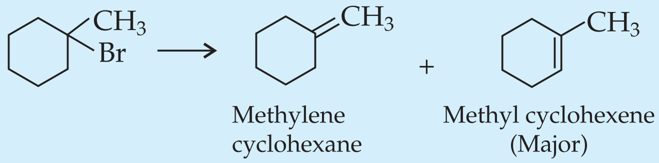
(*iii*) $CH_2 = CH - CH_2Br$ will react faster as C – Br bond in it has lesser bond dissociation energy. C – Br bond in $CH_2 = CH - Br$ has acquired somewhat double character.

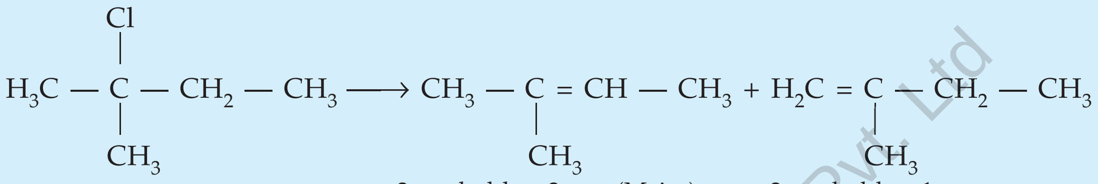
5. *Predict all the alkenes that would be formed by dehydrohalogenation of the following compounds and identify the major alkene*

(*i*) *1-bromo-1-methyl cyclohexane* (*ii*) *2-chloro-2-methyl butane 2-methyl but-l-ene*

(*iii*) *2,2,3-trimethyl-3-bromopentane*

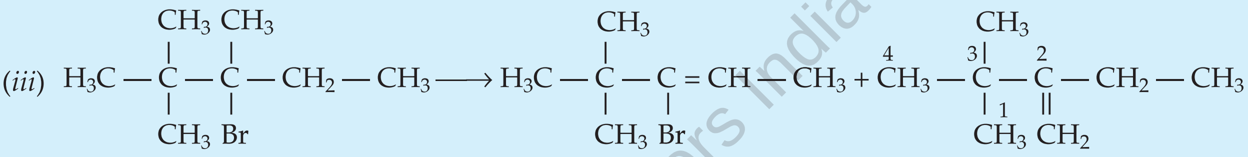
Ans.

(*i*) 

(*ii*) 

$$H_3C - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - CH_3 \longrightarrow CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{C} = CH - CH_3 + H_2C = \underset{\underset{\displaystyle CH_3}{|}}{C} - CH_2 - CH_3$$

2-methyl but-2-ene (Major) 2-methyl but-1-ene

(*iii*) 

$$H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} - CH_2 - CH_3 \longrightarrow H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - \underset{\underset{\displaystyle Br}{|}}{C} = CH - CH_3 + \overset{4}{CH_3} - \overset{\overset{\displaystyle CH_3}{3|}}{\underset{\underset{\displaystyle CH_3}{|\,1}}{C}} - \overset{2}{\underset{\underset{\displaystyle CH_2}{\|}}{C}} - CH_2 - CH_3$$

6. *How will you bring about the following conversions in not more than two steps?*

(*i*) *Ethanol to but-1-yne* (*ii*) *Ethene to bromoethene*

(*iii*) *Propene to 1-nitro propane* (*iv*) *Toluene to benzyl alcohol*

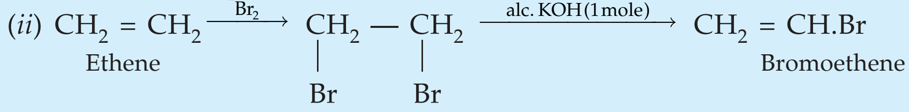
(*v*) *Propene to propyne* (*vi*) *Ethanol to ethyl fluoride*

(*vii*) *Bromomethane to propyne* (*viii*) *But-1-ene to but-2-ene*

(*ix*) *1-chloro butane to n-octane* (*x*) *Benzene to biphenyl*

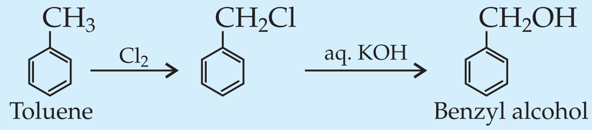
Ans.

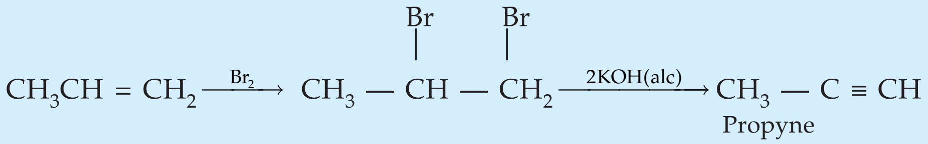
(*i*) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PBr_3} CH_3CH_2Br \xrightarrow{NaC\equiv CH} \underset{\text{But-1-yne}}{CH_3CH_2.C \equiv CH}$

(*ii*) 

$$\underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow{Br_2} \underset{\underset{\displaystyle Br}{|}}{CH_2} - \underset{\underset{\displaystyle Br}{|}}{CH_2} \xrightarrow{\text{alc. KOH (1 mole)}} \underset{\text{Bromoethene}}{CH_2 = CH.Br}$$

(*iii*) $\underset{\text{Propane}}{CH_3 - CH = CH_2} \xrightarrow[(C_6H_5CO)_2\,O_2]{HBr} CH_3 - CH_2CH_2Br \xrightarrow{AgNO_2} \underset{\text{1-nitropropane}}{CH_3CH_2CH_2NO_2}$

(*iv*) 

(v) 

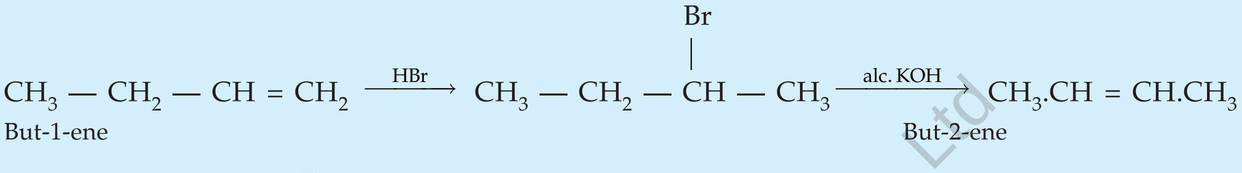
$$CH_3CH = CH_2 \xrightarrow{Br_2} CH_3 - \underset{}{\overset{Br}{\overset{|}{C}H}} - \overset{Br}{\overset{|}{C}H_2} \xrightarrow{2KOH(alc)} \underset{\text{Propyne}}{CH_3 - C \equiv CH}$$

(vi) $CH_3CH_2OH \xrightarrow{P/I_2} CH_3CH_2I \xrightarrow{AgF} CH_3CH_2F$

Ethanol

(vii) $CH_3Br \xrightarrow{Na-C\equiv CH} CH_3 - C \equiv CH$

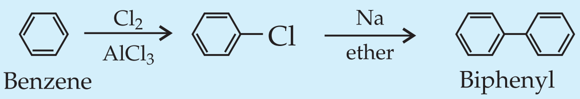
Bromo methane ... Propyne

(viii) 

$$\underset{\text{But-1-ene}}{CH_3 - CH_2 - CH = CH_2} \xrightarrow{HBr} CH_3 - CH_2 - \overset{Br}{\overset{|}{C}H} - CH_3 \xrightarrow{alc.\ KOH} \underset{\text{But-2-ene}}{CH_3.CH = CH.CH_3}$$

(ix) $CH_3CH_2CH_2CH_2Cl \xrightarrow[ether]{Na} CH_3(CH_2)_6.CH_3$

1-chlorobutane ... n-octane

(x) 

7. *Write the structure of the major organic product in each of the following reactions:*

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[heat]{acetone}$

(ii) $(CH_3)_3C.Br + KOH \xrightarrow[heat]{ethanol}$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{water}$

(iv) $CH_3CH_2CH_2Br + KCN \xrightarrow{eq.\ ethanol}$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

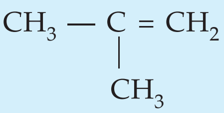
(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(vii) $CH_3.CH_2.CH = CH_2 + HBr \xrightarrow{Peroxide}$

(viii) $CH_3 - CH = C(CH_3)_2 + HBr \longrightarrow$

Ans.

(i) $CH_3CH_2CH_2I$

(ii) 

$$CH_3 - \underset{CH_3}{\underset{|}{C}} = CH_2$$

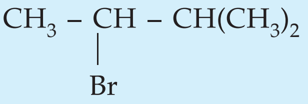
(iii) $CH_3CH(OH)CH_2CH_3$

(iv) $CH_3CH_2CH_2CN$

(v) $C_6H_5OC_2H_5$

(vi) $CH_3CH_2CH_2Cl$

(vii) $CH_3CH_2CH_2CH_2Br$

(viii) 

$$CH_3 - \underset{Br}{\underset{|}{C}H} - CH(CH_3)_2$$

QUICK SCAN (FOR REVISION)

1. Alcohols react with halogen acids to give alkyl halides. The order of reactivity of halogen acids is: HI > HBr > HCl
   The order of reactivity of alcohols is $3^\circ > 2^\circ > 1^\circ$
2. (*i*) $RCH = CH_2 + HX \rightarrow R - CHX - CH_3$
   (*Markownikov's rule*)

   (*ii*) $RCH = CH_2 + HBr \xrightarrow{\text{Peroxide}} R - CH_2 - CH_2 - Br$
   (*Peroxide effect*)

   (*iii*) Peroxide effect is observed only with HBr and not with HCl or HI.
3. $CH_4 + Cl_2 \xrightarrow{520\text{ K or } h\nu} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$
4. Ease of abstraction of hydrogens: $3^\circ > 2^\circ > 1^\circ$ but their relative rates of abstraction respectively are:
   (*i*) 5 : 3.8 : 1 by Cl_2 at 298 K and
   (*ii*) 1600 : 82 : 1 by Br_2 at 400 K.
5. Density changes in the order: RI > RBr > RCl > RF.
6. Gradation in boiling points:

   Boiling points
   (*i*) RI > RBr > RCl > RF
   (*ii*) $RCH_2X > R_2CHX > R_3CX$ ($1^\circ > 2^\circ > 3^\circ$)
   (*iii*) For isomeric alkyl halides, boiling points decrease with branching, *i.e.*

   $CH_3CH_2CH_2CH_2Cl > (CH_3)_2CHCH_2Cl > (CH_3)_3CCl$
7. Stability follows the order:
   (*i*) RF > RCl > RBr > RI
   (*ii*) $2R - I \xrightarrow{h\nu} R - R + I_2$
8. Alkyl halides undergo nucleophilic substitution reaction. These are of two types, SN^1 and SN^2.
9. **SN^1 reactions.** Rate ∝ [RX]. Reaction occurs in two steps involving carbocation intermediates. Such reactions are favoured by polar solvents and low concentration of nucleophiles. Order of reactivity of alkyl halides: $3^\circ > 2^\circ > 1^\circ$. During SN^1 reactions. *Optically active alkyl halides give racemic products.*
10. **SN^2 reactions.** Rate ∝ $[RX\ [Nu^-]$. It occurs in one-step through a transition state, favoured by solvents of low polarity and high concentration of nucleophiles. Order of reactivity of alkyl halides: $1^\circ > 2^\circ > 3^\circ$. During SN^2 reaction, attack of the nucleophile occurs from the back side resulting in inversion of configuration (Walden inversion). Optically active alkyl halides give optically active substitution products.
11. On hydrolysis with aqueous KOH or Ag_2O in boiling water, alkyl halides give alcohols.
12. On heating with an alcoholic solution of KOH, alkyl halides undergo dehydrohalogenation to form alkenes.
13. Reactivity of alkyl halides follows the order:

    RI > RBr > RCl > RF
14. Nucleophilicity of halide ions:

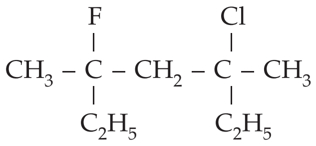
    $I^- > Br^- > Cl^- > F^-$
15. If an alkyl halide can undergo dehydrohalogenation in two different ways, then the more highly substituted alkene is the major product – **Saytzeff Rule**.
16. Vinyl halides being less reactive than alkyl halides undergo dehydrohalogenation with stronger bases such as $NaNH_2$ in liq. NH_3.
17. Ease of dehydrohalogenation of alkyl halides:

    $3^\circ > 2^\circ > 1^\circ$
18. Alkyl halides react with sodium or potassium alkoxides to form *ethers* – **Williamson's synthesis**.
19. Ethers are also formed when alkyl halides are heated with dry Ag_2O.
20. With sodium nitrite, alkyl halides give *alkyl nitrites* but with silver nitrite, they give *nitroalkanes*.
21. Alkyl halides react with an alcoholic solution of KCN to give *cyanides* as the major product while with AgCN, *isocyanides* is the major product.
22. Alkyl halides on heating with an ethanolic solution of NH_3 in a sealed tube at 373 K, yield a mixture of 1°, 2° and 3° amines along with quaternary ammonium salts – **Hofmann ammonolysis of alkyl halides**.
23. On heating with an ethanolic solution of silver salt of a fatty acid, alkyl halides give *esters*.
24. Alkyl iodides on reduction with HI and red P at 420 K give *alkanes*.
25. Alkyl halides react with metallic sodium in dry ether, to give alkanes containing even number of carbon atoms – **Wurtz reaction**. Alkanes containing odd number of carbon atoms can be prepared by **Corey-House reaction**.
26. On heating to 573 K or on heating in the presence of anhyd. $AlCl_3$, alkyl halides undergo isomerisation.
27. Alkyl halides react with Mg turnings in dry ether to form **Grignard reagents**.

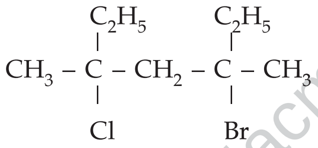
EXERCISES

Very Short Answer Type Questions

1. Which of the following is optically active? Butane-1-ol or 2-chlorobutane.
2. Under what conditions, 2-methylpropene can be converted into isobutyl bromide by hydrogen bromide?
3. Write the order in which formation of alcohol from haloalkane takes place.
4. Which alkyl halide has the highest density and why?
5. An alkyl halide having molecular formula C_4H_9Cl is optically active. What is its structure?
6. Arrange the following in order of the increasing boiling point:
   (*i*) $CH_3CH_2CH_2CH_2Br$ (*ii*) $(CH_3)_3CBr$
   (*iii*) $(CH_3)_2CHCH_2Br$.
7. Write the structure of the main product obtained by the action of conc. H_2SO_4 on 2-methyl-1-butanol.
8. Which is a better nucleophile, a bromide ion or an iodide ion?
9. Write the structural formula of 2-chloro-2-methyl propane.
10. Give the IUPAC names of the following compounds:

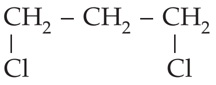
(*i*) 

$CH_3-\overset{F}{\underset{C_2H_5}{C}}-CH_2-\overset{Cl}{\underset{C_2H_5}{C}}-CH_3$

(*ii*) 

$CH_3-\overset{C_2H_5}{\underset{Cl}{C}}-CH_2-\overset{C_2H_5}{\underset{Br}{C}}-CH_3$

11. How will you obtain 1-bromopropane from propene?
12. Write a chemical reaction to illustrate Saytzeff's rule.
13. Which of the following compounds would show optical isomerism and why?
   (*i*) 1-Bromobutane
   (*ii*) 2-Bromobutane.
14. Arrange the following in order of their increasing reactivity in nucleophilic substitution reactions:
   CH_3F, CH_3I, CH_3Br and CH_3Cl.
15. Give the IUPAC name for

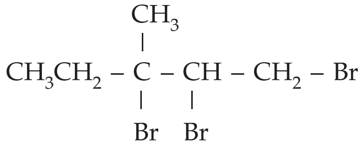


$\underset{Cl}{CH_2}-CH_2-\underset{Cl}{CH_2}$

16. Write the complete reactions involved in
   (*a*) Stephen's reaction (*b*) Wurtz reaction

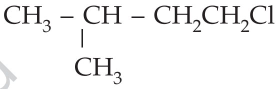
Short Answer Type Questions

1. Give the IUPAC names of the following:

(*i*) 

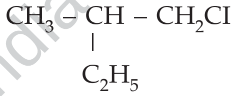
$CH_3CH_2-\overset{CH_3}{\underset{Br}{C}}-\underset{Br}{CH}-CH_2-Br$

   (*ii*) $C_6H_5CH_2CH_2Cl$
   (*iii*) $CH_3CHClCHBrCH_2CH_3$
2. Give the IUPAC names of the following:
   (*i*) $BrCH_2CH_2Br$ (*ii*)



$CH_3-\underset{CH_3}{CH}-CH_2CH_2Cl$

   (*iii*) $(CH_3)_3CCl$
   (*iv*) $CH_3CHClCH_2CH_3$
   (*v*) $ClCH_2CH_2Cl$
   (*vi*) $CH_3-CHBr-CH_2-CH_2Br$
   (*vii*)



$CH_3-\underset{C_2H_5}{CH}-CH_2Cl$

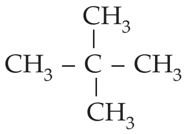
   (*viii*) $BrCH_2-CH_2-CH_2-CH_2Cl$
3. Write the possible structural isomers of C_4H_9Br. Point out optical isomers, if any.
4. Write the structural formulae and the IUPAC names for two optically active halides containing five carbon atoms each in their molecules.
   [**Ans.** 2-Bromopentane and 1-bromo-2-methyl butane]
5. Write the name and possible structures for the compounds having the molecular formula, C_3H_7Cl.
6. Why do alkyl halides show nucleophilic substitution reactions?
7. Rearrange the following in the order of increasing ease of dehydrohalogenation:
   CH_3CH_2Cl, $CH_3CHClCH_3$ and $CH_3CCl(CH_3)_2$. Give reasons.
8. How will you convert ethyl bromide into:
   (*i*) ethane (*ii*) butane
   (*iii*) propanoic acid and (*iv*) ethoxyethane?
9. What different products are obtained when ethyl bromide reacts separately with:
   (*i*) KNO_2 and $AgNO_2$?
   (*ii*) aqueous KOH and alcoholic KOH?
   (*iii*) KCN and AgCN?
10. How will you convert *n*-propyl bromide into isopropyl bromide?

11. Discuss briefly the mechanism of SN^1 and SN^2 reactions.
12. Give the names of the predominant products obtained when bromoethane is treated with:
    - (*i*) sodium metal in dry ether.
    - (*ii*) magnesium metal in dry ether followed by ethanol.
    - (*iii*) an aqueous alkali.
    - (*iv*) an alcoholic potassium hydroxide solution.
13. With the help of chemical equations, show how will you convert:
    - (*i*) 1-propanol to 2-bromopropane?
    - (*ii*) 2-bromopropane to 1-bromopropane?
14. What type of reactions are called nucleophilic substitution reactions? Give one example of this type of reaction.
15. How is ethyl iodide converted into (*i*) diethyl ether (*ii*) ethylene?
16. How are the following conversions achieved?
    - (*i*) 1-Propanol to 1-bromopropane.
    - (*ii*) 1-Iodopropane to propene
    - (*iii*) 2-Butanol to 2-chlorobutane
    - (*iv*) 1-Chloropropane to 1-propanol
    - (*v*) Bromomethane to methylmagnesium bromide
17. Haloalkanes react with potassium cyanide to give alkyl cyanides but give alkyl isocyanides with silver cyanide. Explain.

Long Answer Type Questions

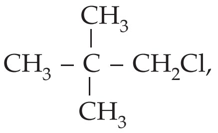
1. What are haloalkanes? How are they named according to the IUPAC system? How can haloalkanes prepared from (*i*) alcohols and (*ii*) alkanes?
2. Describe the synthetic reactions of alkyl halides, illustrating how a wide variety of organic compounds can be prepared from them.
3. Write any five chemical properties of alkyl halides to show their synthetic importance.
4. A compound A contains carbon and hydrogen only and has a molecular mass of 72. Its photochlorination gives a mixture containing only one monochloro and two dichloro hydrocarbons. Deduce the structure of the starting compound A and the chlorinated products.

[**Ans.**

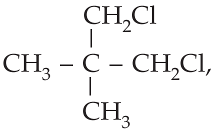


$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}$$

Chlorinated products are:

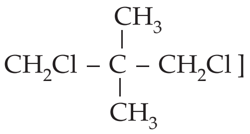


$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_2Cl, \\ | \\ CH_3 \end{array}$$



$$\begin{array}{c} CH_2Cl \\ | \\ CH_3-C-CH_2Cl, \\ | \\ CH_3 \end{array}$$

and



$$\begin{array}{c} CH_3 \\ | \\ CH_2Cl-C-CH_2Cl \\ | \\ CH_3 \end{array}$$

]

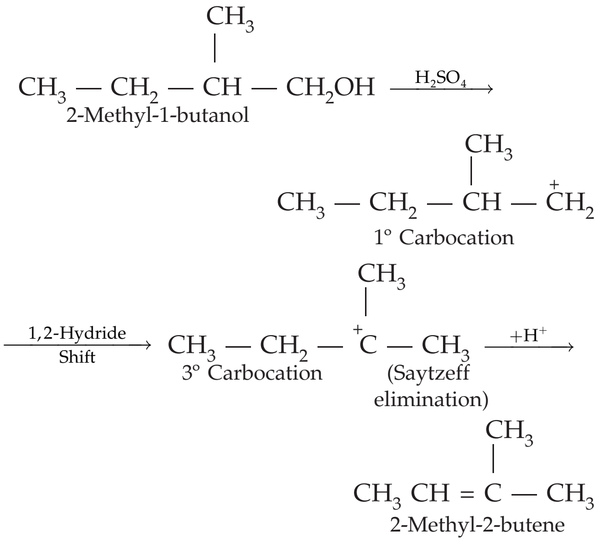
5. How will you convert:
    - (*i*) 1-bromopropane to 2-bromopropane?
    - (*ii*) Propanone to iodoform?
6. What happens when
    - (*i*) Chlorine is passed through ethyl alcohol
    - (*ii*) Ethyl chloride is reacted with sodium-ethoxide
    - (*iii*) Ethyl bromide is treated with aqueous solution of caustic soda
    - (*iv*) Ethyl bromide is treated with alcoholic KOH?
7. Complete the following equations:
    - (*i*) $C_2H_5Cl + KOH\,(aq) \rightarrow ...$
    - (*ii*) $... + HI \rightarrow CH_3CH_2I$
8. Complete and balance the following equation and name the organic compound formed.
   $C_2H_5NH_2 + CHCl_3 + 3KOH \rightarrow$
9. Give a brief account of the following with one example of each.
    - (*i*) Wurtz reaction (*ii*) Markownikov's rule
    - (*iii*) Kharasch effect
10. Identify the compounds, X, Y and Z in each of the following sequence of reactions:
    - (*i*) $C_2H_5Br \xrightarrow{\text{alc.KOH}} X \xrightarrow{Br_2} Y \xrightarrow{\text{alc.KOH}} Z$
    - (*ii*) $C_2H_4 \xrightarrow{HBr} X \xrightarrow{\text{aq.KOH}} Y \xrightarrow{I_2.NaOH} Z$
    - (*iii*) $C_2H_6 \xrightarrow{Cl_2} X \xrightarrow{KCN} Y \xrightarrow{H_2/Ni} Z$

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. 2-Chlorobutane since it contains one chiral carbon atom.
2. In the presence of peroxides.
3. C—I > C—Br > C—Cl > C—F
4. CH_3I; because of its smallest carbon content and heaviest halogen, *i.e.* I.
5. $CH_3–CHCl–CH_2CH_3$ (2-chlorobutane).
6. $(CH_3)_3CBr < (CH_3)_2CHCH_2Br < CH_3CH_2CH_2CH_2Br$.

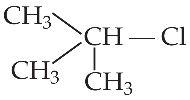
7. 2-Methyl-2-butene; the initially formed 1° carbocation rearranges to the more stable 3° carbocation by a 1, 2-hydride shift which then eliminates a proton to give 2-methyl-2-butene as the main product in accordance with the **Saytzeff's rule**.



$$\underset{\text{2-Methyl-1-butanol}}{CH_3-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2OH} \xrightarrow{H_2SO_4} \underset{1^\circ\text{ Carbocation}}{CH_3-CH_2-\overset{CH_3}{\overset{|}{C}H}-\overset{+}{C}H_2}$$

$$\xrightarrow[\text{Shift}]{\text{1,2-Hydride}} \underset{3^\circ\text{ Carbocation}}{CH_3-CH_2-\overset{CH_3}{\overset{|}{\overset{+}{C}}}-CH_3} \xrightarrow[\text{(Saytzeff elimination)}]{+H^+} \underset{\text{2-Methyl-2-butene}}{CH_3\,CH=\overset{CH_3}{\overset{|}{C}}-CH_3}$$

8. Iodide ion.

9. 

$$(CH_3)_2\underset{\underset{CH_3}{|}}{C}H-Cl$$

10. (*i*) 3-Chloro-5-fluoro 3, 5-dimethylheptane
    (*ii*) 3-Bromo-5-chloro-3, 5-dimethylheptane

11. With HBr in presence of peroxides.

12. $CH_3CHBrCH_2CH_3 \xrightarrow[\Delta]{\text{Alc.KOH}} \underset{80\%}{CH_3CH = CHCH_3} + \underset{20\%}{CH_3CH_2CH = CH_2}$

13. 2-Bromobutane because it contains a chiral carbon.

14. $CH_3F < CH_3Cl < CH_3Br < CH_3I$

15. 1, 3-Dichloropropane.

16. (*a*) Stephen's reaction:

$$CH_3CH_2CN \xrightarrow[HCl]{SnCl_2} CH_3CH_2CH = NH.HCl \xrightarrow[-NH_4Cl]{H_2O/H^+} CH_3CH_2CHO$$

(*b*) Wurtz reaction:

$$2RX + 2Na \xrightarrow{\text{ether}} R - R + 2NaX.$$

COMPETITION FILE

NUMERICAL PROBLEMS

Problem 1. *A chloro compound (A) showed the following properties:*

(*i*) *Decolourised bromine in* CCl_4.
(*ii*) *Absorbed hydrogen catalytically.*
(*iii*) *Gave precipitate with ammonical cuprous chloride.*

[**Ans.** $ClCH_2C \equiv CH$ (propargyl chloride or 3-chloropropyne)]

Problem 2. *n-Butane is produced by monobromination of ethane followed by Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g of n-butane, if the bromination takes place with 90 per cent yield and Wurtz reaction with 85 per cent yield.* [**Ans.** 5.53 litre]

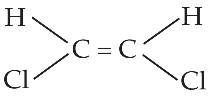
Problem 3. *An organic compound (X), on analysis gives 24.24% C and 4.04% H. Further, sodium extract of 1.0 g of (X) gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound (X) can be represented by two isomeric structures (Y) and (Z). (Y) on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while (Z) on similar treatment gives ethanal. Find out the molecular formula of (X) and give the structures of (Y) and (Z).*

[**Ans.** $X = C_2H_4Cl_2$
$Y = CH_2ClCH_2Cl$
$Z = CH_3CHCl_2$]

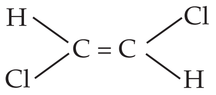
SUBJECTIVE PROBLEMS

Problem 1. *Write the structures of the possible isomers of dichloroethene.*

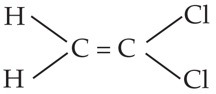
Ans.

(*i*) 

cis-1, 2-Dichloroethene
(μ > 0)

(*ii*) 

trans-1, 2-Dichloroethene
(μ = 0)

(*iii*) 

1, 1-Dichloroethene
(μ > 0)

Problem 2. *Write the structural formulae and IUPAC names for the different alkanes formed when a mixture of 1-bromopropane and 2-bromopropane is reacted with sodium in the presence of ether. What is the name of the reaction?*

Ans.

(*i*) $\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2 - Br} + 2Na + Br - CH_2CH_2CH_3$

$$\xrightarrow{\Delta} \underset{n\text{-Hexane}}{CH_3CH_2CH_2 - CH_2CH_2CH} + 2NaBr$$

(*ii*) $CH_3CH_2CH_2 - Br + 2Na + Br - CH(CH_3)_2 \xrightarrow{\Delta}$

1-Bromopropane 2-Bromopropane

$CH_3CH_2CH_2 - CH(CH_3)_2 + 2NaBr$

2-Methylpentane

(*iii*) $(CH_3)_2CH{-}Br + 2Na + Br - CH(CH_3)_3 \xrightarrow{\Delta}$

2-Bromopropane

$(CH_3)_2CH{-}CH(CH_3) + 2NaBr$

2, 3-Dimethylbutane

The reaction involved is Wurtz reaction.

Problem 3. *Give the IUPAC names of the following compounds:*

(*i*) $CH_3 — C\ (CH_3) — CH_2Cl$

(*ii*) $CH_3 — C\ (CH_3)_2 — Cl$

(*iii*) $CH_3CHClCHBrCH_2CH(CH_3)CH_2CH_2CH_3$

(*iv*) $(CH_3)_2CH - CHCl - CH_3$

Ans.

(*i*) 1-Chloro-2, 2-dimethyl-propane

(*ii*) 2-Choro-2-methyl-propane

(*iii*) 3-Bromo-2-chloro-5-methyloctane

(*iv*) 2-Chloro-3-methylbutane

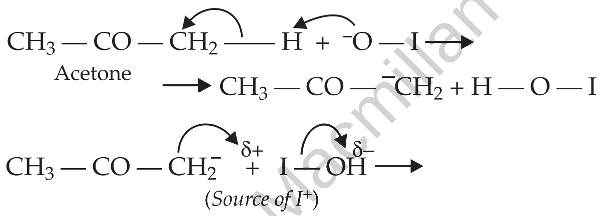
Problem 4. *Give reasons in one or two sentences for the following:*

(*i*) *Triiodomethane is obtained by the reaction of acetone with hypiodite but not with iodide ion. Give reasons.*

(*ii*) *Trichloromethane is stored in dark coloured bottles.*

Ans.

(*i*) To prepare triiodomethane from acetone, I ions is required which is supplied by IO^- but not I^- as shown by the following equations.



$CH_3 — CO — CH_2I + OH$

$CH_3COCH_2I \rightarrow CH_3COCHI_2 \rightarrow CH_3COCI_3 \rightarrow$
$CHI_3 + CH_3COO^-$

(*ii*) Trichloromethane is stored in coloured bottles to prevent oxidation of $CHCl_3$ to poisonous phosgene $(COCl_2)$ gas by atmospheric O_2 and light.

$$Cl_3C - H \xrightarrow{\frac{1}{2}O_2,\,h\nu} [Cl_3C - OH] \xrightarrow[-HCl]{} O = CCl_2$$

(Phosgene)

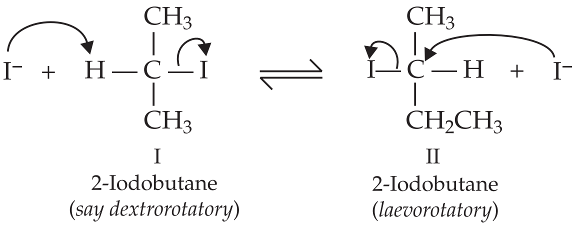
Problem 5. *Complete the following reactions:*

(*i*) Ethanol $\xrightarrow{I_2/NaOH}$ (*ii*) $CH_3COCH_3 \xrightarrow{\text{bleaching powder}}$

Ans. (*i*) CHI_3 (*ii*) $CHCl_3$

Problem 6. *Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain.*

Ans. Optically active 2-iodobutane on treatment with NaI in acetone undergoes inversion and racemization and hence, the product does not show optical activity as explained below:



I
2-Iodobutane
(*say dextrorotatory*)

II
2-Iodobutane
(*laevorotatory*)

When 2-iodobutane (I) is treated with I^- ion, it undergoes *Walden inversion* (SN^2 reaction) to 2-iodobutane (II) which is the enantiomer of I. Now 2-iodobutane (II) undergoes Walden inversion to give enantiomers I. As a result of these two Walden inversions, untimely a 50 : 50 mixture of the two enantiomers is obtained.

Problem 7. *Use Markownikov's rule to predict the products of the following reactions: (i) HCl with $CH_3CCl = CH_2$ (ii) HCl with $CH_3CH = C(CH_3)_2$*

Ans. The products of the reactions are: (*i*) $CH_3CCl_2CH_3$ (*ii*) $CH_3CH_2CCl(CH_3)_2$

Problem 8. *A compound is formed by the substitution of two chlorine atoms for two hydrogen atoms in propane. What is the number of structural isomers possible?*

Ans. Four, various isomers are as follows: 1, 1, 1, 2-; 1, 3- and 2, 2-dichloropropanes.

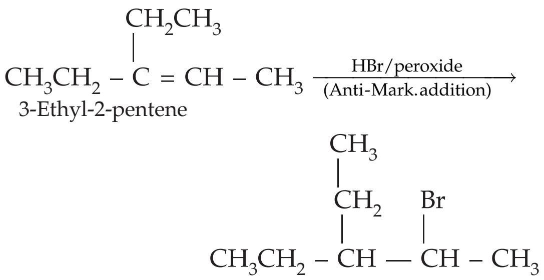
Problem 9. *Give the structure of the major organic products from 3-ethyl-2-pentane under each of the following conditions:*

(*a*) *HBr in the presence of peroxide.*

(*b*) *Br_2/H_2O*

(*c*) *$Hg(OAc)_2/H_2O$; $NaBH_4$*

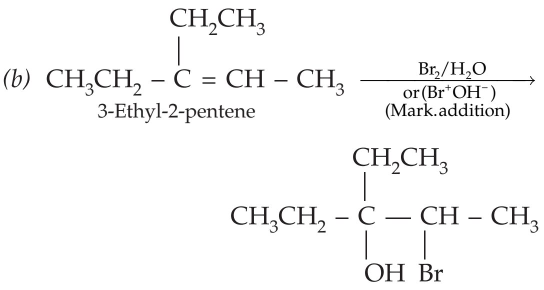
Ans. (*a*)



$$CH_3CH_2 - \overset{\overset{\displaystyle CH_2CH_3}{|}}{C} = CH - CH_3 \xrightarrow[\text{(Anti-Mark.addition)}]{\text{HBr/peroxide}} CH_3CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\overset{\displaystyle CH_2}{\overset{|}{CH}}} — \overset{\overset{\displaystyle Br}{|}}{CH} - CH_3$$

3-Ethyl-2-pentene

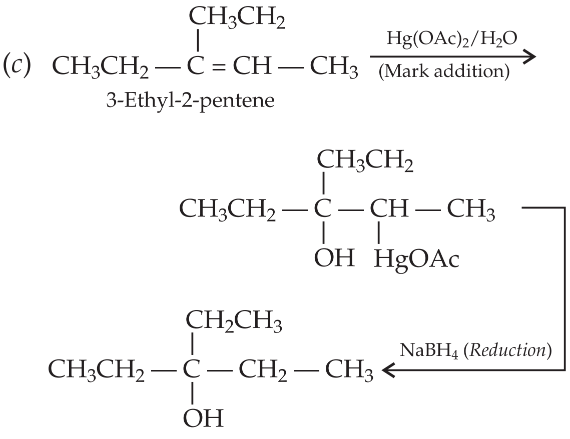
2-Bromo-3-ethylpentane



(b) $CH_3CH_2-\overset{CH_2CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow[\text{or}(Br^+OH^-)\ (\text{Mark.addition})]{Br_2/H_2O} CH_3CH_2-\overset{CH_2CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-\underset{Br}{\underset{|}{CH}}-CH_3$

3-Ethyl-2-pentene

2-Bromo-3-ethyl-3-pentanol

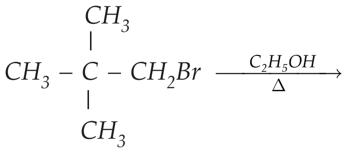


(c) $CH_3CH_2-\overset{CH_3CH_2}{\overset{|}{C}}=CH-CH_3 \xrightarrow[\text{(Mark addition)}]{Hg(OAc)_2/H_2O} CH_3CH_2-\overset{CH_3CH_2}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-\underset{HgOAc}{\underset{|}{CH}}-CH_3 \xrightarrow{NaBH_4\ (Reduction)} CH_3CH_2-\overset{CH_2CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_2-CH_3$

3-Ethyl-2-pentene

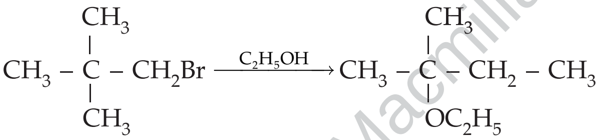
3-Ethyl-3-pentanol

Problem 10. *What would be the major product in the following reaction:*



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2Br \xrightarrow[\Delta]{C_2H_5OH}$

Ans. The reaction proceeds via SN mechanism with rearrangement of neopentyl carbocation to tert. pentyl carbocation.



$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2Br \xrightarrow{C_2H_5OH} CH_3-\overset{CH_3}{\overset{|}{\underset{OC_2H_5}{\underset{|}{C}}}}-CH_2-CH_3$

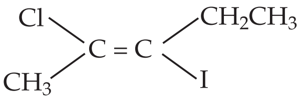
Ethyl tert pentyl ether

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

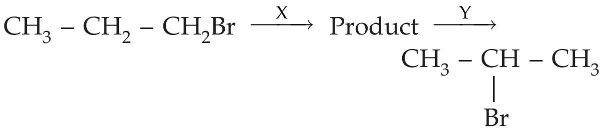
Choose the correct answer:

1. Substitution in chlorine takes place readily at higher temperature in
   (*a*) $CH_3CH = CH_2$ (*b*) $H_2C = CH_2$
   (*c*) $HC \equiv CH$ (*d*) None of these
2. IUPAC name for the compound



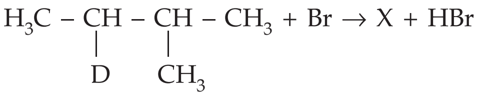
is

   (*a*) *Trans*-2-chloro-3-iodo-2-pentene
   (*b*) *Cis*-2-chloro-3-iodo-2-pentene
   (*c*) *Trans*-3-iodo-4-chloro-3-pentene
   (*d*) *Cis*-2-iodo-4-chloro-3-pentene
3. Identify Z in the reaction:
   $C_2H_5I \xrightarrow{\text{alc. KOH}} X \xrightarrow{Br_2} Y \xrightarrow{KCN} Z$
   (*a*) CH_3CH_2CN (*b*) $CNCH_2CH_2CN$
   (*c*) $BrCH_2CH_2CN$ (*d*) $Br\,CH = CHCN$
4. 1-Chlorobutane, on reaction with alcoholic potash gives
   (*a*) 1-Butene (*b*) 1-Butanol
   (*c*) 2-Butene (*d*) 2-Butanol
5. Which of the following will react with water?
   (*a*) $CHCl_3$ (*b*) Cl_3CCHO
   (*c*) CCl_4 (*d*) $ClCH_2CH_2Cl$
6. The order of reactivities of the following alkyl halides for a SN^2 reaction is
   (*a*) RF > RCl > RBr > RI
   (*b*) RF > RBr > RCl > RI
   (*c*) RCl > RBr > RF > RI
   (*d*) RI > RBr > RCl > RF
7. Which of the following has the highest nucleophilicity?
   (*a*) F^- (*b*) OH^-
   (*c*) CH_3^- (*d*) NH_2^-
8. An SN^2 reaction at an asymmetric carbon of a compound always gives
   (*a*) an enantiomer of the substrate
   (*b*) a product with opposite optical rotation
   (*c*) a mixture of diastereomers
   (*d*) a single stereoisomer
9. Identify the set of reagent/reaction conditions 'X' and 'Y' in the following set of transformations



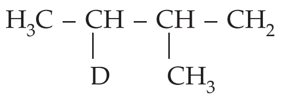
$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{Br}{\underset{|}{CH}}-CH_3$

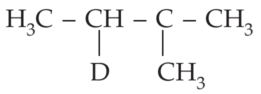
   (*a*) X = dilute aqueous NaOH, 20ºC; Y = HBr/acetic acid, 20ºC
   (*b*) X = conc. alcoholic NaOH, 80ºC; Y = $Br/CHCl_3$, 0ºC.
   (*c*) X = dil. aqueous NaOH, 20ºC; Y = $Br_2/CHCl_3$, 0ºC
   (*d*) X = conc. alcoholic NaOH, 80ºC; Y = $Br_2/CHCl_3$, 0ºC
10. Consider the following reaction:

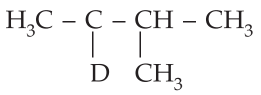


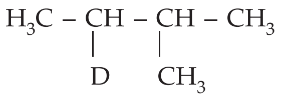
$H_3C-\underset{D}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3 + Br \rightarrow X + HBr$

Identify the structure of the major product 'X'

(*a*) 
$H_3C-\underset{D}{CH}-\underset{CH_3}{CH}-CH_2$

(*b*) 
$H_3C-\underset{D}{CH}-\underset{CH_3}{C}-CH_3$

(*c*) 
$H_3C-\underset{D}{C}-\underset{CH_3}{CH}-CH_3$

(*d*) 
$H_3C-\underset{D}{CH}-\underset{CH_3}{CH}-CH_3$

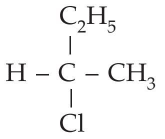
11. How many chiral compounds are possible on mono chlorination of 2-methyl butane?

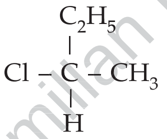
(*a*) 2	(*b*) 4
(*c*) 6	(*d*) 8

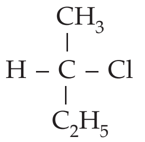
12. Which of the following will have a meso-isomer also?
    (*a*) 2-Chlorobutane (*b*) 2, 3-Dichlorobutane
    (*c*) 2, 3-Dichloropentane
    (*d*) 2-Hydroxypropanoic acid

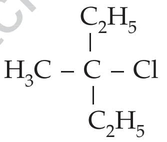
13. $CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$
    The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) *A* to *D* is
    [Nu^- = (*A*) PhO^-, (*B*) AcO^-, (*C*) HO^-, (*D*) CH_3O^-]
    (*a*) $D > C > A > B$ (*b*) $D > C > B > A$
    (*c*) $A > B > C > D$ (*d*) $B > D > C > A$

14. $CH_3 - CHCl - CH_2 - CH_3$ has a chiral centre. Which one of the following represents its R-configuration?

(*a*) 
$H-\overset{C_2H_5}{\underset{Cl}{C}}-CH_3$

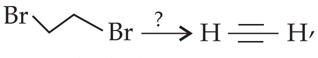
(*b*) 
$Cl-\overset{C_2H_5}{\underset{H}{C}}-CH_3$

(*c*) 
$H-\overset{CH_3}{\underset{C_2H_5}{C}}-Cl$

(*d*) 
$H_3C-\overset{C_2H_5}{\underset{C_2H_5}{C}}-Cl$

15. Which of the following is the correct order of decreasing S_N2 reactivity?
    (*a*) $R_2CHX > R_3CX > RCH_2X$
    (*b*) $RCHX > R_3CX > R_2CHX$
    (*c*) $RCH_2X > R_2CHX > R_3CX$
    (*d*) $R_3CX > R_2CHX > RCH_2X$.
    (X is a halogen)

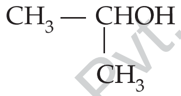
16. The reagent(s) for the following conversion



is/are
    (*a*) alcoholic KOH
    (*b*) alcoholic KOH followed by $NaNH_2$
    (*c*) aqueous KOH followed by $NaNH_2$
    (*d*) Zn/CH_3OH

17. Which one of the following is most reactive towards SN^1 reaction?
    (*a*) $C_6H_5CH(C_6H_5)Br$ (*b*) $C_6H_5CH(CH_3)Br$
    (*c*) $C_6H_5C(CH_3)(C_6H_5)Br$ (*d*) $C_6H_5CH_2Br$

18. The synthesis of 3–octyne is achieved by adding a bromoalkane into a mixture of sodium oxide and an alkyne. The bromoalkane and alkyne respectively are
    (*a*) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C \equiv CH$
    (*b*) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2CH_3$
    (*c*) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C \equiv CH$
    (*d*) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C \equiv CH$

19. The following compounds are given
    (*i*) CH_3CH_2OH (*ii*) CH_3COCH_3
    (*iii*) 
    $CH_3-\underset{CH_3}{CHOH}$
    (*iv*) CH_3OH.
    Which of the above compound(s) on being warmed with iodine solution and NaOH, will give iodoform?
    (*a*) (*i*), (*iii*) and (*iv*) (*b*) only (*ii*)
    (*c*) (*i*), (*ii*) and (*iii*) (*d*) (*i*) and (*ii*).

(B) Fill in the Blanks

Fill in the blank spaces:

1. Alkyl halides are insoluble in water because they do not form .... with water.
2. Carbon tetrachloride is used as a fire extinguisher since it is a .... liquid.
3. The boiling point of an alkyl halide is higher than that of the corresponding alkane because of ....
4. Small quantity of .... is added to chloroform to avoid oxidation of chloroform into phosgene.
5. Butane nitrile can be prepared by heating .... with alcoholic KCN.
6. 2, 2-Dichloropropane reacts with aq. KOH to yield .... as the main product.

(C) True/False Statements

Write T for true and F for false statements:

1. Iodide ion is a better nucleophile than bromide ion.
2. Carbon tetrachloride is inflammable.
3. Carbon tetrachloride burns in air when lighted to give phosgene.
4. 2, 3, 4-Trichloropentane has three asymmetric carbon atoms.
5. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markownikov's rule.

6. The formation of CH_3Cl by the gas phase ultraviolet irradiation of a mixture of CH_4 and Cl_2 involves free radical intermediate.
7. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2- methylpropane and 2-bromo-2-methylpropane in the ratio 9 : 1.

(D) Assertion-Reason Type Questions

In the following questions, two statements are given, one labelled as **Assertion A** and the other as **Reason R**. Examine the two statements carefully and mark the correct choice, (*a*), (*b*), (*c*) or (*d*) according to instructions below:

(*a*) If both A and R are correct and R is the correct explanation of A.

(*b*) If both A and R are correct but R is not the explanation of A.

(*c*) If A is correct but R is not correct.

(*d*) If A is not correct but R is correct.

1. **Assertion A** : Chloroalkanes are obtained by treating alcohols with HCl in the presence of anhydrous zinc chloride.
   Reason R : Anhdrous zinc chloride is a dehydrating agent.
2. **Assertion A** : Reactivity of halogen acids towards alcohols is in the order: HCl > HBr > HI.
   Reason R : Bond dissociation energy of HI is less than that of HBr which in turn is less than that of HCl.
3. **Assertion A** : It is not possible to prepare fluoro compounds by the fluorination of alkanes.
   Reason R : Iodination of alkanes is carried out in the presence of oxidising agents like HIO_3.
4. **Assertion A** : Order of reactivity of various alkyl halides in SN^2 mechanism is : 3° > 2° > 1°.
   Reason R : In case, the haloalkanes can eliminate hydrogen halide in two different ways, the preferred alkene is the one which has minimum alkylation.

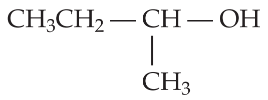
SOME ADDITIONAL QUESTIONS

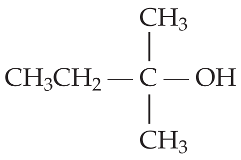
I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. The order of reactivity of following alcohols with halogen acids is _________.

(A) $CH_3CH_2 - CH_2 - OH$

(B)

$CH_3CH_2-\underset{\substack{|\\CH_3}}{CH}-OH$

(C)

$CH_3CH_2-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}-OH$

(*a*) (A) > (B) > (C) (*b*) (C) > (B) > (A)
(*c*) (B) > (A) > (C) (*d*) (A) > (C) > (B)

2. Which reagent will you use for the following reaction?

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

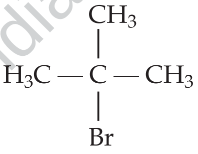
(*a*) Cl_2/*uv* light
(*b*) $NaCl + H_2SO_4$
(*c*) Cl_2 gas in dark
(*d*) Cl_2 gas in the presence of iron in dark

3. Arrange the following compounds in increasing order of their boiling points.

(*i*)

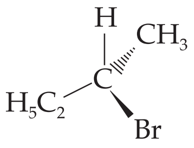
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH-CH_2Br$

(*ii*) $CH_3CH_2CH_2CH_2Br$

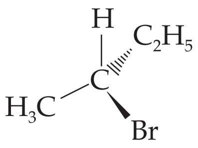
(*iii*)

$H_3C-\underset{\substack{|\\Br}}{\overset{\substack{CH_3\\|}}{C}}-CH_3$

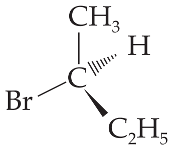
(*a*) (*ii*) < (*i*) < (*iii*) (*b*) (*i*) < (*ii*) < (*iii*)
(*c*) (*iii*) < (*i*) < (*ii*) (*d*) (*iii*) < (*ii*) < (*i*)

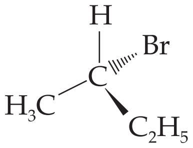
4. Which of the following structures is enantiomeric with the molecule (A) given below:

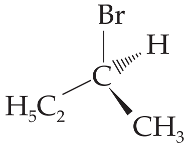


(A)

(*a*)


(*b*)


(*c*)


(*d*)


5. Which of the following is an example of *vic*-dihalide?

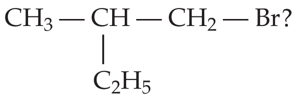
(*a*) Dichloromethane
(*b*) 1, 2-dichloroethane
(*c*) Ethylidene chloride
(*d*) Allyl chloride

6. Ethylidene chloride is a/an ________.
   (*a*) ***vic***-dihalide (*b*) ***gem***-dihalide
   (*c*) allylic halide (*d*) vinylic halide

7. A primary alkyl halide would prefer to undergo _______.
   (*a*) S_N1 reaction (*b*) S_N2 reaction
   (*c*) α-Elimination (*d*) Racemisation

8. Which of the following alkyl halides will undergo S_N1 reaction most readily?
   (*a*) $(CH_3)_3C—F$ (*b*) $(CH_3)_3C—Cl$
   (*c*) $(CH_3)_3C—Br$ (*d*) $(CH_3)_3C—I$

9. Which is the correct IUPAC name for



$CH_3—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—CH_2—Br$?

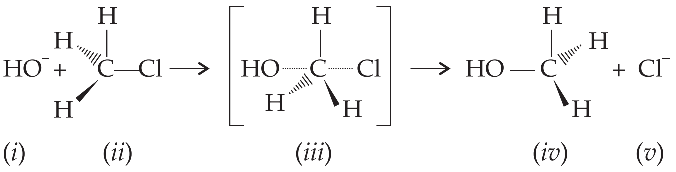
   (*a*) 1-Bromo-2-ethylpropane
   (*b*) 1-Bromo-2-ethyl-2-methylethane
   (*c*) 1-Bromo-2-methylbutane
   (*d*) 2-Methyl-1-bromobutane

10. What should be the correct IUPAC name for diethylbromomethane?
   (*a*) 1-Bromo-1, 1-diethylmethane
   (*b*) 3-Bromopentane
   (*c*) 1-Bromo-1-ethylpropane
   (*d*) 1-Bromopentane

11. Molecules whose mirror image is non superimposable over them are known as chiral. Which of the following molecules is chiral in nature?
   (*a*) 2-Bromobutane (*b*) 1-Bromobutane
   (*c*) 2-Bromopropane (*d*) 2-Bromopropan-2-ol

12. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows __________.
   (*a*) S_N1 mechanism
   (*b*) S_N2 mechanism
   (*c*) Any of the above two depending upon the temperature of reaction
   (*d*) Saytzeff rule

Consider the following reaction and answer the questions from 13 to 15.

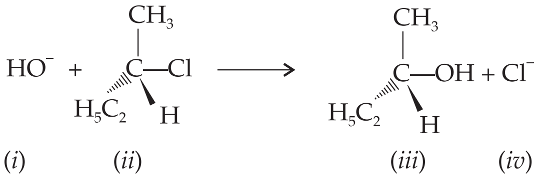


13. Which of the statements are correct about above reaction?
   (*a*) (*i*) and (*v*) both are nucleophiles.
   (*b*) In (*iii*) carbon atom is sp^3 hybridised.
   (*c*) In (*iii*) carbon atom is sp^2 hybridised.
   (*d*) (*i*) and (*v*) both are electrophiles.

14. Which of the following statements are correct about this reaction?
   (*a*) The given reaction follows SN^2 mechanism.
   (*b*) (*ii*) and (*iv*) have opposite configuration.
   (*c*) (*ii*) and (*iv*) have same configuration.
   (*d*) The given reaction follows SN^1 mechanism.

15. Which of the following statements are correct about the reaction intermediate?
   (*a*) Intermediate (*iii*) is unstable because in this carbon is attached to 5 atoms.
   (*b*) Intermediate (*iii*) is unstable because carbon atom is sp^2 hybridised.
   (*c*) Intermediate (*iii*) is stable because carbon atom is sp^3 hybridised.
   (*d*) Intermediate (*iii*) is less table than the reactant (*ii*).

Consider the following reaction and answer the questions from 16 to 21.



16. Which of the following statements are correct about the mechanism of this reaction?
   (*a*) A carbocation will be formed as an intermediate in the reaction.
   (*b*) OH^- will attach the substrate (*ii*) from one side and Cl^- will leave it simultaneously from the other side.
   (*c*) An unstable intermediate will be formed in which OH^- and Cl^- will be attached by weak bonds.
   (*d*) Reaction proceeds through S_N1 mechanism.

17. Which of the following statements are correct about the kinetics of this reaction?
   (*a*) The rate of reaction depends on the concentration of only (*ii*).
   (*b*) The rate of reaction depends on the concentration of both (*i*) and (*ii*).

(*c*) Molecularity of reaction is one.
(*d*) Molecularity of reaction is two.

18. Haloalkanes contain halogen atom(s) attached to the *sp*^{3} hybridised carbon atom of an alkyl group. Identify haloalkane from the following compounds.
    (*a*) 2-Bromopentane
    (*b*) Vinyl chloride (chloroethene)
    (*c*) 2-chloroacetophenone
    (*d*) Trichloromethane

19. Ethylene chloride and ethylidene chloride are isomers. Identify the correct statements.
    (*a*) Both the compounds form same product on treatment with alcoholic KOH.
    (*b*) Both the compounds form same product on treatment with aq. NaOH.
    (*c*) Both the compounds form same product on reduction.
    (*d*) Both the compounds are optically active.

20. Which of the following compounds are ***gem***-dihalides?
    (*a*) Ethylidene chloride (*b*) Ethylene dichloride
    (*c*) Methylene chloride (*d*) Benzyl chloride

21. Which of the following are secondary bromides?
    (*a*) $(CH_3)_2CHBr$ (*b*) $(CH_3)_3CCH_2Br$
    (*c*) $CH_3CH(Br)CH_2CH_3$ (*d*) $(CH_3)_2CBrCH_2CH_3$

II. Assertion-Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

(*i*) Assertion and reason both are correct and reason is correct explanation of assertion.
(*ii*) Assertion and reason both are wrong statements.
(*iii*) Assertion is correct but reason is wrong statement.
(*iv*) Assertion is wrong but reason is correct statement.
(*v*) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

1. **Assertion** : The boiling points of alkyl halides decrease in the order:

   RI > RBr > RCl > RF

   Reason : The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

2. **Assertion** : KCN reacts with methyl chloride to give methyl isocyanide.

   Reason : CN^- is an ambident nucleophile.

3. **Assertion** : *tert*-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

   Reason : In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

III. Short Answer Type Questions

1. Why is the solubility of haloalkanes in water very low?
2. Compound ‘A’ with molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound ‘A’ only. When another optically active isomer ‘B’ of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.
   (*i*) Write down the structural formula of both compounds ‘A’ and ‘B’.
   (*ii*) Out of these two compounds, which one will be converted to the product with inverted configuration.
3. Write the structures and names of the compounds formed when compound ‘A’ with molecular formula, C_7H_8 is treated with Cl_2 in presence of $FeCl_3$.
4. Write down the structure and IUPAC name for neo-pentylbromide.
5. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloro derivative and two dichloro derivatives on photochlorination. Give the structure of the hydrocarbon.

IV. Long Answer Type Questions

1. Some alkylhalides undergo substitution reaction whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.
2. Some halogen containing compounds are useful in daily life. Some compounds of this class are responsible for exposure of flora and fauna to more and more of UV light which causes destruction to a great extent. Name the class of these halocompounds. In your opinion, what should be done to minimise harmful effects of these compounds.

ANSWERS

(A) Multiple Choice Questions

1. (*a*) 2. (*a*) 3. (*b*) 4. (*a*) 5. (*b*) and (*d*) 6. (*d*) 7. (*c*) 8. (*d*)
9. (*b*) 10. (*b*) 11. (*b*) 12. (*b*) 13. (*a*) 14. (*b*) 15. (*c*) 16. (*b*)
17. (*c*) 18. (*d*) 19. (*c*)

(B) Fill in the Blanks

1. hydrogen bonds 2. non-inflammable 3. dipole-dipole interactions
4. ethyl alcohol 5. *n*-propyl chloride 6. propanone

(C) True/False Statements

1. T 2. F 3. F 4. F 5. T 6. T 7. F

(D) Assertion-Reason Type Questions

1. (*a*) 2. (*d*) 3. (*b*) 4. (*c*)

Some Additional Questions

I. Multiple Choice Questions

1. (*b*) 2. (*a*) 3. (*c*) 4. (*a*) 5. (*b*) 6. (*b*) 7. (*b*)
8. (*d*) 9. (*c*) 10. (*b*) 11. (*a*) 12. (*a*) 13. (*a*), (*c*) 14. (*a*), (*b*)
15. (*a*), (*d*) 16. (*a*), (*d*) 17. (*a*), (*c*) 18. (*a*), (*d*) 19. (*a*), (*d*) 20. (*a*), (*c*) 21. (*a*), (*c*)

II. Assertion-Reason Type Questions

1. (*v*) 2. (*iv*) 3. (*i*)

13

CHAPTER

Alcohols

LEARNING OBJECTIVES

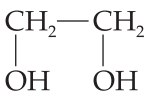
- List the IUPAC rules to nomenclature simple alcohols.
- Classify alcohols as primary alcohol, secondary alcohol or tertiary alcohol and name them accordingly.
- Explain the general methods of preparation of alcohols.
- Analyze the structures of alcohols.
- Discuss the physical properties of alcohols.
- Discuss the chemical properties of alcohols.

13.1 INTRODUCTION

Alcohols are compounds, containing-OH (alcoholic) groups attached to an alkyl group in the molecule. They are classified as *mono*, *di* and *tri* hydric alcohols accordingly as one, two or three –OH groups are present in the molecule. Some examples of *mono*, *di* and *tri* hydric alcohols are given below:

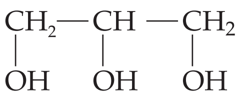
CH_3CH_2OH

Ethanol or Ethyl alcohol
(*Monohydric*)



$$\begin{array}{cc} CH_2 - & CH_2 \\ | & | \\ OH & OH \end{array}$$

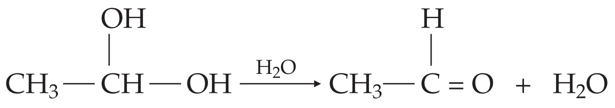
Ethane-1, 2-diol or Ethylene glycol
(*Dihydric*)



$$\begin{array}{ccc} CH_2 - & CH - & CH_2 \\ | & | & | \\ OH & OH & OH \end{array}$$

Propane-1, 2, 3-triol or Glycerol
(*Trihydric*)

It may be noted that alcohols containing more than one –OH group linked to the same carbon atom are highly unstable and lose water to form more stable aldehydes or ketones.



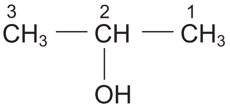
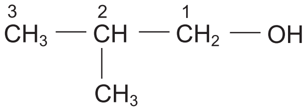
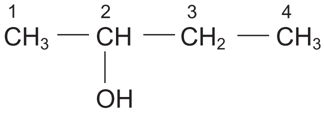
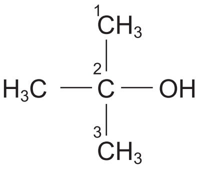
$$CH_3 - \overset{\overset{\displaystyle OH}{|}}{C}H - OH \xrightarrow{H_2O} CH_3 - \overset{\overset{\displaystyle H}{|}}{C} = O + H_2O$$

Unstable   Ethanal

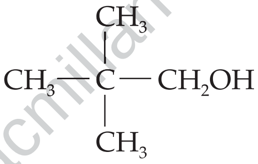
13.2 NOMENCLATURE OF ALCOHOLS

Monohydric Alcohols: In the common system of nomenclature, alcohols are named as *alkyl alcohols.* In IUPAC system, the names of alcohols are derived from corresponding alkanes by replacing *'e'* of alkanes by *'ol'*. The IUPAC names of alcohols are given in the Table 13.1. Position of the alcoholic group is indicated by a numeral.

Table 13.1

Formula	Common Name	IUPAC Name
CH_3OH	Methyl alcohol	Methanol
CH_3-CH_2-OH	Ethyl alcohol	Ethanol
$\overset{3}{CH_3}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$	*n*-Propyl alcohol	Propan-1-ol
 $\overset{3}{CH_3}-\underset{\displaystyle OH}{\overset{2}{CH}}-\overset{1}{CH_3}$	*iso*-Propyl alcohol	Propan-2-ol
$\overset{4}{CH_3}-\overset{3}{CH_2}-\overset{2}{CH_2}-\overset{1}{CH_2}-OH$	*n*-Butyl alcohol	Butan-1-ol
 $\overset{3}{CH_3}-\underset{\displaystyle CH_3}{\overset{2}{CH}}-\overset{1}{CH_2}-OH$	*iso*-Butyl alcohol	2-Methylpropan-1-ol
 $\overset{1}{CH_3}-\underset{\displaystyle OH}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_3}$	*sec*-Butyl alcohol	Butan-2-ol
 $H_3C-\underset{\displaystyle \overset{3}{CH_3}}{\overset{\displaystyle \overset{1}{CH_3}}{\overset{2}{C}}}-OH$	*tert*-Butyl alcohol	2-Methylpropan-2-ol

Some more examples of alcohols are given below:

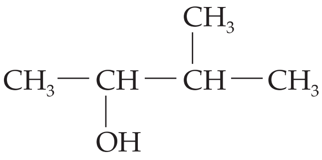


$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_2OH$$

2, 2-Dimethylpropan-1-ol
(*Common name* Neo-pentyl alcohol)

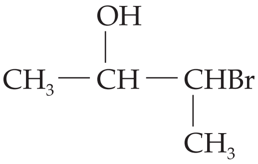
$$HC\equiv C-CH_2-OH$$

2 - Propyn-l-ol
(*Common name* Propargyl alcohol)



$$CH_3-\underset{\displaystyle OH}{CH}-\overset{\displaystyle CH_3}{CH}-CH_3$$

3-Methylbutan-2-ol



$$CH_3-\overset{\displaystyle OH}{CH}-\underset{\displaystyle CH_3}{CHBr}$$

3-Bromobutan-2-ol

Dihydric Alcohols: In IUPAC system, nomenclature of dihydric alcohols are named as *alkanediols.* For example,

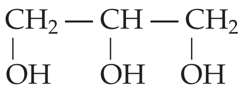
$$HO-CH_2-CH_2-OH$$

1, 2-Ethanediol

$$HO-CH_2-CH_2-CH_2-OH$$

1, 3-Propanediol

Trihydric Alcohols: In IUPAC system, nomenclature of trihydric alcohols are named as *alkanetriols*. For example,



$$\underset{\mathrm{OH}}{\mathrm{CH_2}}-\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{OH}}{\mathrm{CH_2}}$$

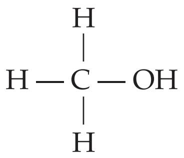
Propane-1, 2, 3-triol (Glycerol)

13.3 PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

Monohydric alcohols are classified as under:

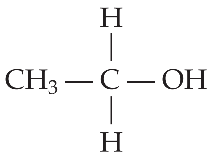
(*a*) **Primary (1°) alcohols** *are those alcohols which have just one (or none) alkyl group linked to the carbon attached directly to hydroxyl group*. They have the general formula: $R-CH_2-OH$

For example,



$$\mathrm{H}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH}$$

Methyl alcohol

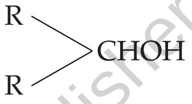


$$\mathrm{CH_3}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{OH}$$

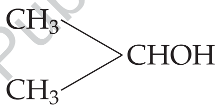
Ethyl alcohol

Therefore, primary alcoholic group is $-CH_2OH$.

(*b*) **Secondary (2°) alcohols** *are those alcohols which have two alkyl groups linked to the carbon attached directly to hydroxyl group*. They have the general formula:



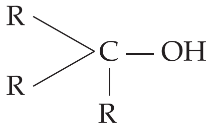
For example,



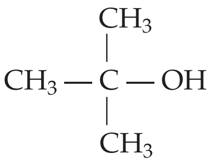
Iso-propyl alcohol

Therefore, secondary alcoholic group is > CHOH.

(*c*) **Tertiary (3°) alcohols** *are those alcohols which have three alkyl groups linked to the carbon attached directly to hydroxyl group*. They have the general formula:



For example,



$$\mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{OH}$$

tert-Butyl alcohol

Therefore, tertiary alcoholic group is $\geq$C — OH.

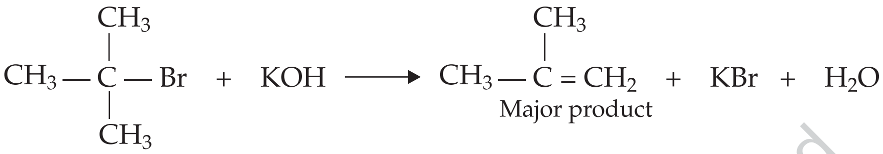
13.4 GENERAL METHODS OF PREPARATION OF ALCOHOLS

General methods of preparation of alcohols are given as under:

1. **By the Hydrolysis of Haloalkanes:** Haloalkanes on boiling with aqueous solution of an alkali hydroxide or moist silver oxide give alcohols.

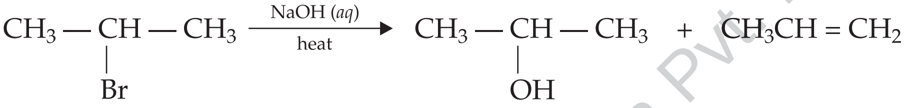
$$RX + KOH(aq) \longrightarrow ROH + KX$$
$$C_2H_5Br + KOH(aq) \longrightarrow C_2H_5OH + KBr$$

Primary alkyl halides give good yield of alcohols. But, tertiary alkyl halides yield mainly alkene due to dehydrohalogenation.



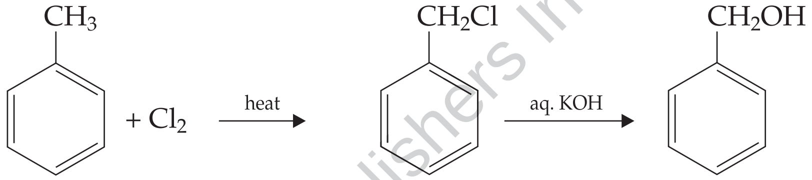
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + KOH \longrightarrow \underset{\text{Major product}}{CH_3-\overset{CH_3}{C}=CH_2} + KBr + H_2O$$

Secondary alkyl halides show an intermediate behaviour and give a mixture of alcohol and alkene.



$$CH_3-\underset{Br}{CH}-CH_3 \xrightarrow[\text{heat}]{NaOH\,(aq)} CH_3-\underset{OH}{CH}-CH_3 + CH_3CH=CH_2$$

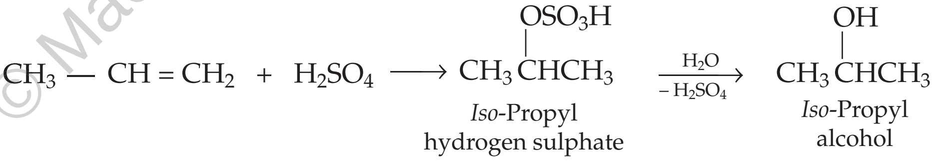
Aromatic alcohols can be obtained by the following sequence of reactions:



Toluene Benzyl chloride Benzyl alcohol

2. **Hydration of Alkenes:** Addition of H_2SO_4 to alkenes furnishes alkyl hydrogen sulphate which on hydrolysis with hot water gives alcohol. For example,

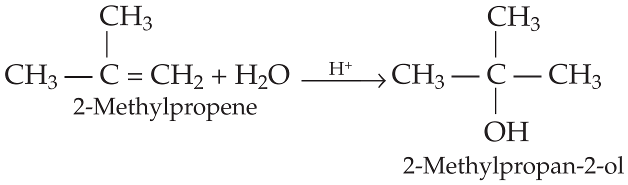
$$\underset{\text{Ethane}}{CH_2=CH_2} + H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2HSO_4} \xrightarrow[-H_2SO_4]{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH}$$



$$CH_3-CH=CH_2 + H_2SO_4 \longrightarrow \underset{\substack{\textit{Iso}\text{-Propyl}\\ \text{hydrogen sulphate}}}{CH_3\overset{OSO_3H}{C}HCH_3} \xrightarrow[-H_2SO_4]{H_2O} \underset{\substack{\textit{Iso}\text{-Propyl}\\ \text{alcohol}}}{CH_3\overset{OH}{C}HCH_3}$$

Addition takes place on unsymmetrical alkenes in accordance with Markownikov's rule.

Some reactive alkenes undergo direct hydration in the presence of mineral acids which act as catalysts.



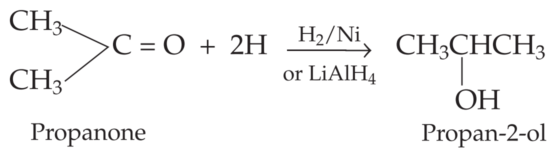
$$\underset{\text{2-Methylpropene}}{CH_3-\overset{CH_3}{C}=CH_2} + H_2O \xrightarrow{H^+} \underset{\text{2-Methylpropan-2-ol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3}$$

This method is widely used for the manufacture of alcohols, as alkenes are readily obtained by the cracking of petroleum.

3. From Aldehydes and Ketones

(*a*) Reduction. Aldehydes and Ketones on reduction give primary alcohols and secondary alcohols respectively. $LiAlH_4$, $NaBH_4$, Na/C_2H_5OH or H_2 with Ni, Pt or Pd are used as catalysts.

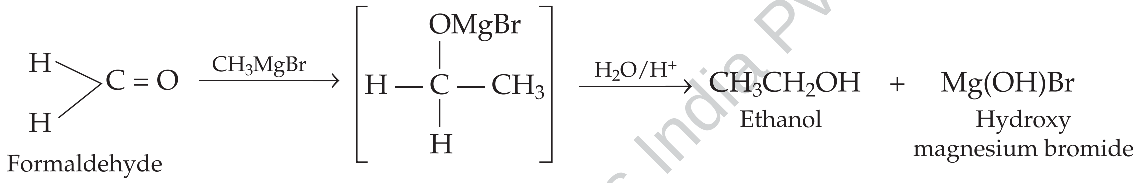
$$\underset{\text{Ethanal}}{CH_3CHO} + 2H \xrightarrow[\text{or } LiAlH_4]{H_2/Ni} \underset{\text{Ethanol}}{CH_3CH_2OH}$$



Propanone

Propan-2-ol

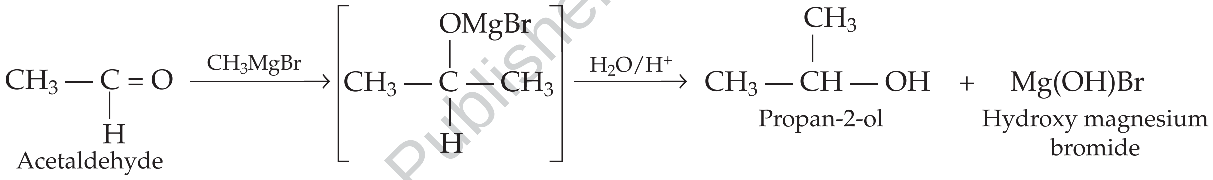
(*b*) Using Grignard reagent. Grignard reagent reacts with aldehydes and ketones to form products which decompose with dil. HCl or dil. H_2SO_4 to give primary, secondary and tertiary alcohols. Formaldehyde gives primary alcohol whereas all other aldehydes give secondary alcohols. Tertiary alcohols are obtained from ketones.



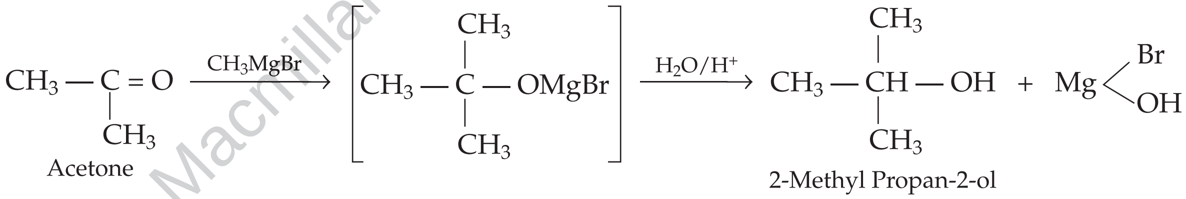
Formaldehyde

Ethanol

Hydroxy magnesium bromide



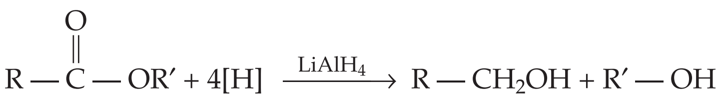
$$\underset{\text{Acetaldehyde}}{CH_3-\underset{\underset{H}{|}}{C}=O} \xrightarrow{CH_3MgBr} \left[CH_3-\overset{\overset{OMgBr}{|}}{\underset{\underset{H}{|}}{C}}-CH_3\right] \xrightarrow{H_2O/H^+} \underset{\text{Propan-2-ol}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-OH} + \underset{\text{Hydroxy magnesium bromide}}{Mg(OH)Br}$$



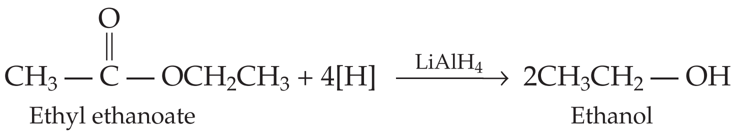
$$\underset{\text{Acetone}}{CH_3-\underset{\underset{CH_3}{|}}{C}=O} \xrightarrow{CH_3MgBr} \left[CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OMgBr\right] \xrightarrow{H_2O/H^+} \underset{\text{2-Methyl Propan-2-ol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{CH}}-OH} + Mg\begin{matrix}Br\\OH\end{matrix}$$

4. From Esters

(*a*) By reduction. $LiAlH_4$ or Na/C_2H_5OH reduce esters to primary alcohols.

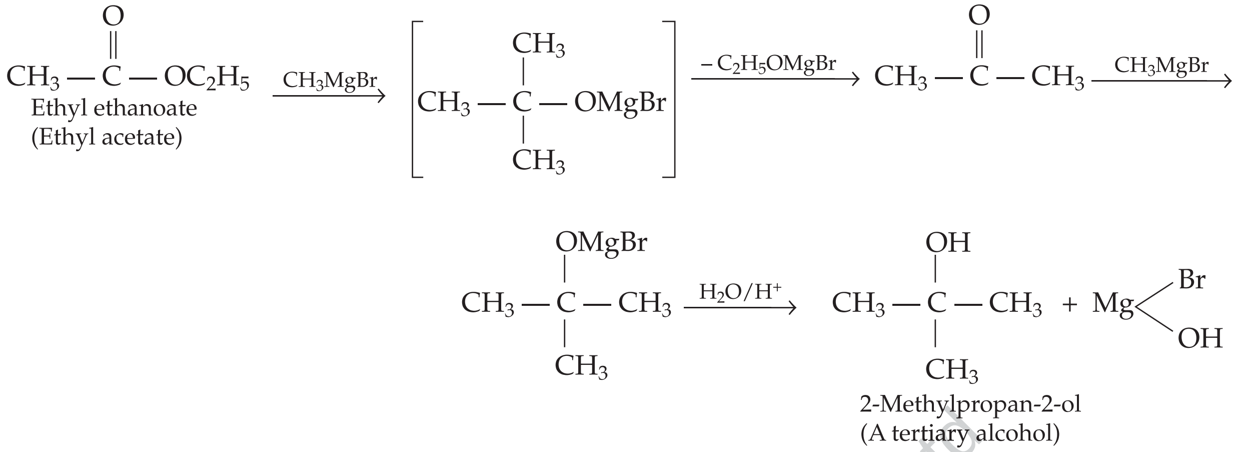


$$R-\overset{\overset{O}{\|}}{C}-OR' + 4[H] \xrightarrow{LiAlH_4} R-CH_2OH + R'-OH$$



$$\underset{\text{Ethyl ethanoate}}{CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_3} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{2CH_3CH_2-OH}$$

(*b*) Using Grignard's reagent. Esters of formic acid yield secondary alcohols while those of other acids yields tertiary alcohols on reaction with Grignard reagents.

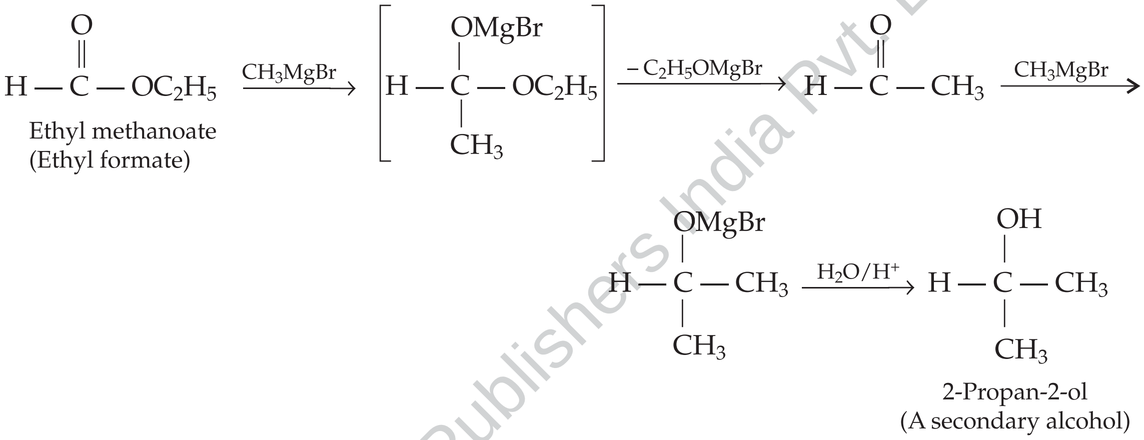


$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow{CH_3MgBr} \left[CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OMgBr\right] \xrightarrow{-C_2H_5OMgBr} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{CH_3MgBr}$$

Ethyl ethanoate
(Ethyl acetate)

$$CH_3-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H_2O/H^+} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 + Mg\begin{matrix}\diagup Br\\ \diagdown OH\end{matrix}$$

2-Methylpropan-2-ol
(A tertiary alcohol)

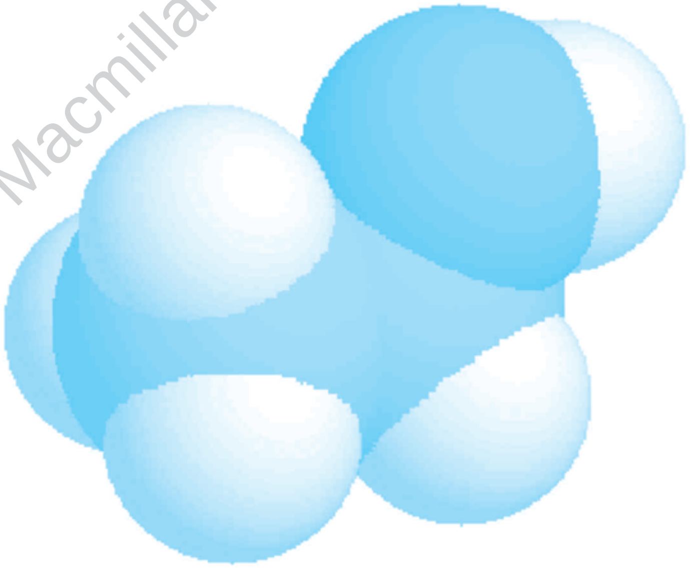


$$H-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow{CH_3MgBr} \left[H-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-OC_2H_5\right] \xrightarrow{-C_2H_5OMgBr} H-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{CH_3MgBr}$$

Ethyl methanoate
(Ethyl formate)

$$H-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 \xrightarrow{H_2O/H^+} H-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

2-Propan-2-ol
(A secondary alcohol)



Space model of ethyl alcohol

13.5 MANUFACTURE OF ALCOHOLS

Fermentation of Carbohydrates: Formation of ethyl alcohol by the fermentation of sugar (obtained from molasses) is a prominent method. Sucrose is first converted into glucose and fructose with the help of an enzyme *invertase.* Glucose and fructose are then converted into ethyl alcohol with the help of an enzyme *zymase.*

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

Barley, rice, maize and potatoes which contain plenty of starch are treated with enzymes *diastase* and *maltase* to obtain ethyl alcohol.

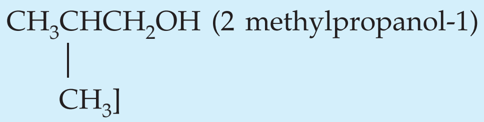
$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

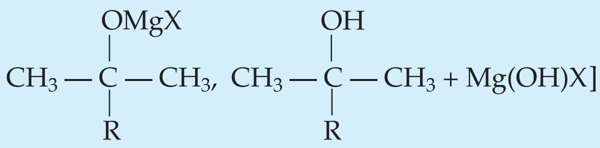
$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

PROBLEMS FOR PRACTICE

1. Name the Grignard reagent required for converting
   (*i*) formaldehyde to *n*-butyl alcohol (*ii*) acetaldehyde into sec. butyl alcohol.
   [**Ans.** (*i*) *n*-Propylmagnesium bromide; (*ii*) ethyl magnesium bromide.]

2. Which isomeric alcohols with formula $C_4H_{10}O$ can be prepared by hydrogenation of aldehydes?
   [**Ans.** Primary alcohols are obtained by hydrogenation of aldehydes. Thus, the alcohols that can be obtained are
   (*i*) $CH_3CH_2CH_2CH_2OH$
   Butanol-1
   (*ii*)
   
   $\underset{\displaystyle CH_3}{CH_3\overset{}{C}HCH_2OH}$ (2 methylpropanol-1)]

3. Which alcohol with formula $C_4H_{10}O$ cannot be prepared by the reduction of aldehyde or ketone?
   [**Ans.** Tert. butyl alcohol]

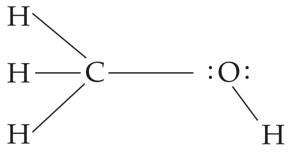
4. Complete the following equation:
   $$(CH_3)_2C = O \xrightarrow{\text{RMgX}} ? \xrightarrow{H^+/H_2O} ?$$
   [**Ans.**
   
   $CH_3-\underset{R}{\overset{OMgX}{C}}-CH_3,\ CH_3-\underset{R}{\overset{OH}{C}}-CH_3 + Mg(OH)X$]

5. Name the reagent which is most effective in carrying out anti-Markownikov's addition of H_2O across enthylenic double bond. Give example.
   [**Ans.** Hydrolysis of alkene with $B_2H_6/\ H_2O_2/\ OH^-$]

13.6 STRUCTURE OF ALCOHOLS

The general formula of alcohols is R—OH, where R is some alkyl group. The –OH group is attached to carbon of the alkyl group.

The C–O–H bonds in alcohols is not linear. The structure of methyl alcohol can be represented as under:



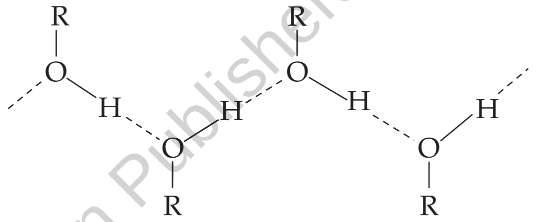
Methanol

As oxygen is more electronegative than carbon and hydrogen, therefore, C—O and O—H bonds in alcohols and phenols are polar bonds and, hence, both alcohols and phenols possess a net dipole moment. Methanol has a higher dipole moment of 1.71 D compared to a dipole moment of 1.54 D for phenol. *The smaller dipole moment of phenol is due to the electron withdrawing effect of phenyl group in contrast to the electron releasing effect of alkyl group in alcohols.*

13.7 PHYSICAL PROPERTIES OF ALCOHOLS

(*i*) The lower members of alcohols are colourless volatile liquids with a characteristic alcoholic smell and burning taste whereas higher alcohols are odourless, tasteless and waxy solids.

(*ii*) **Boiling Points.** Boiling points of alcohols are much higher than those of alkanes, haloalkanes or ethers of comparable molecular masses. This is because of intermolecular hydrogen bonding that exists between alcohol molecules.



Compounds	Mol. Mass	Boiling Point
CH_3CH_2OH (Ethanol)	46	351 K
CH_3OCH_3 (Methoxymethane)	46	297 K
CH_3Cl (Chloromethane)	50.5	249 K
$CH_3CH_2CH_3$ (Propane)	44	231 K

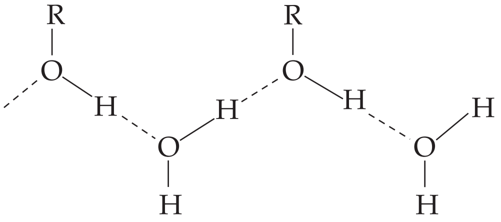
For isomeric alcohols, the boiling points follow the order: Primary alcohol > Secondary alcohol > Tertiary alcohol.

This can be explained in terms of decreasing surface area and hence, decreasing van der Waals' forces as we move from primary to tertiary alcohol.

It is because of this reason that alcohols cannot be derived with anhydrous $CaCl_2$ *and* $MgCl_2$*.*

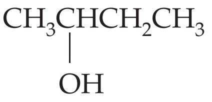
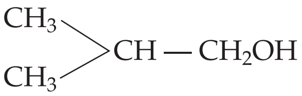
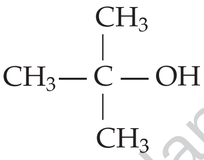
(*iii*) **Solubility of Alcohols.** The first three members are completely miscible with water. It is observed that solubility rapidly decreases with the increase in molecular mass. The higher members are almost insoluble in water but are soluble in organic solvents.

The solubility of lower alcohols can be explained in terms of hydrogen bonds between water and polar O–H group of alcohol molecules as illustrated below:



The solubility of alcohols in water decreases with the increase in molecular mass *because, the non-polar alkyl group becomes dominant and hinders the formation of hydrogen bonds.*

Among the isomeric alcohols, the solubility increases with branching of chain. *It is because the surface area of non-polar part in the molecule decreases, thus, enhancing the solubility.* Solubility data of isomeric alcohols with molecular formula C_4H_9OH as listed below, confirms this view.

Alcohol	Structure	Solubility g/ 100 g of H_2O
n-Butyl alcohol	$CH_3CH_2CH_2CH_2OH$	7.9
sec-Butyl alcohol	 $CH_3\underset{\mid \atop OH}{CH}CH_2CH_3$	12.5
iso-Butyl alcohol	 $(CH_3)_2CH-CH_2OH$	10.0
tert-Butyl alcohol	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$	Extremely soluble

Alcohol breathalyser is used to check drunken driving

(*iv*) **Intoxicating Effects.** Alcohols are known to have intoxicating effects. Methanol is poisonous and cause blindness if consumed. Ethanol, on the other hand, is used for drinking purposes.

13.8 CHEMICAL PROPERTIES OF ALCOHOLS

The reactions of alcohols can be studied under three headings:

1. *Reactions involving the cleavage of oxygen-hydrogen bond.*
2. *Reactions involving the cleavage of carbon-oxygen bond.*
3. *Reactions involving both the alkyl and the hydroxyl groups.*

13.8.1 Reactions Involving the Cleavage of Oxygen-Hydrogen R — O — H Bond

(*i*) **Acidic Character.** Alcohols are very weak acids even weaker than water. When treated with active metals like sodium or potassium, alcohols liberate hydrogen with the formation of alkoxides.

$$R-O-H + Na \longrightarrow \underset{\text{Sod. alkoxide}}{R-\bar{O}\overset{+}{Na}} + \frac{1}{2}H_2$$

$$\underset{\text{Ethanol}}{C_2H_5OH} + Na \longrightarrow \underset{\text{Sod. alkoxide}}{C_2H_5-\overset{-}{O}\overset{+}{Na}} + \frac{1}{2}H_2$$

However, there is no effect of alcohol on blue litmus.

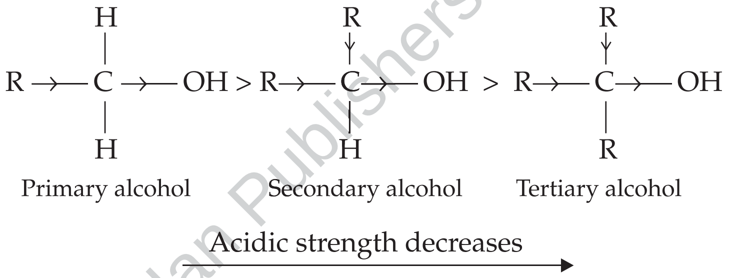
Alcohols behave as acids because of the presence of polar O—H group. Due to greater electronegativity of oxygen atom, the shared pair between O and H is drawn more towards the oxygen atom. This results in release of H^+ ion. However, alcohols are very very weak acids. This is explainable on the basis of electron releasing nature of alkyl group present in alcohols. Alkyl group increases electron density around the oxygen atom due to which the polarity of the O–H bond decreases.

$$\underset{\text{Alcohol}}{R\rightarrow\ddot{\underset{..}{O}}-H} \rightleftharpoons \underset{\text{Alkoxide ion}}{R\rightarrow\ddot{\underset{..}{O}}:^{-}} + H$$

Thus, the release of H^+ ion is difficult. This explains the weak acidic character of alcohols.

The order of **acidic strength** among various alcohols is: Primary > Secondary > Tertiary.

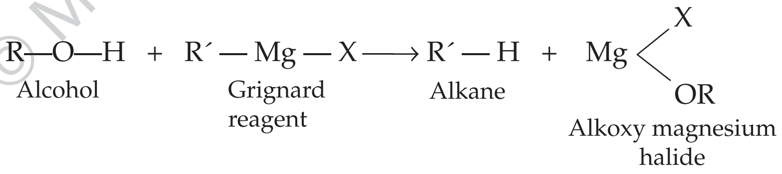
The order can again be explained in terms of electron releasing inductive effect of alkyl groups. Greater is the number of alkyl groups attached to the carbon carrying the –OH group smaller will be the polarity of —OH group and, hence, smaller will be the acidic character. In tertiary alcohols, the carbon atom carrying —OH group, is attached to three alkyl groups due to which electron density on oxygen is maximum in their case, hence, cleavage of C—H bond is difficult. Thus, tertiary alcohols are least acidic whereas primary alcohols (with only one alkyl group) are most acidic. Secondary alcohols show intermediate character.



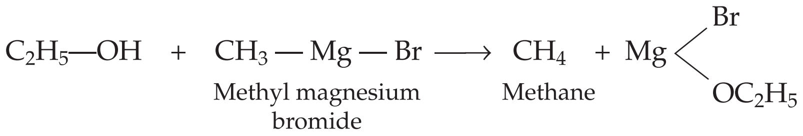
$$\underset{\text{Primary alcohol}}{R\rightarrow\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}\rightarrow OH} > \underset{\text{Secondary alcohol}}{R\rightarrow\overset{\overset{R}{\downarrow}}{\underset{\underset{H}{|}}{C}}\rightarrow OH} > \underset{\text{Tertiary alcohol}}{R\rightarrow\overset{\overset{R}{\downarrow}}{\underset{\underset{R}{|}}{C}}\rightarrow OH}$$

Acidic strength decreases →

(ii) Reaction with Grignard Reagent. (*Zerewitnoff's Reaction*). Alcohols react with Grignard reagent to form alkanes. In these reactions, the alkane is obtained from the alkyl part of Grignard reagent. This is because alcohols contain active hydrogen in the form of —OH group.



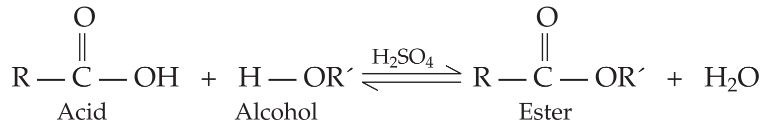
$$\underset{\text{Alcohol}}{R-O-H} + \underset{\text{Grignard reagent}}{R'-Mg-X} \longrightarrow \underset{\text{Alkane}}{R'-H} + \underset{\text{Alkoxy magnesium halide}}{Mg\genfrac{}{}{0pt}{}{X}{OR}}$$



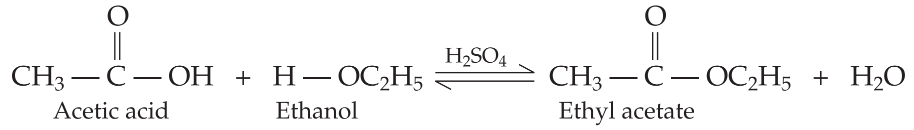
$$C_2H_5-OH + \underset{\text{Methyl magnesium bromide}}{CH_3-Mg-Br} \longrightarrow \underset{\text{Methane}}{CH_4} + Mg\genfrac{}{}{0pt}{}{Br}{OC_2H_5}$$

This reaction is used for the estimation of alcohlic group (**Zerewitnoff reaction**).

(iii) Reaction with Monocarboxylic Acids (*Esterification*). Alcohols react with monocarboxylic acids in the presence of conc. sulphuric acid to form esters. Conc. H_2SO_4 acts as a protonating agent as well as dehydrating agent and helps to increase the yield.



$$\underset{\text{Acid}}{R-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Alcohol}}{H-OR'} \xrightleftharpoons{H_2SO_4} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'} + H_2O$$



$$\underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Ethanol}}{H-OC_2H_5} \xrightleftharpoons{H_2SO_4} \underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} + H_2O$$

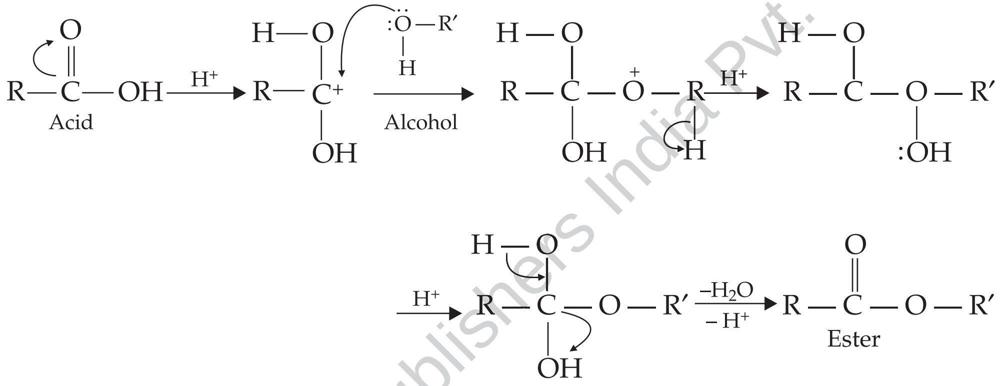
This reaction is reversible in nature and the equilibrium can be shifted to the right by removing water as soon as it is formed. When HCl gas is used as a catalyst in this reaction, it is called as **Fischer-Speier esterification.**

Mechanism of esterification of alcohol: The following steps are involved in the reaction:

(*i*) Protonation of carbonyl oxygen of the carboxylic acid with proton released from mineral acid.

(*ii*) Nucleophilic attack by the oxygen of the alcohol to the protonated carboxylic acid.

(*iii*) Conversion into ester as depicted below:



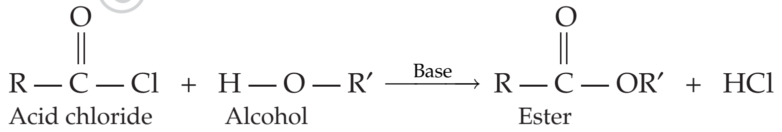
Rate of esterification decreases as the size of group R in the acid or group R′ in the alcohol increases. Order of reactivity of alcohol in esterification follows the sequence:

$$CH_3OH > C_2H_5OH > (CH_3)_2CHOH > (CH_3)_3COH$$

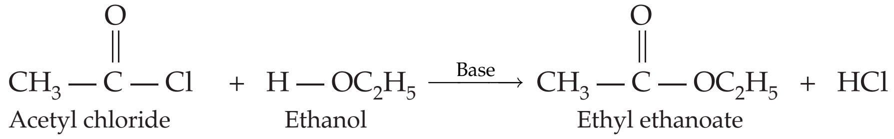
Order of reactivity of acids in esterification has the sequence:

$$HCOOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$$

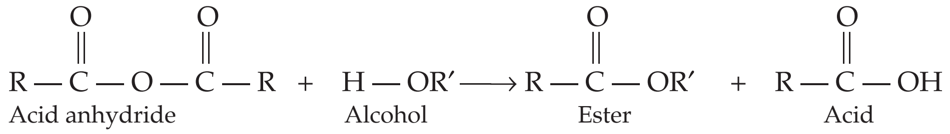
(*iv*) **Reaction with Acid Chloride or Acid Anhydride (*Acylation*).** Alcohols on treatment with acid chloride or acid anhydride in the presence of bases like pyridine or dimethylaniline (as catalyst) form esters. This reaction is called **acylation** or **acetylation.** Following equations illustrate:



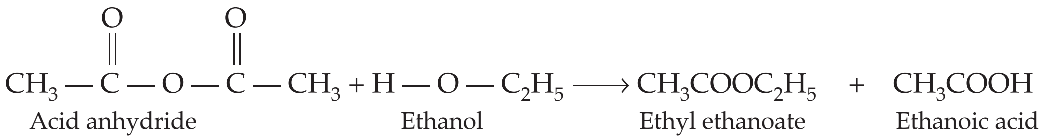
$$\underset{\text{Acid chloride}}{R-\overset{\overset{O}{\|}}{C}-Cl} + \underset{\text{Alcohol}}{H-O-R'} \xrightarrow{\text{Base}} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'} + HCl$$



$$\underset{\text{Acetyl chloride}}{CH_3-\overset{\overset{O}{\|}}{C}-Cl} + \underset{\text{Ethanol}}{H-OC_2H_5} \xrightarrow{\text{Base}} \underset{\text{Ethyl ethanoate}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} + HCl$$



$$\underset{\text{Acid anhydride}}{R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R} + \underset{\text{Alcohol}}{H-OR'} \longrightarrow \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'} + \underset{\text{Acid}}{R-\overset{\overset{O}{\|}}{C}-OH}$$

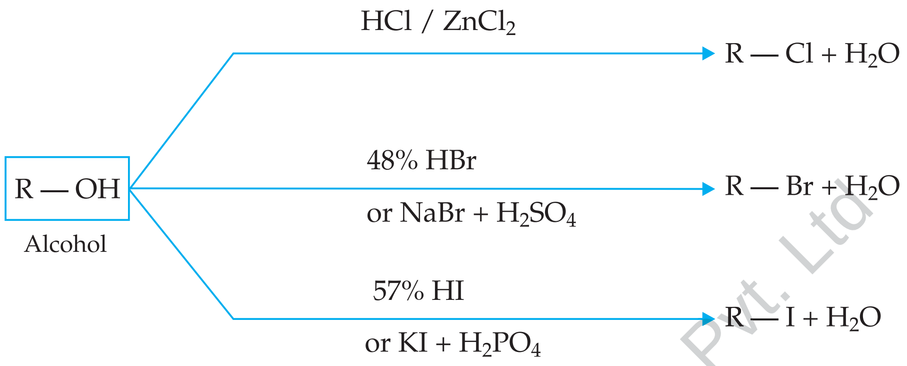


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H-O-C_2H_5 \longrightarrow CH_3COOC_2H_5 + CH_3COOH$$

Acid anhydride Ethanol Ethyl ethanoate Ethanoic acid

13.8.2 Reactions Involving Cleavage of Carbon-Oxygen R—C—OH Bond

Reaction with Hydrogen Halides. Alcohols react with hydrogen halides to form alkyl halides. Some representative reactions are given below:



The order of reactivity of various alcohols towards this reaction is **Tertiary > Secondary > Primary.**

The reactivity of various hydrogen halides follows the order: **HI > HBr > HCl.**

Mechanism of reaction with halogen acids

Primary alcohols react through **SN^2 mechanism.**

1. $R-OH + HX \rightleftharpoons R-\overset{+}{O}H_2 + :X^- \text{(slow)}$

2. $:X^- + R-\overset{+}{O}H_2 \longrightarrow [\overset{\delta-}{X}.....R....\overset{\delta-}{O}H_2] \longrightarrow X-R + H_2O$

For secondary and tertiary alcohols a **SN^1 mechanism** is proposed.

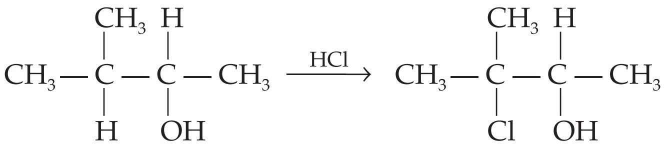
1. $R-OH + HX \rightleftharpoons R-\overset{+}{O}H_2 + :\bar{X}$

2. $R-\overset{+}{O}H_2 \rightleftharpoons R^+ + H_2O \text{ (slow)}$

3. $R + :X^- \longrightarrow R-X \text{ (fast)}$

In step 1, the alcohol accepts hydrogen ion to form the protonated alcohol which dissociates into *carbocation* and water. In step 2, the carbocation then combines with halide ion to form alkyl halide.

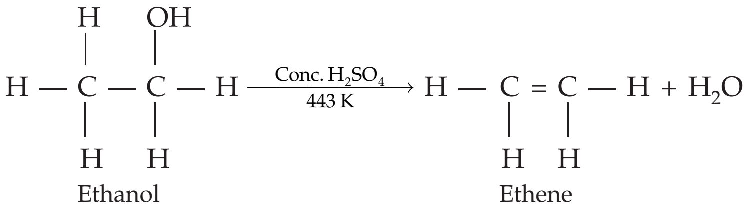
In case of alcohols reacting through SN^1 mechanism, the alkyl group may undergo rearrangements due to rearrangement in the intermediate carbocation.

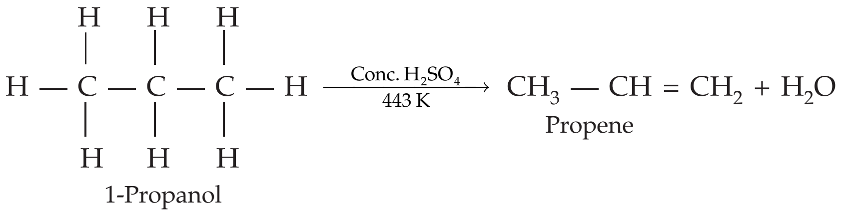


$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{OH}{\overset{H}{C}}-CH_3 \xrightarrow{HCl} CH_3-\underset{Cl}{\overset{CH_3}{C}}-\underset{OH}{\overset{H}{C}}-CH_3$$

13.8.3 Reactions Involving Both the Alkyl and the Hydroxyl Groups

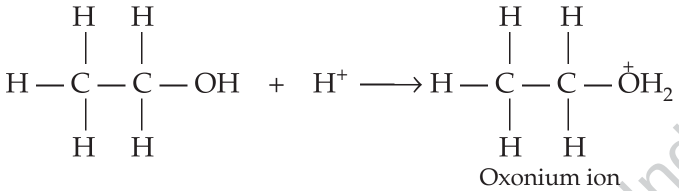
(*i*) **Dehydration (*Formation of alkenes*).** When heated with conc. H_2SO_4, phosphoric acid or boric acid, alcohols undergo dehydration to form alkenes. The reaction with conc. sulphuric acid is carried at 443 K whereas phosphoric and boric acids require higher temperature for the reaction to take place.



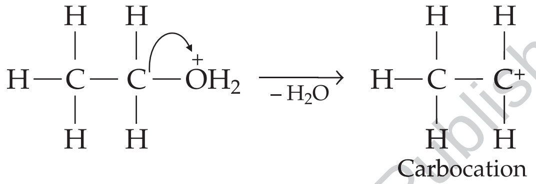


Mechanism of dehydration of alcohols: Following steps are involved in the mechanism of dehydration of alcohols:

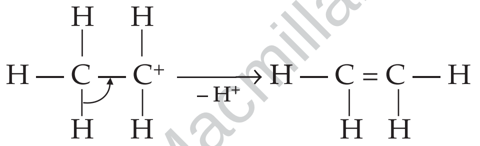
1. **Protonation of alcohol**



2. **Removal of water**



3. **Loss of proton:** The ease of dehydration of alcohols is found to follow the order:



Tertiary alcohol > Secondary alcohol > Primary alcohol.

Alcohols can also be dehydrated by passing vapours of alcohol over alumina at 620 K.

$$\underset{\text{Ethanol}}{CH_3CH_2OH\,(g)} \xrightarrow[-H_2O]{Al_2O_3,\,620\text{ K}} \underset{\text{Ethene}}{CH_2 = CH_2}$$

The reaction between ethanol and sulphuric acid produces different products under different reaction conditions.

(*a*) **At 383 K,** *ethyl alcohol forms ethyl hydrogen sulphate.*

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \xrightarrow{383\text{ K}} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

(*b*) **Distillation under reduced pressure yields,** *diethyl sulphate.*

$$2C_2H_5OH + H_2SO_4 \xrightarrow{\text{heat}} \underset{\text{Diethyl sulphate}}{(C_2H_5)_2SO_4} + 2H_2O$$

(*c*) *With excess of alcohol at 413 K, two molecules of alcohol lose one water molecule and ether is obtained.*

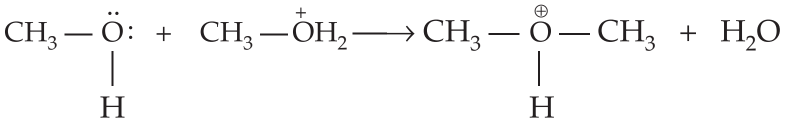
$$2C_2H_5OH \xrightarrow[413\ K]{\text{conc. } H_2SO_4} \underset{\substack{\text{Ethoxyethane}\\ \text{(Diethyl ether)}}}{C_2H_5OC_2H_5} + H_2O$$

Mechanism of reaction: The mechanism of this reaction involves the following steps. The mechanism has been explained as under taking the example of dehydration of methyl alcohol.

1. **Protonation of alcohol molecule**

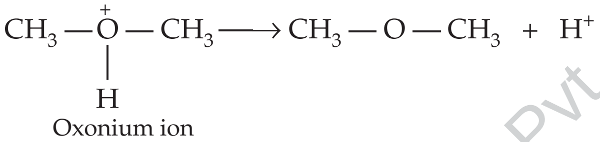
$$CH_3-OH + H^+ \longrightarrow CH_3\overset{\oplus}{O}H_2$$

2. **Combination of unprotonated molecule with protonated molecule with removal of water**



$$CH_3-\underset{\underset{\displaystyle H}{|}}{\ddot{O}:} + CH_3-\overset{+}{O}H_2 \longrightarrow CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\oplus}{O}}-CH_3 + H_2O$$

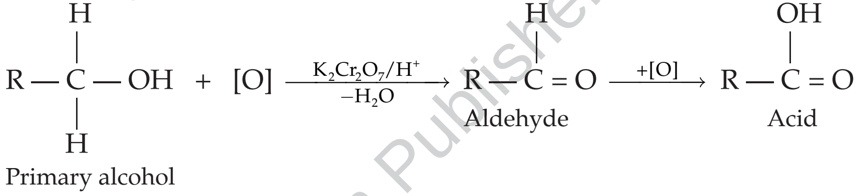
3. **Loss of proton from oxonium ion**



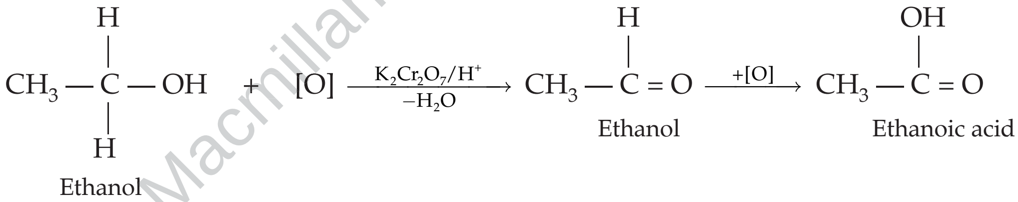
$$\underset{\text{Oxonium ion}}{CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{+}{O}}-CH_3} \longrightarrow CH_3-O-CH_3 + H^+$$

(*ii*) **Oxidation of Alcohols.** Alcohols undergo oxidation with oxidising agents such as chromium trioxide (CrO_3), potassium dichromate, potassium permanganate or dilute nitric acid.

(*a*) **A primary alcohol** on oxidation with acidified potassium dichromate first gives an aldehyde which on further oxidation gives an acid with the same number of carbon atoms as the original alcohol. The following reactions illustrate:

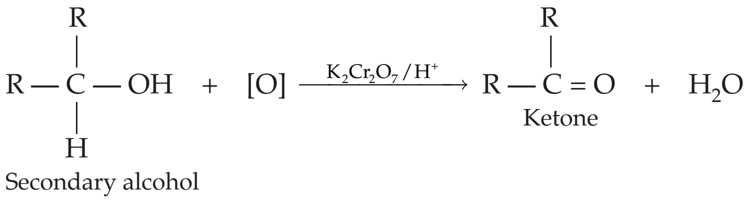


$$\underset{\text{Primary alcohol}}{R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-OH} + [O] \xrightarrow[-H_2O]{K_2Cr_2O_7/H^+} \underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle H}{|}}{C}=O} \xrightarrow{+[O]} \underset{\text{Acid}}{R-\overset{\overset{\displaystyle OH}{|}}{C}=O}$$

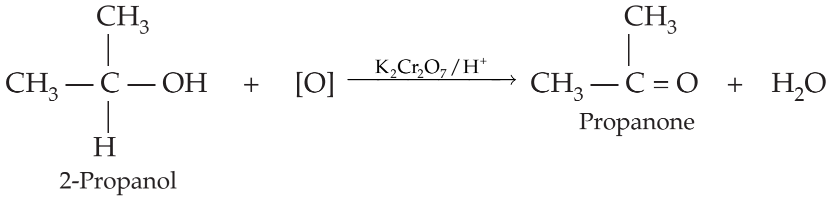


$$\underset{\text{Ethanol}}{CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-OH} + [O] \xrightarrow[-H_2O]{K_2Cr_2O_7/H^+} \underset{\text{Ethanol}}{CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O} \xrightarrow{+[O]} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=O}$$

(*b*) **A secondary alcohol** on oxidation gets oxidised to a ketone with the same number of carbon atoms as the original alcohol.

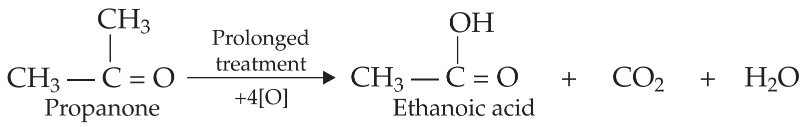


$$\underset{\text{Secondary alcohol}}{R-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}-OH} + [O] \xrightarrow{K_2Cr_2O_7/H^+} \underset{\text{Ketone}}{R-\overset{\overset{\displaystyle R}{|}}{C}=O} + H_2O$$



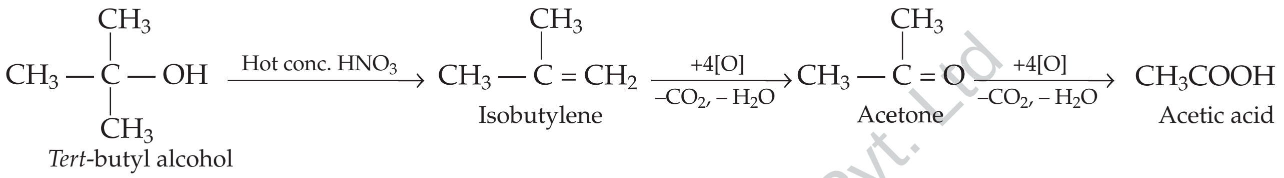
$$\underset{\text{2-Propanol}}{CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH} + [O] \xrightarrow{K_2Cr_2O_7/H^+} \underset{\text{Propanone}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O} + H_2O$$

Prolonged treatment with the oxidising agent converts ketones into acids with smaller number of carbon atoms than the alcohols. The reaction is called **oxidative degradation** of alcohols.



$$\underset{\text{Propanone}}{CH_3-\overset{\overset{\Large CH_3}{|}}{C}=O} \xrightarrow[+4[O]]{\text{Prolonged treatment}} \underset{\text{Ethanoic acid}}{CH_3-\overset{\overset{\Large OH}{|}}{C}=O} + CO_2 + H_2O$$

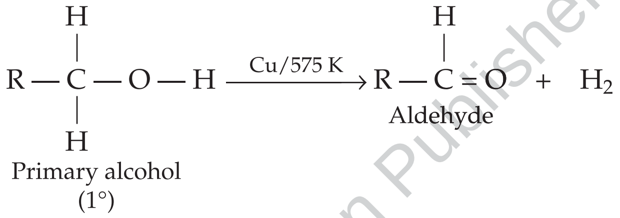
(*c*) Tertiary alcohols are not oxidised with mild oxidising agents in aqueous, alkaline or under neutral conditions. Strong oxidation of tertiary alcohols in acidic medium brings about dehydration of alcohols to alkenes and subsequent degradation to ketones and acids having smaller number of carbon atoms than the alcohols.



$$\underset{\textit{Tert}\text{-butyl alcohol}}{CH_3-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-OH} \xrightarrow{\text{Hot conc. } HNO_3} \underset{\text{Isobutylene}}{CH_3-\overset{\overset{\Large CH_3}{|}}{C}=CH_2} \xrightarrow[-CO_2,\ -H_2O]{+4[O]} \underset{\text{Acetone}}{CH_3-\overset{\overset{\Large CH_3}{|}}{C}=O} \xrightarrow[-CO_2,\ -H_2O]{+4[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

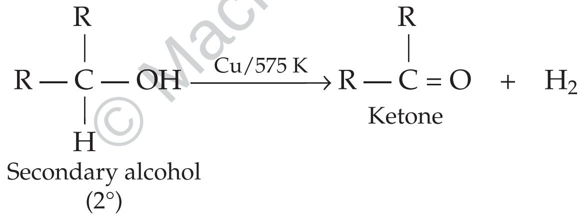
(*iii*) Dehydrogenation (*Reaction with Hot Reduced Copper*). Primary, secondary and tertiary alcohols give different products when their vapours are passed over reduced copper at 575 K.

(*a*) A *primary alcohol gets dehydrogenated to aldehyde.*



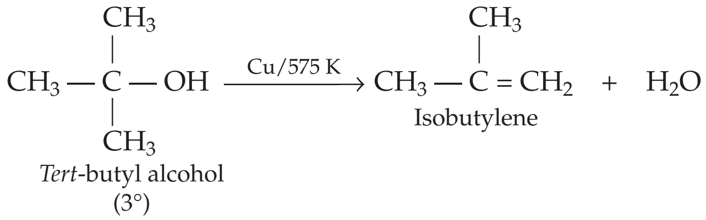
$$\underset{\substack{\text{Primary alcohol}\\(1°)}}{R-\underset{\underset{\Large H}{|}}{\overset{\overset{\Large H}{|}}{C}}-O-H} \xrightarrow{Cu/575\ K} \underset{\text{Aldehyde}}{R-\overset{\overset{\Large H}{|}}{C}=O} + H_2$$

(*b*) *A secondary alcohol gets dehydrogenated to ketone.*



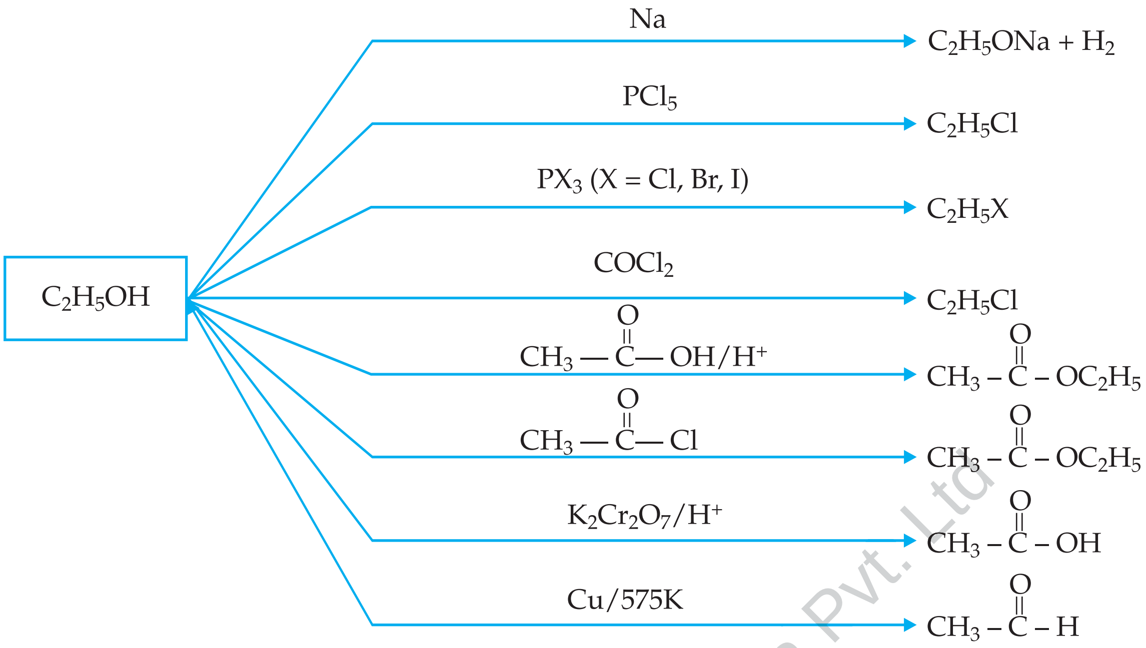
$$\underset{\substack{\text{Secondary alcohol}\\(2°)}}{R-\underset{\underset{\Large H}{|}}{\overset{\overset{\Large R}{|}}{C}}-OH} \xrightarrow{Cu/575\ K} \underset{\text{Ketone}}{R-\overset{\overset{\Large R}{|}}{C}=O} + H_2$$

(*c*) *A tertiary alcohol does not contain hydrogen, hence, dehydrogenation does not take place. However, it gets dehydrated to form an alkene.*



$$\underset{\substack{\textit{Tert}\text{-butyl alcohol}\\(3°)}}{CH_3-\underset{\underset{\Large CH_3}{|}}{\overset{\overset{\Large CH_3}{|}}{C}}-OH} \xrightarrow{Cu/575\ K} \underset{\text{Isobutylene}}{CH_3-\overset{\overset{\Large CH_3}{|}}{C}=CH_2} + H_2O$$

The reactions of alcohols are summarised as under:



PROBLEMS FOR PRACTICE

1. What is Zerewitnoff's reaction?

[**Ans.** $C_2H_5OH + CH_3MgBr \longrightarrow \underset{\text{Methane}}{CH_4} + Mg(OC_2H_5)Br$]

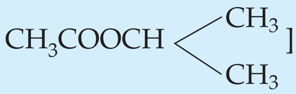
2. Arrange these compounds in order of acid strength: *n*-butyl alcohol, *sec*-Butyl alcohol, *iso* butyl alcohol and *tert*-butyl alcohol.

[**Ans.** *Tert*-butyl alcohol < *Sec*-butyl alcohol < *Iso*-butyl alcohol < *n*-butyl alcohol]

3. Out of neopentyl alcohol and *n*-pentyl alcohol which has higher boiling point?

[**Ans.** *n*-pentyl alcohol, due to larger surface area.]

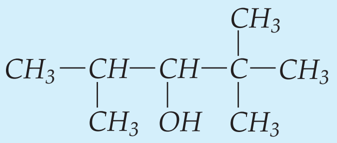
4. Which ester is formed when isopropyl alcohol is treated with ethanoic acid and conc. H_2SO_4? Give reaction.

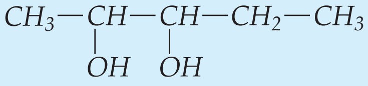
[**Ans.** Isopropyl acetate:  $CH_3COOCH\begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix}$]

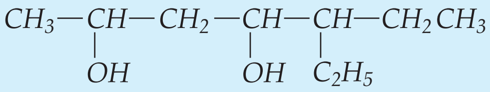
5. Outline the mechanism of esterification of alcohol.

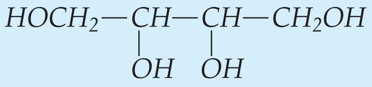
MISCELLANEOUS SOLVED QUESTIONS

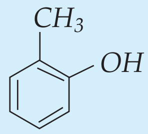
1. *Write IUPAC names of the following compounds:*

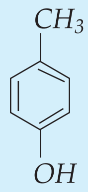
(*i*) 
$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

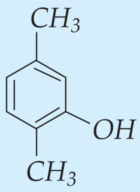
(*iii*) 
$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$

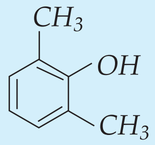
(*ii*) 
$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{C_2H_5}{\underset{|}{CH}}-CH_2CH_3$

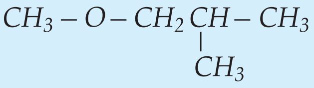
(*iv*) 
$HOCH_2-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_2OH$

(*v*) 

(*vi*) 

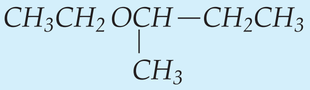
(*vii*) 

(*viii*) 

(*ix*) 

$CH_3-O-CH_2CH(CH_3)-CH_3$

(*x*) $C_6H_5OC_2H_5$ (*xi*) $C_6H_5O.nC_7H_{15}$

(*xii*) 

$CH_3CH_2OCH(CH_3)-CH_2CH_3$

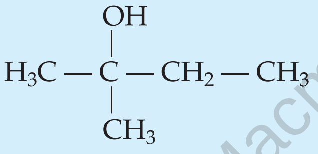
Ans.

(*i*) 2, 2, 4-trimethyl pentan-3-ol
(*ii*) 5-ethyl heptan-2, 4-diol
(*iii*) Pentan-2, 3-diol
(*iv*) Propane, 2, 3-triol
(*v*) 2-methyl phenol
(*vi*) 4-methyl phenol
(*vii*) 2, 5-dimethyl phenol
(*viii*) 2, 6-dimethyl phenol
(*ix*) 1-methoxy 2-methyl propane
(*x*) Ethoxy benzene
(*xi*) 1-phenoxy heptane
(*xii*) 2-ethoxy butane

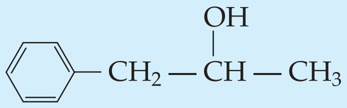
2. *Write structural formula of the compounds whose IUPAC names are as follows:*

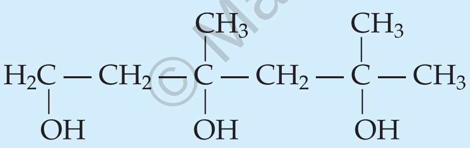
(*i*) *2-methylbutan 2-ol*
(*ii*) *1-phenyl propan-2-ol*
(*iii*) *3, 5-dimethyl hexene-1, 3, 5 triol*
(*iv*) *2, 3-diethyl phenol*
(*v*) *1-ethoxy propane*
(*vi*) *2-ethoxy 3-methyl pentane*
(*vii*) *Cyclohexylmethanol*
(*viii*) *3-cyclohexyl pentan-3-ol*
(*ix*) *Cyclopent 3-en-1-ol*
(*x*) *3-chloromethyl pentan 1-ol*

Ans.

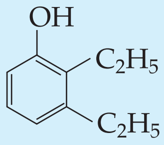
(*i*) 

$H_3C-C(OH)(CH_3)-CH_2-CH_3$

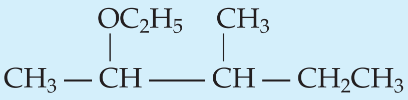
(*ii*) 

(*iii*) 

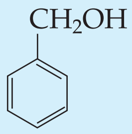
$H_2C(OH)-CH_2-C(CH_3)(OH)-CH_2-C(CH_3)(OH)-CH_3$

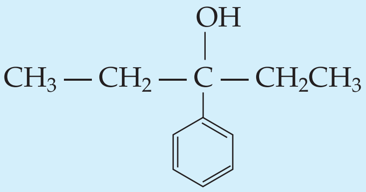
(*iv*) 

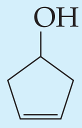
(*v*) $H_5C_2O-CH_2CH_2CH_3$

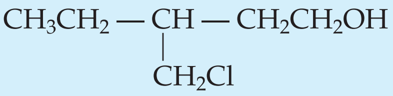
(*vi*) 

$CH_3-CH(OC_2H_5)-CH(CH_3)-CH_2CH_3$

(*vii*) 

(*viii*) 

(*ix*) 

(*x*) 

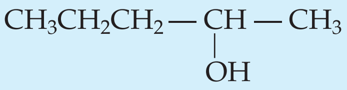
$CH_3CH_2-\underset{CH_2Cl}{\underset{|}{CH}}-CH_2CH_2OH$

3. *Draw the structure of all isomeric alcohols of molecular formula* $C_5H_{12}O$ *and give their IUPAC names. Classify them as primary, secondary and tertiary alcohols.*

Ans.

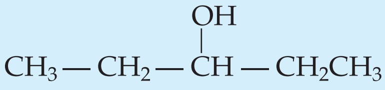
(*i*) $CH_3CH_2CH_2CH_2OH$

Pentan-1-ol
(Primary)

(*ii*) 

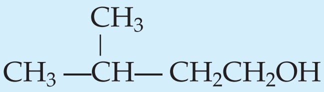
$CH_3CH_2CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$

Pentan-2-ol
(Secondary)

(*iii*) 

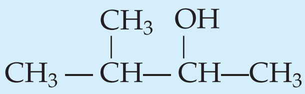
$CH_3-CH_2-\overset{OH}{\overset{|}{CH}}-CH_2CH_3$

Pentan-3-ol
(Secondary)

(*iv*) 

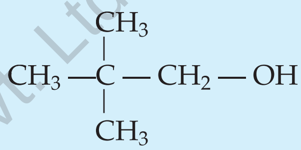
$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2CH_2OH$

3-methyl butan-1-ol
(Primary)

(*v*) 

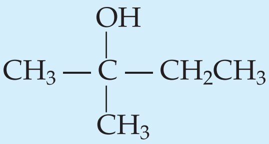
$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{OH}{\overset{|}{CH}}-CH_3$

3-methyl butan-2-ol
(Secondary)

(*vi*) 

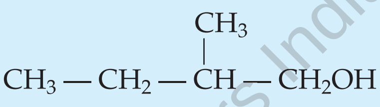
$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-OH$

2,2-dimethyl propan-1-ol
(Primary)

(*vii*) 

$CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2CH_3$

2-methyl butan-2-ol
(Tertiary)

(*viii*) 

$CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2OH$

2-methyl butan-1-ol
(Primary)

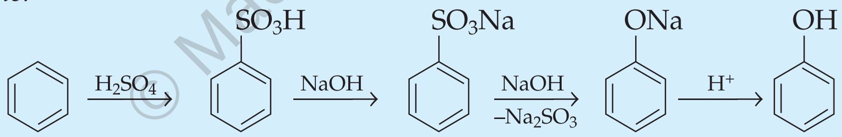
4. *Explain why does propanol have higher boiling point than that of hydrocarbon, butane.*

Ans. This is due to intermolecular H-bonding in propanol whereas in butane there is no H-bonding.

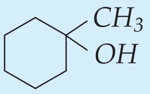
5. *Alcohols are comparatively more soluble in water than the hydrocarbons of comparable molecular masses. Explain this fact.*

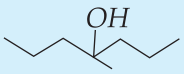
Ans. Alcohols are capable of forming H-bonds with water whereas hydrocarbons cannot.

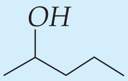
6. *You are given benzene, conc.* H_2SO_4 *and NaOH. Write the equations for the preparation of phenol using these reagents.*

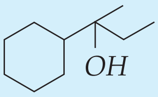
Ans. 

7. *Show how would you synthesize the following alcohols from appropriate alkenes?*

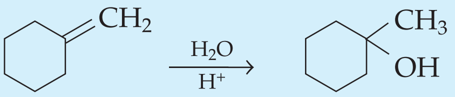
(*i*) 

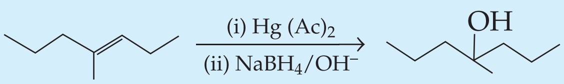
(*ii*) 

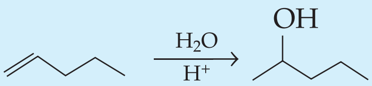
(*iii*) 

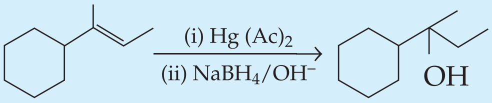
(*iv*) 

Ans.

(*i*) 

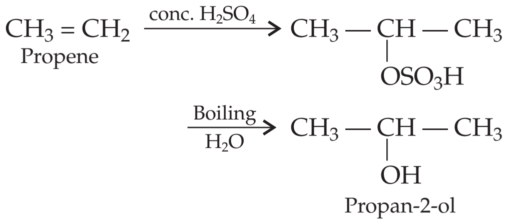
(*ii*) 

(*iii*) 

(*iv*) 

QUICK SCAN (FOR REVISION)

1. Alcohols are classified as monohydric, dihydric or trihydric accordingly as they contain one, two or three alcoholic groups.
2. Alcohols are obtained by:
   (*i*) hydrolysis of alkyl halides with aqueous KOH or moist silver oxide (AgOH),
   (*ii*) reduction of aldehydes and ketones with H_2/Ni, Pt or Pd; Na/alcohol and $NaBH_4$ or $LiAlH_4$.
   (*iii*) reduction of esters with $LiAlH_4$ or Na/alcohol **(Bouveault-Blanc reduction).**
3. Alcohols can also be obtained by *Markownikov's addition of water to alkenes.*
   (*i*) **By hydration of alkenes**



$$\underset{\text{Propene}}{CH_3=CH_2} \xrightarrow{\text{conc. } H_2SO_4} CH_3-\underset{\substack{|\\ OSO_3H}}{CH}-CH_3 \xrightarrow[H_2O]{\text{Boiling}} \underset{\text{Propan-2-ol}}{CH_3-\underset{\substack{|\\ OH}}{CH}-CH_3}$$

4. Alcohols are obtained by addition of Grignard reagent (followed by hydrolysis with dil. HCl) on carbonyl compounds.
   (*i*) Formaldehyde gives 1° alcohols.
   (*ii*) Aldehydes other than formaldehyde give 2° alcohols.
   (*iii*) Ketones and esters give 3° alcohols.
5. Nitrous acids reacts with 1° aliphatic amines to give 1° alcohols.
6. Ethyl alcohol can be obtained by:
   (*i*) **Fermentation of sugar:**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

   (*ii*) **Fermentation of starch:**

$$2(C_6H_{10}O_5) + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

7. Lower alcohols are highly soluble in H_2O due to intermolecular H–bonding, but the solubility decreases as the molecular mass of the alcohol increases. This is due to decrease in the extent of H–bonding with increase in size of alkyl group.
8. **Acidity of alcohols.** It follows the order 1° > 2° > 3°.
9. **Esterification.** Alcohols react with carboxylic acids in the presence of a few drops of conc. H_2SO_4 or dry HC1 gas to form *esters.*

   Reactivity of alcohols:

   $CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$

   Reactivity of acids:

   $HCOOH > CH_3COOH > (CH_3)_2CHCOOH > (CH_3)_3CCOOH$
10. Alcohols react with conc. H_2SO_4 at different temperatures to form different products:

    (*i*) **At 383 K,** *alkyl hydrogen sulphates are formed* which when heated under reduced pressure form dialkyl sulphates, (*ii*) **At 413 K,** alkyl hydrogen sulphates react with excess of alcohol to form *ethers.* (*iii*) **At 443 K,** in the presence of excess of conc. H_2SO_4, alkyl hydrogen sulphates eliminate the molecules of H_2SO_4 to form *alkenes.*
11. **Oxidation.** Reagents used for oxidation of alcohols are: neutral, acidic or alkaline $KMnO_4$, acidified $K_2Cr_2O_7$ and dil. HNO_3.
    (*i*) **1° Alcohol** gives first *aldehydes* and then carboxylic acids both with the same number of C-atoms as the original alcohol.
    (*ii*) **2° Alcohol** gives first *ketones* with the same number of carbon atoms and then *acids* with smaller number of carbon atoms than the original alcohol.
    (*iii*) **3° Alcohol** gives first *ketones* and then *carboxylic acids* both with smaller number of carbon atoms than the original alcohol.
12. **Distinction between 1°, 2° and 3° Alcohols:**
    Action of hot copper. When vapours of alcohol are passed over heated copper at 573 K, **1° alcohols** give *aldehydes,* **2° alcohols** give *ketones* while 3° alcohols give *alkenes.*
13. Methanol also called *wood spirit* is commercially obtained by catalytic hydrogenation of CO at 573 K under a pressure of 200 atmospheres in the presence of a catalyst consisting of oxides of Cu, Zn and not Cr. Drinking of methyl alcohol causes blindness.
14. **Absolute alcohol** is prepared from rectified spirit by *azeotropic distillation.*

15. **Rectified spirit** contains 95% alcohol and 5% water and is obtained by fermentation of carbohydrates (molasses, starch, etc.).

16. **Methylated spirit or denatured alcohol** is obtained by adding methyl alcohol, acetone and pyridine to alcohol to make it unfit for drinking.

17. **Power alcohol** is a mixture of absolute alcohol and petrol in the ratio 1 : 4 and is used for running automobiles.

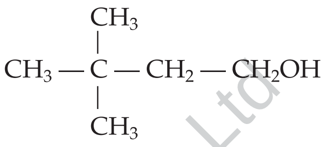
EXERCISES

Very Short Answer Type Questions

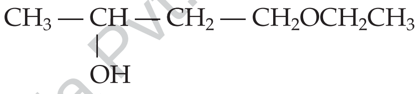
1. Name the enzyme which converts starch into maltose.
2. What product is obtained when 1, 2-ethanediol is treated with HIO_4?
3. What is the order of reactivity of HCl, HBr and HI with alcohols?
4. With the help of chemical equations, show how will you convert ethanol into ethylene glycol in two steps.
5. What is usually added to ethyl alcohol to make it unfit for drinking purposes?
6. Alcohols react with sodium metal to give H_2 gas. What do you conclude about the nature of alcohols?
7. What is the order of acidic character of primary, secondary and tertiary alcohols?
8. What is absolute alcohol?
9. Name any two reagents used for bringing about the oxidation of alcohols.
10. Name the enzymes present in yeast which convert sucrose into glucose and fructose and then to ethyl alcohol.
11. What is the main product obtained when vapours of *t*-butyl alcohol are passed over copper at 573 K?
12. Name the alcohol with lowest molecular weight and which is optically active.
13. Arrange the following in order of decreasing acid strength: CH_3OH, H_2O, C_6H_5OH.
14. Alcohols react with organic acids to form esters. What is the reaction called?
15. What is the order of dehydration of primary, secondary and tertiary alcohols?
16. What is 'power alcohol'?
17. What is the increasing order of reactivity of sodium metal towards primary, secondary and tertiary alcohols?
18. Why are alcohols soluble in water?
19. Name the only primary alcohol which gives iodoform test.
20. Anhydrous $CaCl_2$ is not recommended as a drying agent for alcohols and amines. Why?

Short Answer Type Questions

1. Give the IUPAC names of the following:

(*i*) 

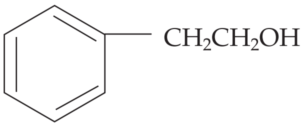
$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_2OH$$

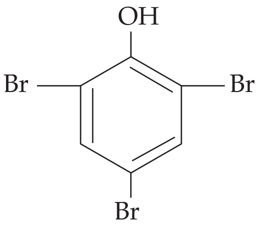
(*ii*) 

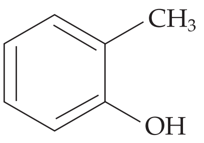
$$CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2-CH_2OCH_2CH_3$$

(*iii*) $HOCH_2—CHOH—CH_2OH$

(*iv*) $HOCH_2—CH_2—CH_2OH$

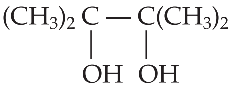
(*v*) 

(*vi*) 

(*vii*) 

(*viii*) $HOCH_2CH_2OH$

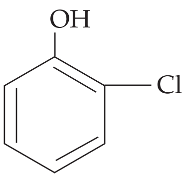
(*ix*) $(CH_3)_3COH$

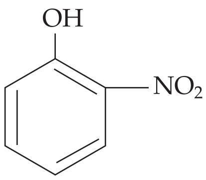
(*x*) 

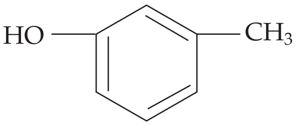
$$(CH_3)_2\underset{\underset{\displaystyle OH}{|}}{C}-\underset{\underset{\displaystyle OH}{|}}{C}(CH_3)_2$$

2. What are primary, secondary and tertiary alcohols? Give one example of each.

3. Discuss briefly a method by which primary, secondary and tertiary alcohols be distinguished.
4. Write the names of the following compounds:

(*i*)


(*ii*)


(*iii*)


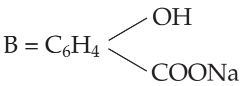
5. Give the IUPAC names of the following:
   - (*i*) Isobutyl alcohol
   - (*ii*) Benzyl alcohol
   - (*iii*) Isopropyl alcohol
   - (*iv*) *t*-Butyl alcohol.
6. How are alcohols obtained from:

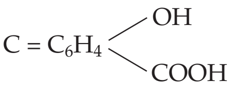
   (*i*) haloalkanes (*ii*) aldehydes and ketones? Give one example in each case.
7. What is Grignard reagent? How is it useful for the preparation of primary, secondary and tertiary alcohols?
8. How many isomers are possible for the molecular formula $C_4H_{10}O$? Which one is optically active and why?
9. Show with the help of chemical equations, what happens when cumene hydroperoxide is treated with dilute H_2SO_4.
10. What is fermentation? How is ethyl alcohol obtained from molasses?
11. What are primary, secondary and tertiary alcohols? How can these be obtained with the help of Grignard reagent?
12. Account for the following:
    - (*i*) The order of reactivity of halogen acids towards alcohols is: HI > HBr > HCl.
    - (*ii*) The order of acidity of alcohols falls in the order: primary > secondary > tertiary.
13. What happens when primary, secondary and tertiary alcohols are:
    - (*i*) oxidised using alkaline potassium permanganate?
    - (*ii*) passed over heated copper at 570 K?
14. How will you obtain the following, starting from ethanol:

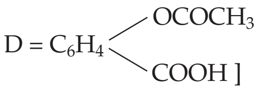
    (*i*) ethyl ethanoate, (*ii*) bromoethane, (*iii*) sod. ethoxide, (*iv*) ethanal, (*v*) ethene, (*vi*) iodoform and (*vii*) diethyl ether?
15. What happens when excess of ethyl alcohol is heated with conc. H_2SO_4 at 413 K?
16. Write balanced chemical equation for the dehydration of ethanol.

Long Answer Type Questions

1. What is fermentation? How is ethanol obtained by fermentation of molasses giving chemical equations?
2. How will you obtain the following, starting from ethyl alcohol?
   - (*i*) ethyl bromide
   - (*ii*) iodoform
   - (*iii*) sodium ethoxide
   - (*iv*) diethyl ether
   - (*v*) acetaldehyde.
3. An organic compound A having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. A on treatment with CO_2 and NaOH at 400 K under pressure gives B which on acidification gives a compound C. C reacts with acetyl chloride to give D which is a popular pain-killer. Deduce the structures of A, B, C, and D.

[Ans. A = C_6H_5OH,

$B = C_6H_4\begin{cases} OH \\ COONa \end{cases}$


$C = C_6H_4\begin{cases} OH \\ COOH \end{cases}$


$D = C_6H_4\begin{cases} OCOCH_3 \\ COOH \end{cases}$]

4. Draw the structures of eight isomeric pentyl alcohols, $C_5H_{11}OH$ and name each alcohol according to IUPAC system.
5. Give the names of the chief products expected from the reaction, if any, of ethanol with:

   (*i*) Cu at 573 K (*ii*) P + Br_2 (*iii*) H_2SO_4 heat (*iv*) HBr.
6. What are primary, secondary and tertiary alcohols? What happens when these three classes of alcohols are:
   - (*i*) passed over heated copper
   - (*ii*) oxidised with $K_2Cr_2O_7$ and H_2SO_4?
7. How can ethanol be prepared from: (*i*) ethene (*ii*) bromoethane? How does it react with sulphuric acid as: (*i*) at 383 K (*ii*) when distilled under reduced pressure at 383 K (*iii*) with excess alcohol at 413 K and (*iv*) with excess sulphuric acid at 440 K? Write the chemical equations for the reactions involved.

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. Diastase
2. Formaldehyde (methanal)
3. HI > HBr > HCl
4. $CH_3—CH_2OH \xrightarrow[\text{433 – 433 K}]{\text{conc. } H_2SO_4} CH_2 = CH_2$

   $\xrightarrow[\text{(Baeyer's reagent)}]{\text{alk. } KMnO_4} HO — CH_2 — CH_2 — OH$
5. Methanol and pyridine
6. Acidic
7. Primary > secondary > tertiary.
8. 100% ethyl alcohol is called absolute alcohol
9. Acidic or alkaline $KMnO_4$, acidic $K_2Cr_2O_7$.
10. Invertase, zymase
11. Isobutylene
12. 2-Butanol
13. $C_6H_5OH > H_2O > CH_3OH$.
14. Esterification
15. Tertiary > secondary > primary
16. A mixture of absolute alcohol (20%), petrol (80%) and some benzene.
17. Tertiary < secondary < primary.
18. Due to intermolecular H-bonding between alcohol and water molecules.
19. Ethanal
20. Alcohols and amines combine with anhyd. $CaCl_2$ to form complexes. For example, with C_2H_5OH it gives a complex of molecular formula $CaCl_2–3C_2H_5OH$.

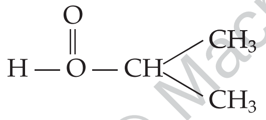
COMPETITION FILE

SUBJECTIVE PROBLEMS

1. A compound D ($C_8H_{10}O$), on treatment alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E ($C_7H_6O_6$). Write the structures of D and E and explain the formation of E.

   [**Ans.** (D) = 1–Phenylethanol and (E) = Benzoic acid]

2. An ester A ($C_4H_8O_2$), on treatment with excess methyl magnesium chloride followed by acidification gives an alcohol B as the sole organic product. Alcohol B, on oxidation with NaOCl followed by acidification, gives acetic acid. Deduce the structures of A and B. Show the reactions involved.

   [**Ans.** A =  and

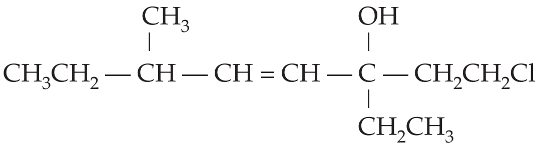
   B = $CH_3CH(CH_3)OH$]

3. Sodium metal may be used to remove last traces of H_2O from benzene but not from elhanol. Why?

   [**Ans.** Sodium metal reacts with ethanol.]

4. Draw the structures of the following:
   (*i*) 1, 2, 3-propanetriol.
   (*ii*) l-chloro-6-methyl-3-ethyloct-4-en-3-ol.

   [**Ans.** (*i*) $HOCH_2CHOHCH_2OH$

   (*ii*) 

   $CH_3CH_2 — \underset{}{\overset{CH_3}{\overset{|}{CH}}} — CH = CH — \underset{\underset{CH_2CH_3}{|}}{\overset{\overset{OH}{|}}{C}} — CH_2CH_2Cl$

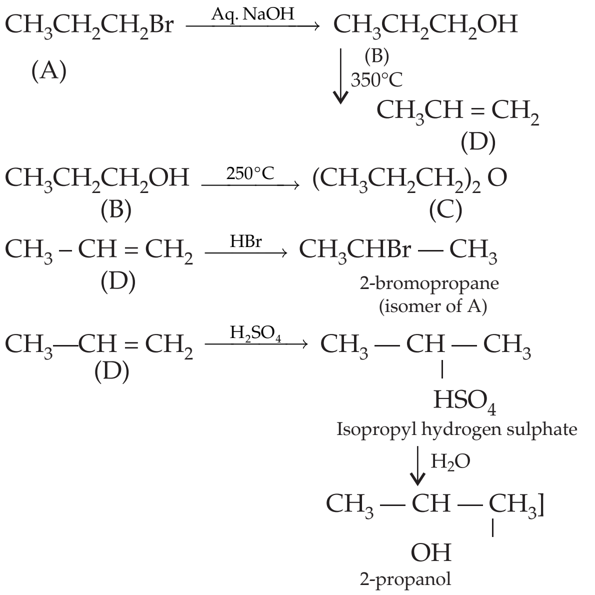
5. *0.369g of a bromo derivative of a hydrocarbon (A) when vaporised occupied 67.2 mL at N.T.P. (A) on reaction with aqueous NaOH gives (B). (B) when passed over alumina at 250°C gives a neutral compound (C) while at 350°C, it gives a hydrocarbon (D). (D) when treated with HBr gave an isomer of (A). When (D) is treated with conc. H_2SO_4 and the product is diluted with water and distilled, (E) is obtained. Identify from (A) to (E) and explain the reactions involved.*

   [**Ans.** A = $\underset{\text{(1-bromopropane)}}{CH_3CH_2CH_2Br}$, B = $\underset{\text{1-propanol}}{CH_3CH_2CH_2OH}$,

   C = $\underset{\text{Di-}n\text{-propyl ether}}{(CH_3CH_2CH_2)_2\ O}$,

   D = $\underset{\text{propene}}{CH_3CH = CH_2}$ and E = $\underset{\text{2-propanol}}{CH_3CHOHCH_3}$.

   Mol. formula weight of A on calculation comes out to be 123.

   $$\underset{\text{(A)}}{CH_3CH_2CH_2Br} \xrightarrow{\text{Aq. NaOH}} \underset{\text{(B)}}{CH_3CH_2CH_2OH} \xrightarrow{350°C} \underset{\text{(D)}}{CH_3CH = CH_2}$$

   $$\underset{\text{(B)}}{CH_3CH_2CH_2OH} \xrightarrow{250°C} \underset{\text{(C)}}{(CH_3CH_2CH_2)_2\ O}$$

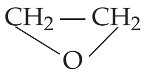
   $$\underset{\text{(D)}}{CH_3 - CH = CH_2} \xrightarrow{\text{HBr}} \underset{\substack{\text{2-bromopropane} \\ \text{(isomer of A)}}}{CH_3CHBr — CH_3}$$

   $$\underset{\text{(D)}}{CH_3—CH = CH_2} \xrightarrow{H_2SO_4} \underset{\text{Isopropyl hydrogen sulphate}}{CH_3 — \underset{\underset{HSO_4}{|}}{CH} — CH_3} \xrightarrow{H_2O} \underset{\text{2-propanol}}{CH_3 — \underset{\underset{OH}{|}}{CH} — CH_3}]$$

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. Reaction of  with RMgX leads to the formation of:

(*a*) RCHOHR (*b*) $RCHOHCH_3$

(*c*) $\begin{matrix}R\\R\end{matrix}\!\!>CHCH_2OH$ (*d*) RCH_2CH_2OH

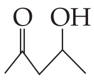
2. Among the following compounds, the strongest acid is

(*a*) $HC\equiv CH$ (*b*) C_6H_6

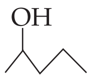
(*c*) C_2H_6 (*d*) CH_3OH

3. Which one of the following will most readily be dehydrated in acidic condition?

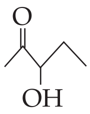
(*a*)



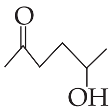
(*b*)



(*c*)



(*d*)



4. The compound that will react most readily with NaOH to form methanol is:

(*a*) $(CH_3)_4N^+I^-$ (*b*) CF_3OCH_3

(*c*) $(CH_3)_3S^+I^-$ (*d*) $(CH_3)_3CCl$

5. Identify the set of reagents/reaction conditions of X and Y in the following set of transformations:

(*a*) X = dilute aqueous NaOH, 20°C, Y = HBr/ acetic acid, 20°C

(*b*) X = concentrated alcoholic NaOH, 80°C; Y = HBr/ acetic acid, 20°C

(*c*) X = dilute aqueous NaOH, 20°C; Y = Br_2/ $CHCl_3$, 0ºC

(*d*) X = concentrated alcoholic NaOH, 80°C; Y = Br_2/ $CHCl_3$, 0°C

6. Consider the following reaction:

$$\text{Ethanol} \xrightarrow{PBr_3} X \xrightarrow{\text{alc. KOH}} Y \xrightarrow[\text{(ii) } H_2O\text{, heat}]{\text{(i) } H_2SO_4\text{, room temperature}} Z;$$

the product Z is

(*a*) $CH_3CH_2—O—CH_2—CH_3$

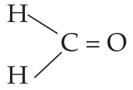
(*b*) $CH_3—CH_2—O—SO_3H$

(*c*) CH_3CH_2OH

(*d*) $CH_2=CH_2$

7. $HOCH_2CH_2OH$ on heating with periodic acid gives

(*a*) 2HCOOH (*b*) $\begin{matrix}CHO\\|\\CHO\end{matrix}$

(*c*) 2  (*d*) $2CO_2$

8. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is

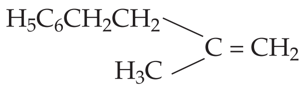
(*a*) 1-Butanol (*b*) 2-Butanol

(*c*) 2-Methylpropan-2-ol (*d*) 2-Methylpropanol

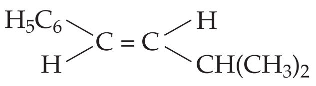
9. The main product of the following reaction is

$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{Conc. } H_2SO_4}$$

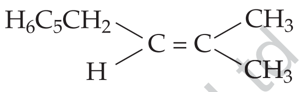
(*a*)



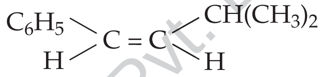
(*b*)

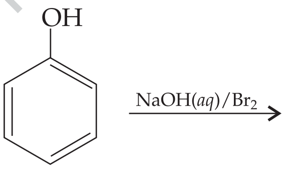


(*c*)

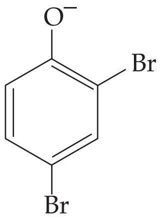


(*d*)

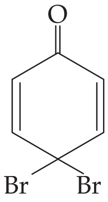


10. In the reaction  the intermediate(s) is (are)

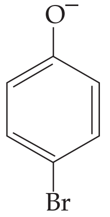
(*a*)



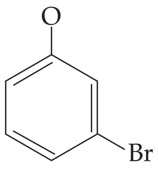
(*b*)



(*c*)



(*d*)



11. Which of the following compounds will show metamerism?

(*a*) $CH_3COC_2H_5$ (*b*) $C_2H_5SC_2H_5$

(*c*) CH_3OCH_3 (*d*) $CH_3OC_2H_5$.

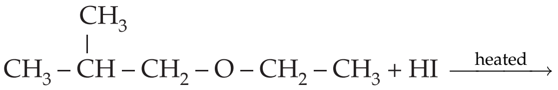
12. The major organic product in the reaction,

$CH_3OCH(CH_3)_2 + HI \longrightarrow$ products is

(*a*) $CH_3I + (CH_3)_2CHOH$ (*b*) $CH_3OH + (CH_3)_2CHI$

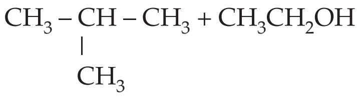
(*c*) $ICH_2OCH(CH_3)_2$ (*d*) $CH_3O\underset{\displaystyle I}{\underset{|}{C}}(CH_3)_2$

13. In the reaction:

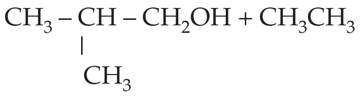


$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-CH_2-O-CH_2-CH_3+HI\xrightarrow{\text{heated}}$$

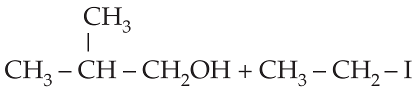
Which of the following compounds will be formed?

(*a*) 

$CH_3-\underset{CH_3}{\underset{|}{C}}H-CH_3+CH_3CH_2OH$

(*b*) 

$CH_3-\underset{CH_3}{\underset{|}{C}}H-CH_2OH+CH_3CH_3$

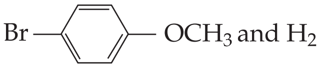
(*c*) 

$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2OH+CH_3-CH_2-I$

(*d*) none of these

14. In the reaction 

the products are

(*a*) 

(*b*) 

(*c*) 

(*d*) 

(B) Fill in the Blanks

Fill in the blank spaces:

1. The halogen acid which is most reactive towards alcohol is _______.
2. Lower alcohols are highly soluble in water due to ____________.
3. Primary, secondary and tertiary alcohols can be distinguished by the actions of _______ copper.
4. Tertiary alcohols when passed over heated copper undergo _______ to form _______.
5. A primary alcohol on oxidation gives an _______ which on further oxidation gives a _______ containing the same number of carbon atoms.

(C) True/False Statements

Write T for true and F for false statements:

1. Tertiary alcohols are more reactive towards halogen acids than secondary alcohols.
2. Sodium ethoxide is prepared by the reaction of ethanol with aqueous sodium hydroxide.
3. Drinking of methyl alcohol causes blindness.
4. Lower alcohols are more soluble in water than higher alcohols.
5. The boiling point of 1-butanol (mol. mass 74) is higher than that of ethylene glycol (mol. mass 62).
6. Dynamite contains 2, 4, 6-trinitrotoluene.
7. Methanol can be distinguished from ethanol by haloform reaction.

(D) Assertion-Reason Type Questions

In the following questions, two statements are given, one labelled as Assertion (A) and the other as Reason (R). Examine the two statements carefully and mark the correct choice out of (a), (b), (c) and (d) according to the instructions below:

If both **A** and **R** are correct and **R** is the correct explanation of A, mark (*a*).

If both **A** and **R** are correct but **R** is not the explanation of **A**, mark (*b*).

If **A** is correct but **R** is wrong, mark *(c).*

If **A** is wrong but **R** is correct, mark *(d).*

1. ***Assertion (A)*** : Alcohol is denatured by the addition of methyl alcohol.

Reason (R) : Drinking of methyl alcohol causes blindness.

2. ***Assertion (A)*** : Methanol can be distinguished from ethanol by haloform reaction.

Reason (R) : Propanol-2 gives haloform reaction.

3. ***Assertion (A)*** : 100% ethyl alcohol cannot be obtained by fractional distillation.

Reason (R) : A mixture of water and alcohol on distillation forms an azeotrope containing 95% alcohol and 5% water.

SOME ADDITIONAL QUESTIONS

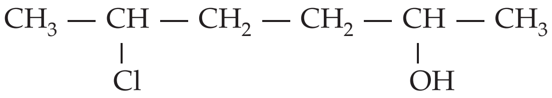
I. Multiple Choice Questions

Choose one or more than one correct answers:

1. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields
   - (*a*) *o*-Cresol
   - (*b*) *m*-Cresol
   - (*c*) 2, 4-Dihydroxytoluene
   - (*d*) Benzyl alcohol
2. How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature?
   - (*a*) 1
   - (*b*) 2
   - (*c*) 3
   - (*d*) 4
3. CH_3CH_2OH can be converted into CH_3CHO by
   - (*a*) catalytic hydrogenation
   - (*b*) treatment with $LiAlH_4$
   - (*c*) treatment with pyridinium chlorochromate
   - (*d*) treatment with $KMnO_4$

4. The process of converting alkyl halides into alcohols involves
   (*a*) addition reaction
   (*b*) substitution reaction
   (*c*) dehydrohalogenation reaction
   (*d*) rearrangement reaction

5. IUPAC name of the compound given below is



$$CH_3-\underset{\substack{|\\Cl}}{CH}-CH_2-CH_2-\underset{\substack{|\\OH}}{CH}-CH_3$$

   (*a*) 2-Chloro-5-hydroxyhexane
   (*b*) 2-Hydroxy-5-chlorohexane
   (*c*) 5-Chlorohexan-2-ol
   (*d*) 2-Chlorohexan-5-ol

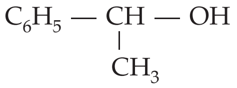
6. IUPAC name of *m*-cresol is
   (*a*) 3-methylphenol
   (*b*) 3-chlorophenol
   (*c*) 3-methoxyphenol
   (*d*) benzene-1, 3-diol

7. Which of the following compounds will react with sodium hydroxide solution in water?
   (*a*) C_6H_5OH
   (*b*) $C_6H_5CH_2OH$
   (*c*) $(CH_3)_3\,COH$
   (*d*) C_2H_5OH

8. Which of the following are used to convert RCHO into RCH_2OH?
   (*a*) H_2/Pd
   (*b*) $LiAlH_4$
   (*c*) $NaBH_4$
   (*d*) Reaction with RMgX followed by hydrolysis

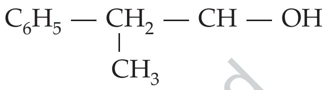
9. Which of the following reagents can be used to oxidise primary alcohols to aldehydes?
   (*a*) CrO_3 in anhydrous medium
   (*b*) $KMnO_4$ in acidic medium
   (*c*) Pyridinium chlorochromate
   (*d*) Heat in the presence of Cu at 573 K

10. Which of the following are benzylic alcohols?
   (*a*) $C_6H_5—CH_2—CH_2OH$
   (*b*) $C_6H_5—CH_2OH$
   (*c*)



$$C_6H_5-\underset{\substack{|\\CH_3}}{CH}-OH$$

   (*d*)



$$C_6H_5-\underset{\substack{|\\CH_3}}{CH_2}-CH-OH$$

II. Short Answer Type Questions

1. Name the factors responsible for the solubility of alcohols in water.
2. What is denatured alcohol?
3. Out of 2-chloroethanol and ethanol which is more acidic and why?
4. Suggest a reagent for conversion of ethanol to ethanal.
5. Suggest a reagent for conversion of ethanol to ethanoic acid.
6. Preparation of alcohols from alkenes involves the electrophilic attack on alkene carbon atom. Explain its mechanism.

ANSWERS

(A) Multiple Choice Questions

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

(B) Fill in the Blanks

1. HI 2. hydrogen bonding 3. hot
4. dehydration, alkene 5. aldehyde, carboxylic acid

(C) True/False Statements

1. True 2. False, with Na metal 3. True 4. True
5. False, glycol has higher b.p. 6. False 7. True

(D) Assertion-Reason Type Questions

1. (*a*) 2. (*b*) 3. (*a*)

Some Additional Questions

I. Multiple Choice Questions

1. (*d*) 2. (*a*) 3. (*c*) 4. (*b*) 5. (*c*) 6. (*a*) 7. (*a*)
8. (*a*), (*b*), (*c*) 9. (*a*), (*c*), (*d*) 10. (*b*), (*c*)

14
CHAPTER

Aromatic Compounds (Benzene and Phenol)

LEARNING OBJECTIVES

- Structure and bonding
  - Explain the structure of benzene and compare the Kekulé and delocalised models for benzene in terms of *p*-orbital overlap forming π-bonds.
  - Use the evidence (e.g. bond lengths, enthalpy of hydrogenation and resistance to reaction compared to alkenes) to explain how this supports the delocalised model for the structure of benzene.
  - Explain that delocalisaton gives stability to the benzene molecule.
- Electrophilic substitution of arenes
  - Describe the reactions of arenes with concentrated nitric acid in the presence of sulphuric acid.
  - Explain the mechanism of electrophilic substitution for the reaction of arenes with concentrated nitric acid in the presence of concentrated sulphuric acid.
  - Explain the mechanism of electrophilic substitution for the reaction of arenes with a halogen in the presence of a halogen carrier.
  - Explain the mechanism of electrophilic substitution for the halogenation reactions of arenes limited to monosubstitution of the arene only.
  - Describe Friedel-Crafts alkylation and acylation reactions.
  - Explain the importance of Friedel-Crafts alkylation in organic synthesis, for example, industrial production of ethylbenzene and manufacture of polystyrene.
  - Explain the mechanism for the alkylation and acylation reactions of arenes using $AlCl_3$ as a catalyst.
- Phenols
  - Describe the industrial preparation of phenol from petroleum oil.
  - Describe the preparation of phenol from sodium benzenesulfonate, chlorobenzene (Dow's process) and from the hydrolysis of diazonium salts.
  - Explain why phenol is more reactive than benzene and therefore more susceptible to electrophilic substitution.
  - Explain the substitution patterns (*ortho* and *para*) for phenol.
  - Describe the reactions of phenol with dilute and concentrated nitric acid and Kolbe's reaction to form salicylic acid (2-hydroxybenzoic acid).

14.1 INTRODUCTION

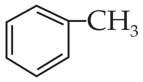
The relatively low number of hydrogen in proportion to the number of carbon is a characteristic of aromatic compounds. Aromatic compounds are usually found in tree and plant oils. While benzaldehyde (C_6H_5CHO) is found in cherries and peaches, toluene may be extracted from balsam tree and benzene is isolated from coal tar obtained from the destructive distillation of coal. Due to their pleasant smell, the name **aromatic**

compounds was given to the members of their family. Many natural products such as the hormone oestrone and the opiate morphine contain aromatic parts. Nowadays, the chemical meaning of the term ‘aromatic’ is no longer correlated with the compound’s smell. Some of the aromatic compounds are actually toxic and foul-smelling. The term “aromatic” now applies to a family of compounds which contain benzene rings. The chemical behaviour of aromatic compounds is considerably different from that of aliphatic compounds.

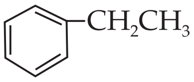
14.2 AROMATIC HYDROCARBONS (ARENES)

Benzene is the simplest aromatic hydrocarbon. Arenes are mixed aromatic-aliphatic compounds. An alkyl, alkenyl or alkynyl group attached to a benzene ring constitutes an arene. Thus, arenes can be classified into the following types:

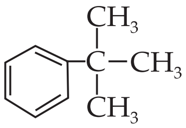
Alkyl benzenes



Toluene

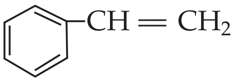


Ethylbenzene

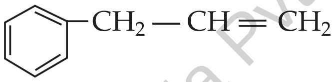


Tert-butyl benzene

Alkenyl benzenes

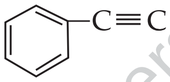


Styrene



3-Phenyl propene-1

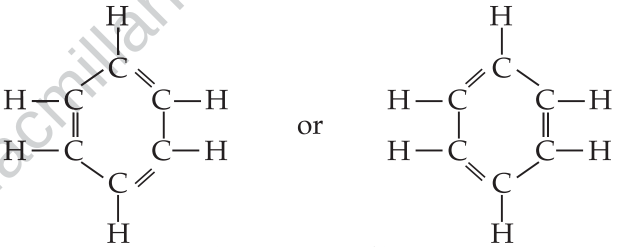
Alkynyl benzenes



Phenyl acetylene

14.3 STRUCTURE OF BENZENE

Kekule’s Structure. According to Kekule, six carbon atoms of benzene are linked to each other by alternate single and double covalent bonds to form a hexagonal ring as shown in the following figure:



Kekule's structure of benzene

Each carbon atom is linked to one hydrogen atom, thus, conforming to its molecular formula.

Drawbacks of Kekule’s Structure. Kekule’s structure does not explain the following observations:

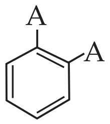
(*i*) **Chemical reactions.** Benzene does not undergo addition reactions and fails to decolorise Baeyer’s reagent. In spite of the presence of three double bonds as established by Kekule’s structure, it readily undergoes electrophilic substitution reaction in which the benzene ring is retained.

(*ii*) **Heat of combustion.** On the basis of Kekule’s structure, the heat of combustion of benzene is expected to be 3449.0 kJ mol^{-1}. But the experimental value is 3298.5 kJ mol^{-1}. Thus, benzene has 150.5 kJ mol^{-1} of energy less than that of Kekule’s structure. Benzene is, therefore, more stable than the structure proposed by Kekule.

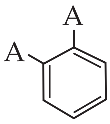
Kekule

(*iii*) **Heat of hydrogenation.** On the basis of Kekule's structure, the heat of formation of benzene is expected to be 358.0 kJ mol^{-1}. But the experimental value is 208.5 kJ mol^{-1}. This again shows that benzene is more stable than expected from Kekule's structure.

(*iv*) ***Ortho*-disubstituted product.** Benzene forms only one *ortho*-disubstituted product, whereas Kekule's structure predicts two *o*-disubstituted products as shown below:



Presence of double bond between the substituents



Presence of single bond between the substituents

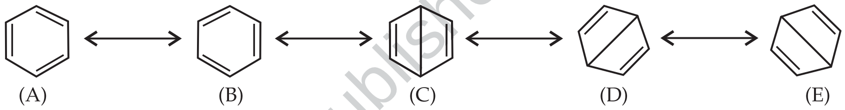
(*v*) **Carbon-carbon bond lengths.** X-ray diffraction studies show that all the carbon-carbon bond lengths are identical, *viz.,* 1.397 Å and lie in between the single and double bonds. This is not in accordance with Kekule's structure which contains two kinds of the carbon-carbon bonds.

The anomalies in the Kekule structure can be explained by resonance structure and molecule orbital structure.

Resonance Structure of Benzene

If a single structure does not explain all the properties of a compound, then a number of different structures each of which explains some properties of the compound, are suggested. These different structures in which the relative position of the atoms is the same are called *resonance* structures or *canonical* structures. The real structure of the molecule is not represented by any one of the canonical structures but is a resonance hybrid of various resonance structures. The various resonance structures are separated by a double headed ($\leftrightarrow$) arrow. This arrow should be clearly distinguished from that used for an equilibrium ($\rightleftharpoons$).

In the light of resonance theory, benzene can be represented as a resonance hybrid of the following structures:



Out of the five resonating structures, major contribution is from structures (A) and (B). Other structures contribute only to a small extent.

Molecular Orbital Structure of Benzene

Structure of benzene can be best described by using the orbital concept. Each carbon atom in benzene is sp^2 hybridised and, thus, forms three σ-bonds, two with adjacent carbon atoms and one with hydrogen. Thus, all the six carbons and six hydrogen atoms lie in the same plane and the angle between two adjacent σ-bonds is 120° [Fig. 14.1(*a*)].

Each carbon is still left with an unhybridised *p*-orbital lying above and below the plane of benzene ring. Each one of these *p*-orbitals overlap sidewise on either sides to form two sets of π-electron clouds [Figs. 14.1(*b*), (*c*)]. π-electrons are delocalised as these can move over all the six carbon atoms [Fig. 14.1(*d*)]. As a result of this delocalisation two continuous ring like electron clouds one above and the other below the plane of carbon atoms [Fig. 14.1(*e*)] are formed. Bond angles and bond lengths in the molecule of benzene are mentioned in [Fig. 14.1(*f*)].

Evidence in Support of Orbital Structure

(*i*) **Unusual stability.** Benzene molecule exhibits unusual stability and resists the formation of addition products. This can easily be understood in terms of delocalisation of π-electrons which is responsible for aromaticity.

(*ii*) **Isomer number.** According to orbital concept, all the six carbons in benzene are completely equivalent. Similarly, all the six hydrogen atoms also occupy identical positions. Thus, benzene should form only one monosubstituted and three disubstituted products. This has been found to be so in actual practice.

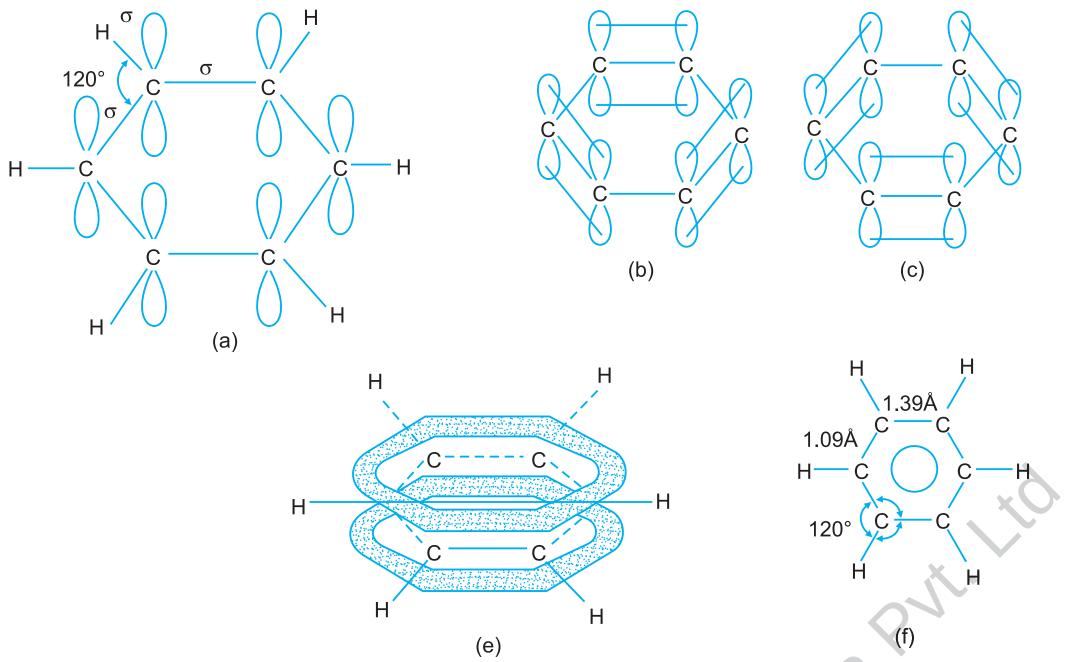


Fig. 14.1: *Orbital structure of benzene*

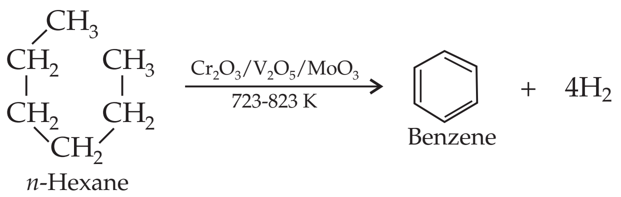
(*iii*) Electrophilic substitution reactions. There are two continuous ring-like π-electrons clouds one above and the other below the plane of carbon atoms. The π-electrons are easily attacked by electrophiles. Hence, benzene undergoes electrophilic substitution reactions.

14.4 METHODS OF OBTAINING BENZENE ON INDUSTRIAL SCALE

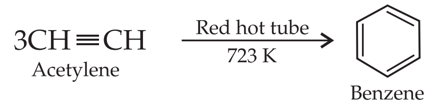
(*i*) From Coal tar (Industrial Method). The light oil fraction (boiling range 353 K to 443 K) of coal tar which contains mainly benzene, toluene and xylene, is treated with conc. H_2SO_4 to remove impurities of pyridine and thiophene. To remove acidic impurities such as phenol, the organic layer is washed successively with water and aqueous KOH and finally after washing with water it is subjected to fractional distillation to obtain three main fractions as given below:

- (*a*) *90% benzol* (boiling range 353 K to 383 K). It consists of 70% benzene, 24% toluene and rest xylene. Its careful fractionation gives benzene, toluene and xylene.
- (*b*) *90% toluol* (boiling range 383 K to 413 K). It consists mainly of xylene and small amounts of benzene and toluene.
- (*c*) *Solvent naphtha or Benzene* (boiling range 413 K to 443 K). It mainly consists of xylene.

(*ii*) From Petroleum (Industrial Method). Aromatic hydrocarbons are synthesized by *catalytic reforming* of alkanes obtained from petroleum which involves cyclization and aromatization. For example, hexane can be converted to cyclohexane and then to benzene by passing its vapours over Cr_2O_3, V_2O_5 or MoO_3 at 723 K to 823 K. Similarly, *n*-heptane gives toluene.

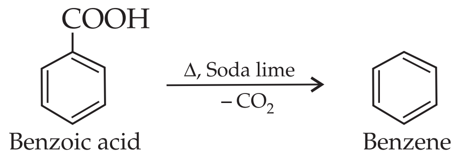


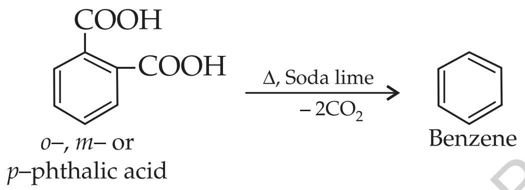
***(iii)* From Acetylene.** Acetylene on passing through a red hot tube trimerizes to benzene.



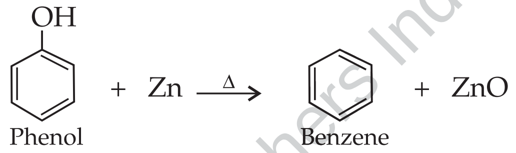
14.5 LABORATORY METHODS OF PREPARING BENZENE

(*a*) Decarboxylation of benzoic acid or phthalic acid with soda lime

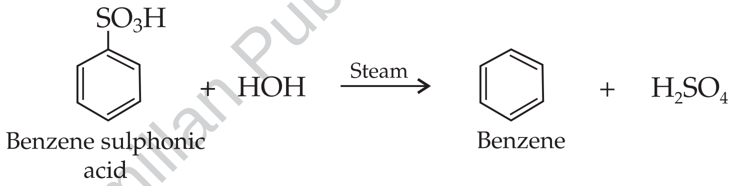




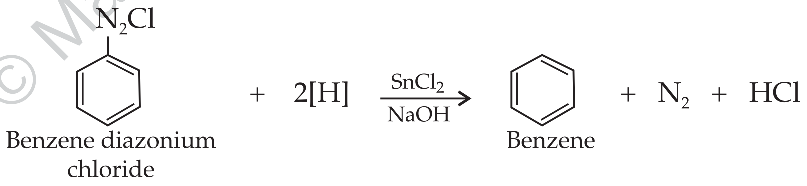
(*b*) Distillation of phenol with zinc dust (reduction)



(*c*) By hydrolysis of benzene sulphonic acid with super heated steam or boiling with HCl under pressure



(*d*) By reduction of benzene diazonium chloride with alkaline sodium stannate



14.6 PROPERTIES OF BENZENE

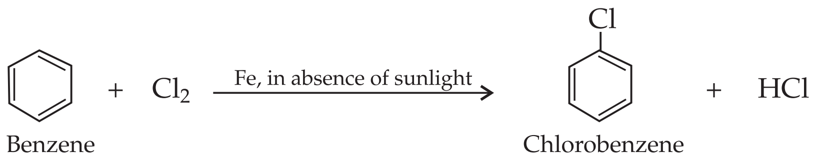
14.6.1 Physical Properties

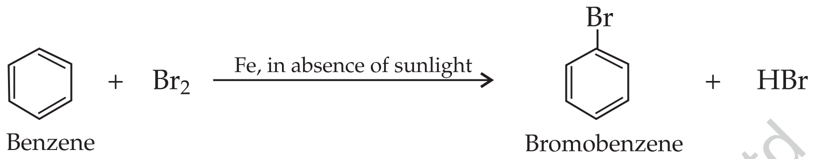
1. Benzene is a colourless liquid with a boiling point of 80.1°C.
2. It gives an aromatic gasoline-like odour.
3. It is lighter than water with a density of 0.8765 g/cm^3.
4. It is almost insoluble in water but dissolves freely in alcohol, $CHCl_3$, CCl_4 and diethyl ether.

14.6.2 Chemical Properties

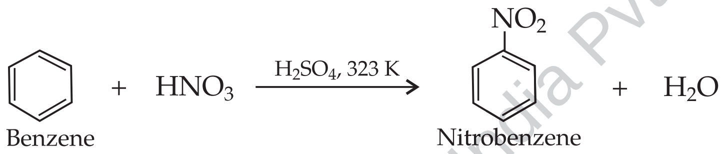
Substitution Reactions of Benzene

(*a*) **Halogenation.** Benzene reacts with chlorine or bromine in the presence of a catalyst (iron, iron halide or aluminium halide) and in the absence of sunlight to form chlorobenzene or bromobenzene. As hydrogen atom is displaced by a halogen, the reaction is called **halogenation.**

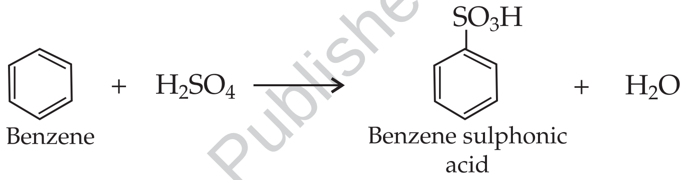




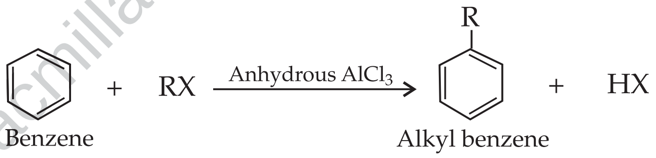
(*b*) **Nitration.** Benzene on warming with a mixture of nitric acid and sulphuric acid forms nitrobenzene. As hydrogen atom is replaced by a nitro group (–NO_2), the reaction is called **nitration.**



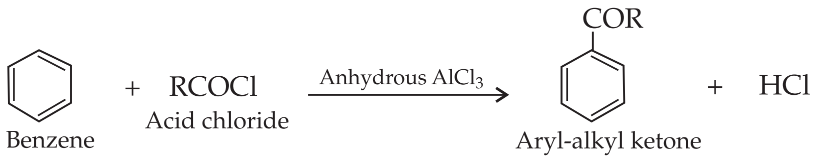
(*c*) **Sulphonation.** Benzene on warming with conc. sulphuric acid forms benzene sulphonic acid. As hydrogen atom is replaced by a sulphonic acid group (—SO_3H), the reaction is called **sulphonation.**

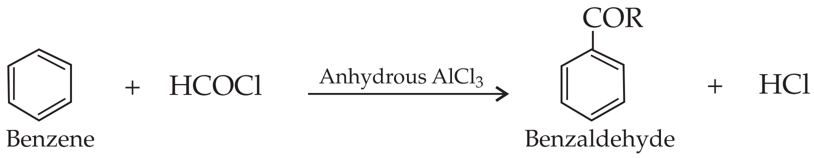


(*d*) **Friedel-Crafts alkylation.** This reaction is used for introducing an alkyl group in a benzene ring.



(*e*) **Friedel-Crafts acylation.** This reaction is used for the preparation of aromatic ketones. Benzene is treated with acid chloride in the presence of anhydrous aluminium chloride.

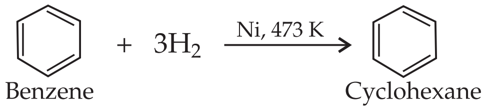




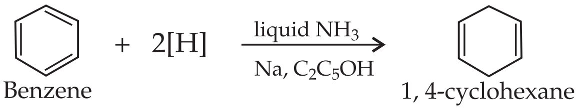
Friedel-Crafts alkylation and Friedel-Crafts acylation are of great synthetic utility to an organic chemist for the preparation of ethyl benzene and polystyrene.

Addition Reactions of Benzene

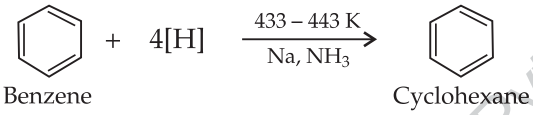
(*a*) **Addition of hydrogen.** When benzene vapours mixed with hydrogen are passed over nickel catalyst at 473 K, cyclohexane is formed.



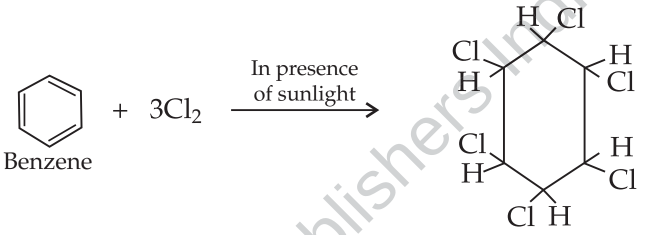
On reduction with sodium and ethanol in the presence of liquid ammonia, benzene gives 1, 4-cyclohexadiene. This reaction is called **Birch reduction.**



At higher temperature, even in the absence of ethanol, Birch reduction takes place and cyclohexane is formed.

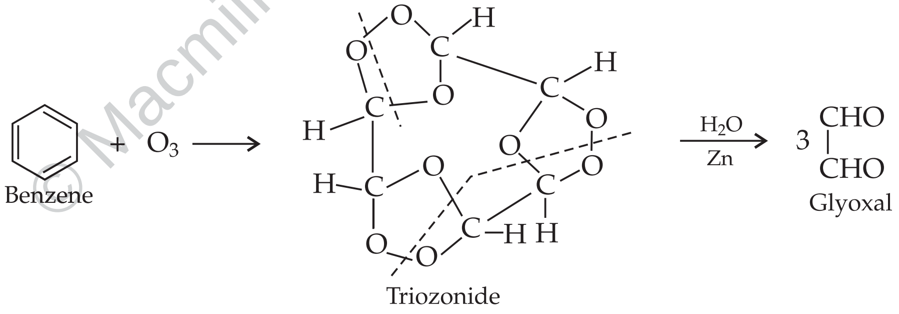


(*b*) **Addition of halogens.** Benzene on treatment with halogens in the presence of sunlight gives benzene hexahalides.



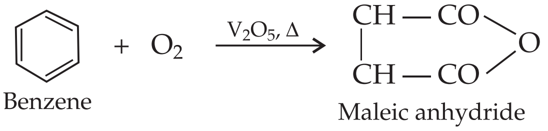
Benzene hexachloride (BHC)
or Hexachlorocyclohexane (HCH)

(*c*) **Addition of ozone.** Benzene reacts with ozone to form a triozonide, which is decomposed by water to give three molecules of glyoxal.



Oxidation Reactions of Benzene

When benzene vapours mixed with air are passed over heated vanadium pentoxide catalyst, maleic anhydride is obtained.



Combustion. When benzene burns in air or oxygen, carbon dioxide and water are formed.

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

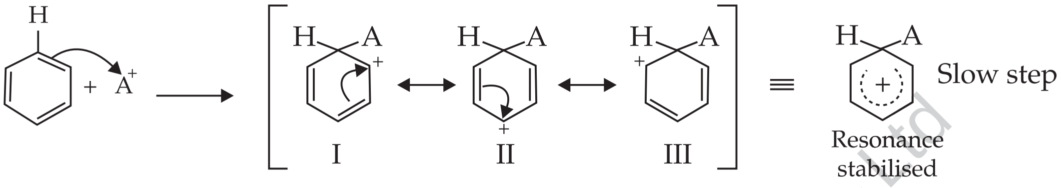
14.7 GENERAL MECHANISM OF ELECTROPHILIC SUBSTITUTION IN BENZENE

Electrophilic substitution reactions are initiated by substances which are either electrophilic themselves or which generate some electrophilic species. General mechanism involves the following sequence of steps:

(I) Generation of electrophile. To start with, there is preliminary reaction which generates an electrophile.

$$\mathrm{A - B} \longrightarrow \underset{\text{Electrophile}}{\mathrm{A^+}} + \mathrm{B^-}$$

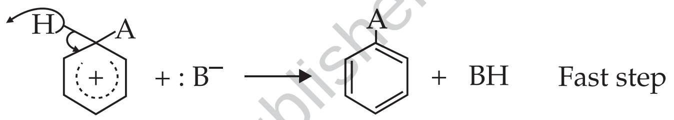
(II) Formation of intermediate carbocation (Carbonium ion). The electrophile attacks the π-electrons cloud of the benzene ring and, thus, brings about an electronic displacement. This results in the formation of **intermediate carbocation** which is resonance stabilized as shown below:



Resonating structures

During the formation of the carbocation, the aromaticity of the benzene ring is destroyed. Consequently, the formation of carbocation becomes slow and, hence, is the **rate determining step.**

(III) Abstraction of a proton from the carbocation. The base present in the reaction mixture abstracts the proton from the carbocation to form the final product. Since the aromatic character of the benzene ring is restored, this step is **fast** and, hence, is not the rate determining step.



Evidence in Support of the Mechanism

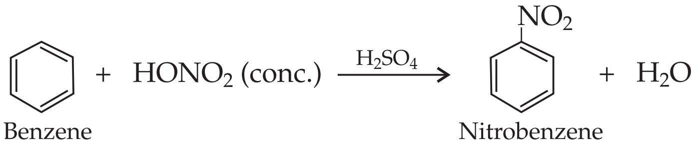
Electrophilic aromatic substitution involves two steps, *viz.*, formation of carbocation and abstraction of proton from carbocation, after the generation of an electrophile. The first step involving the formation of intermediate carbocation is slow and, hence, is the rate determining step of the reaction. The second step which involves the abstraction of a proton from the carbocation is fast hence, is not the rate determining step.

The above mechanism is supported by **isotope tracer technique** as described below:

A carbon-carbon bond is broken more slowly than a bond between carbon and hydrogen. Thus, if a hydrogen is lost in the rate determining step of a reaction, it will show an **isotope effect** on replacing hydrogen by deuterium. But this isotope effect has not been observed in aromatic electrophilic substitution reactions. For example, the rate of nitration of deutero-benzene is the same as the rate of benzene. Thus, proton elimination is not the rate determining step of the reaction. The step leading to the formation of carbocation does not involve the cleavage of carbon-hydrogen bond and, hence, it is the rate determining step of the reaction.

Nitration

This reaction involves the treatment of an aromatic compound with a mixture of nitric acid and sulphuric acid. For example,

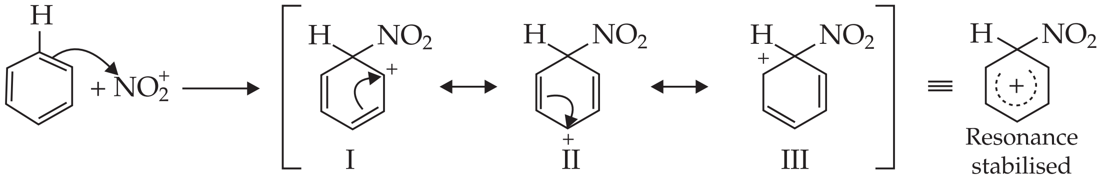


Mechanism. The various steps in the nitration of benzene can be outlined as below:

(I) Generation of electrophile

$$HONO_2 + 2H_2SO_4 \rightleftharpoons \underset{\text{Nitronium ion}}{NO_2^+} + H_3O^+ + 2HSO_4^-$$

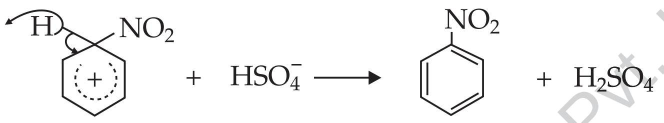
(II) Formation of carbocation



Resonating structures

Resonance stabilised carbocation

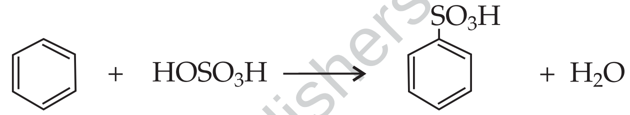
(III) Abstraction of proton from the carbocation



Nitrobenzene

Sulphonation

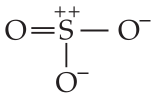
The sulphonation of an aromatic compound can be brought about by the action of conc. H_2SO_4 or oleum. For example,



Benzene

Benzene sulphonic acid

Mechanism. The attacking electrophilic reagent in this reaction is believed to be sulphur trioxide which is present as such in oleum or may be formed by the dissociation of sulphuric acid. The electrophilic nature of SO_3 molecule is due to the presence of electron deficient sulphur atom.



$$O{=}\overset{++}{\underset{\substack{|\\O^-}}{S}}{-}O^-$$

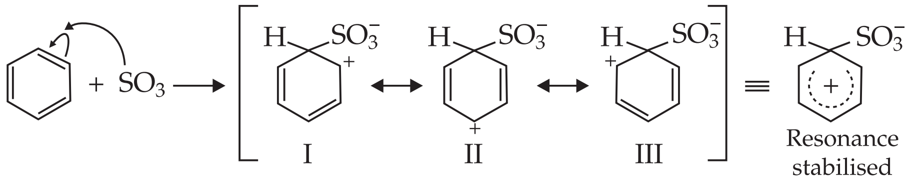
As the positive charge is concentrated on sulphur and negative charges are scattered on two oxygens, SO_3 molecule acts as an electrophile.

The complete mechanism of this reaction may be outlined as follows:

(I) Generation of electrophile

$$2H_2SO_4 \rightleftharpoons \underset{\text{Electrophile}}{SO_3} + HSO_4^- + H_3O^+$$

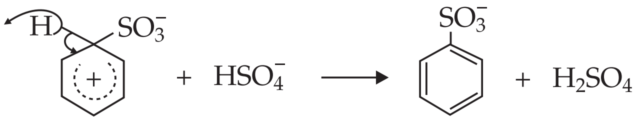
(II) Formation of carbocation



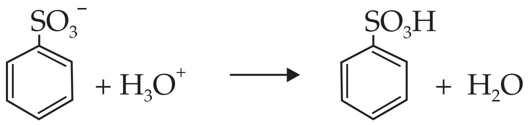
Resonating structures

Resonance stabilised carbocation

(III) Abstraction of proton from the carbocation

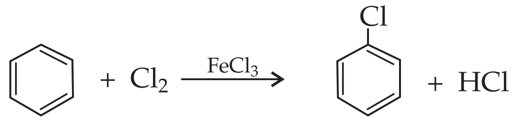


(IV) Formation of final product



Halogenation

Halogenation of benzene can be brought about by treating the compound with halogens in the presence of Lewis acids such as ferric halides and anhydrous aluminium chloride. Chlorination of benzene is considered below:



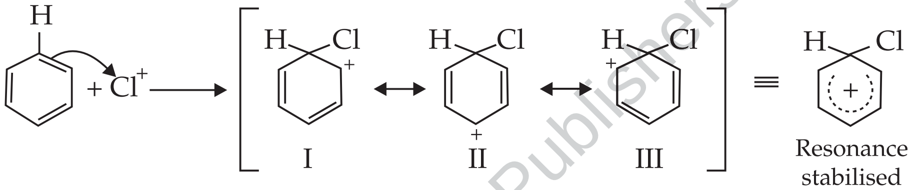
Benzene Chlorobenzene

Mechanism. Various steps involved in the reaction are as follow:

(I) Generation of electrophile

$$Cl - Cl + FeCl_3 \rightleftharpoons \overset{+}{Cl} + FeCl_4^-$$

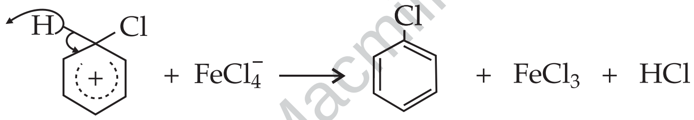
(II) Formation of carbocation



Resonating structures

Resonance stabilised carbocation

(III) Abstraction of proton from the carbocation



Chlorobenzene

Friedel-Crafts Acylation

When benzene is treated with acetyl chloride in the presence of anhydrous aluminium chloride, the formation of acetophenone takes place. This reaction is known is **Friedel-Crafts acylation.**

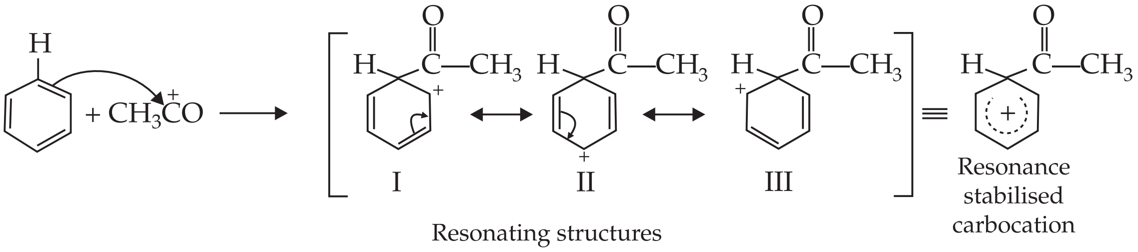
Benzene Acetyl chloride Acetophenone

Mechanism. The most probable mechanism of the above reaction is discussed as under:

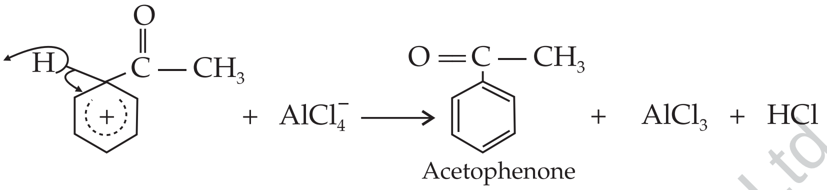
(I) Generation of electrophile

$$\underset{\text{Acetyl chloride}}{CH_3 - \overset{O}{\overset{\|}{C}} - Cl} + AlCl_3 \rightleftharpoons \underset{\text{Acetyl cation}}{CH_3 - \overset{O}{\overset{\|}{C^+}}} + AlCl_4^-$$

(II) Formation of carbocation

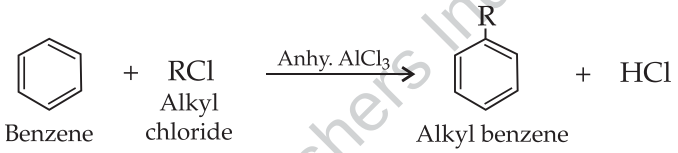


(III) Abstraction of proton from the carbocation



Friedel-Crafts Alkylation

In this reaction benzene or substituted benzene is treated with an alkyl halide in the presence of small amounts of Lewis acids ($AlCl_3$, BF_3, $FeCl_3$, etc.) It leads to the direct introduction of an alkyl group into the benzene ring.

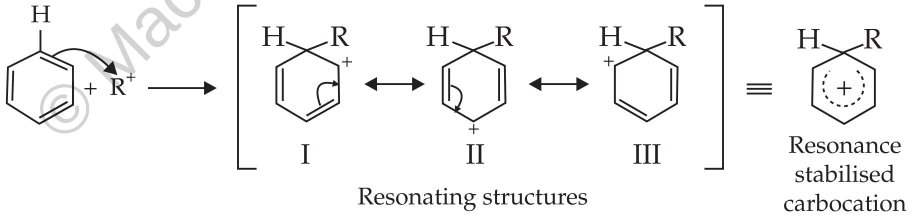


Mechanism. The reaction is believed to take place through the following steps:

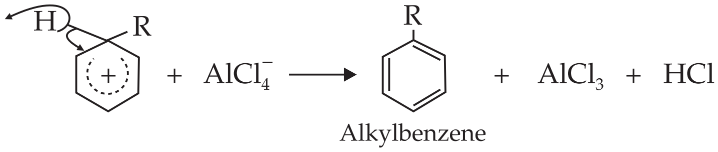
(I) Generation of electrophile

$$R—Cl + AlCl_3 \rightleftharpoons \underset{\text{Electrophile}}{R^+} + AlCl_4^-$$

(II) Formation of carbocation



(III) Abstraction of proton from the carbocation



14.8 EFFECT OF SUBSTITUENTS ON ORIENTATION AND REACTIVITY OF BENZENE

It has been observed that substituents already attached to the benzene ring not only govern the orientation of further substitution but also affect the reactivity of the benzene ring. It is discussed in brief as below:

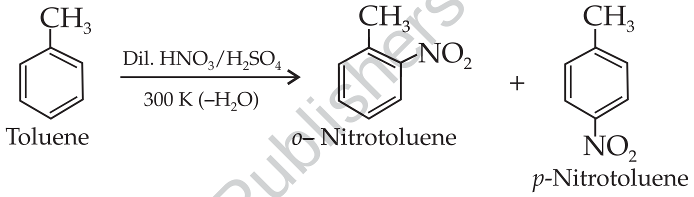
(I) Effect of substituents on orientation. As stated above, the nature of the group already attached to the benzene ring determines the position of the incoming group. In general, groups have been classified into two categories:

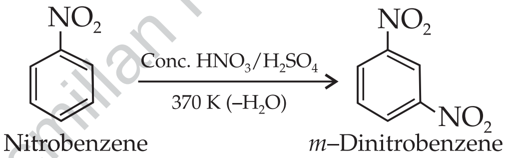
(*a*) *Ortho-para* directing groups. The groups which direct the incoming group towards *ortho* and *para* positions are called *ortho-para* directing groups. Groups such as –R, $–C_6H_5$, –OH, –SH, –OR, $–NH_2$, –NHR, $–NR_2$, –Cl, –Br, –I, etc., are all *ortho-para* directing groups.

(*b*) *Meta* directing groups. The groups which direct the incoming group towards *meta* position are called *meta* directing groups. Groups such as —COOH,—CHO,—CN,$—NO_2$,—COR,$—SO_3H$, etc., are all *meta* directing groups.

It may be mentioned that groups which contain double or triple bond are usually *meta* directing while those which do not contain multiple bonds are *ortho-para* directing. However, there are certain exceptions to this rule.

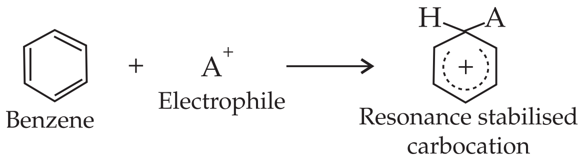
(II) Effect of substituents on reactivity. Reactivity of the benzene ring in electrophilic substitution reactions depends upon the tendency of the substituent group already present in the benzene ring to release or withdraw electrons. A group that releases electrons activates benzene ring while the one which draws electrons deactivates the benzene ring. It is found that except halogens all *ortho-para* directing groups activate the ring and all *meta* directing groups deactivate the ring towards further electrophilic substitution. Thus, nitration of toluene can be carried out at room temperature, while that of nitrobenzene requires more drastic conditions. This is illustrated as below:





Reactivity in Aromatic Compounds on the Basis of Inductive and Resonance Effects

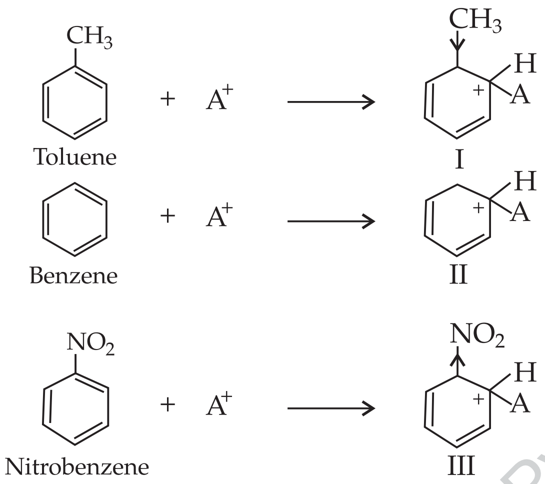
Theory of reactivity. It has been observed that the rate determining step in electrophilic aromatic substitution is the formation of intermediate resonance stabilised carbocation.



It is, thus, clear that any factor which stabilises the intermediate carbocation will also stabilise the transition state leading to its formation. Consequently, the carbocation will be formed more quickly and the rate of the overall reaction will increase. On the other hand, factors which destabilise the carbocation will decrease the case of its formation and, hence, decrease the rate of the reaction.

It is a familiar fact that dispersal of charge leads to the stability of the system. Now electron releasing groups tend to decrease the positive charge on the carbocation and, thus, stabilise the ion. As a result, the rate of the reaction increases. On the other hand, electron withdrawing groups destabilise the carbocation by intensifying the positive charge on it. Consequently, the rate of further electrophilic substitution reaction decreases. It may be mentioned that the release or withdrawal of electrons may occur due to inductive effect alone or through the net result of inductive and resonance effects.

The effect of substituents on reactivity can be illustrated by considering electrophilic substitution in benzene, toluene and nitrobenzene. The relative rates of these three substitution reactions will depend upon the relative stabilities of their corresponding intermediate carbocations formed as shown below:



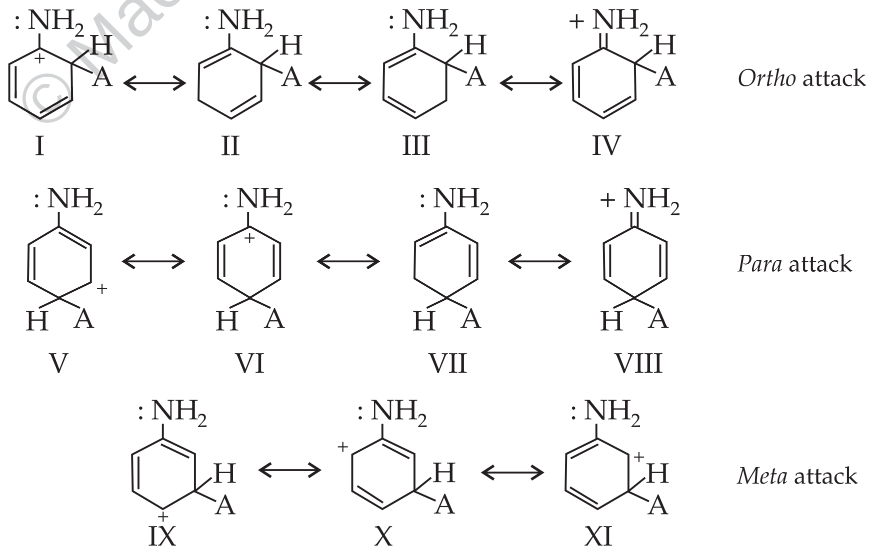
Due to its electron releasing inductive effect, methyl group tends to disperse the positive charge and, thus, stabilises the carbocation (I). As a result, the carbocation (I) is formed more quickly than the carbocation (II) from benzene. Consequently, toluene undergoes electrophilic substitution at a faster rate than benzene does.

On the other hand, the nitro group tends to intensify the positive charge due to its electron withdrawing inductive and resonance effects. This destabilises the carbocation (III) which is, therefore, formed more slowly than the carbocation (II) from benzene. Consequently, nitrobenzene undergoes electrophilic substitution at a slower rate as compared to benzene.

Electronic Interpretation of the *Ortho-para* Directing Influence of Amino Group

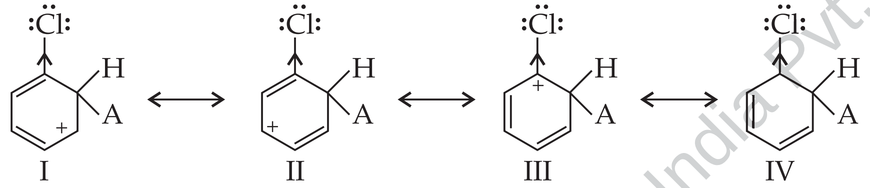
Amino group exerts electron withdrawing (–I) and electron releasing (+M) effects. Of the two opposing effects, the resonance effect dominates and thus overall behaviour of —NH_2 group is electron releasing, *i.e.*, it acts as an activator.

The *ortho* and *para* directing influence of –NH_2 group can be explained by assuming that nitrogen can share more than a pair of electrons with the benzene ring and can accommodate a positive charge. Thus, consider the case of further electrophilic substitution in aniline. The various resonating structures of the carbocations formed by *ortho, para* and *meta* attack are given below:

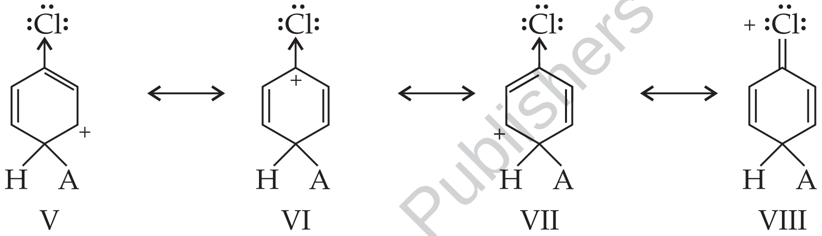


The intermediate carbocation resulting from *ortho* as well as *para* attacks is a resonance hybrid of four structures while the one formed by *meta* attack is a resonance hybrid of three structures. Further, in structures IV and VIII, the positive charge is carried by nitrogen. These structures are more stable since in these structures every atom (except hydrogen) has a complete octet of electrons. No such structure is, however, possible in case of *meta* attack. It is, therefore, clear that the resonance hybrid carbocations resulting from *ortho* and *para* attacks are more stable than the carbocation formed by attack at the *meta* position. Consequently, further electrophilic substitution in aniline occurs faster at the *ortho* and *para* positions than at the *meta* position. In other words, —NH_2 group is an *ortho-para* directing group. **Halogens are electron withdrawing and yet they direct the incoming group to *ortho* and *para* positions.** Halogens exert electron withdrawing (–I) and electron releasing (+M) effects. Due to high electronegativities of halogens, the inductive effect predominates over the mesomeric effect and, thus, the overall behaviour of halogens is electron withdrawing. In other words, halogens act as deactivators for further substitution.

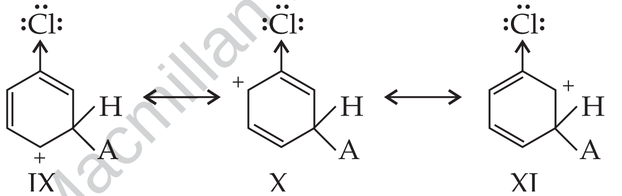
In order to account for their *ortho* and *para* directing nature, it has been assumed that halogens can share more than one pair of electrons with the benzene ring and can accommodate positive charge. Thus, consider the case of further electrophilic substitution in chlorobenzene. The various resonating structures of the carbocation formed by *ortho*, *para* and *meta* attacks are given below:



Ortho attack



Para attack



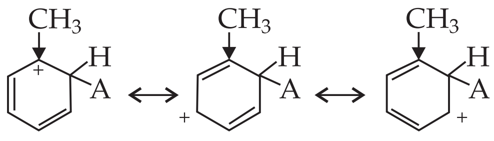
Meta attack

It is clear that the intermediate carbocation resulting from *ortho* as well as *para* attacks is a resonance hybrid of four structures while the one formed by *meta* attack is a resonance hybrid of three structures. Structures (III) and (VI) are highly unstable since in these structures the positive charge is carried by that carbon which is linked to electron withdrawing chlorine atom. However, in structures (IV) and (VIII), the positive charge is carried by chlorine. These structures are extra stable since in them every atom (except hydrogen) has a complete octet of electrons. No such structure is, however, possible in case of *meta* attack. Thus, the resonance hybrid carbocations resulting from *ortho* and *para* attacks are more stable than that formed by attack at the *meta* position. As a result, chlorine is *ortho* and *para* directing. The same is true for other halogens. It may, thus, be concluded that in case of halogens, the reactivity is controlled by the stronger inductive effect and the orientation is determined by mesomeric effect.

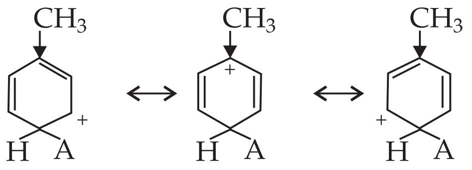
Electronic Interpretation of *Ortho* and *Para* Directing Influence of Alkyl Groups

Alkyl groups exert electron releasing inductive effect (+I effect). Consider the case of further electrophilic substitution in toluene which contains an electron releasing methyl group.

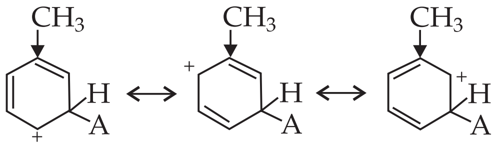
The various resonating structures of the carbocations formed by *ortho*, *para* and *meta* attacks are given below:



I II III *Ortho* attack



IV V VI *Para* attack



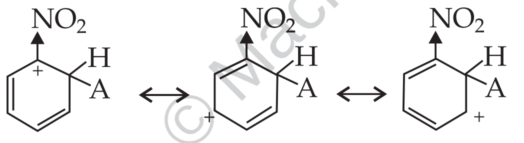
VII VIII IX *Meta* attack

We find that in each case, the intermediate carbocation is a resonance hybrid of three structures. In structures (I) and (V), the positive charge is located on the carbon atom to which electron releasing methyl group is attached. Therefore, the positive charge on such a carbon is highly dispersed and, thus, the corresponding structures (I) and (V) are more stable than all other structures. No such structure is, however, possible in case of *meta* attack. Hence, the resonance hybrid carbocations resulting from *ortho* and *para* attacks are more stable than the one formed by the attack at *meta* position. Therefore, further electrophilic substitution in toluene occurs faster at the *ortho* and *para* positions than at the *meta* position. In other words, methyl group is an *ortho-para* directing group. Other alkyl groups behave similarly.

Deactivating and *Meta* Directing Nature of Nitro Group Towards Electrophilic Aromatic Substitution

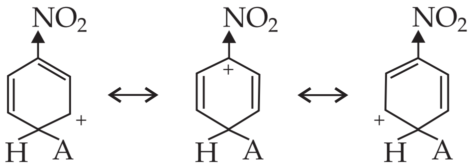
Nitro group is electron withdrawing in nature. In this case, the electron withdrawal occurs through electron withdrawing effect (–I-effect) as well as electron withdrawing resonance effect (–M-effect). Due to its electron withdrawing character, nitro group deactivates the benzene ring towards further electrophilic substitution.

Let us examine the directing influence of —NO_2 group by considering electrophilic substitution in nitrobenzene. The various resonating structures of the carbocations formed by *ortho*, *para* and *meta* attacks are given below:



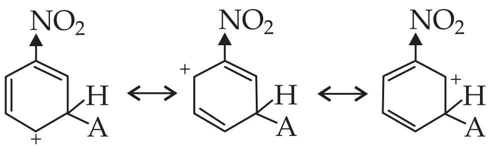
I II III *Ortho* attack

Specially unstable



IV V VI *Para* attack

Specially unstable

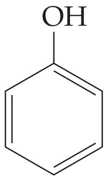


VII VIII IX *Meta* attack

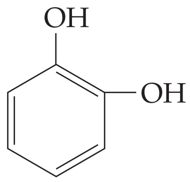
In the contributing structures (I) and (V), the positive charge is located on that carbon atom which is directly linked to electron withdrawing nitro group. Although —NO_2 group withdraws electrons from all positions, it does so most from the carbon directly attached to it. Hence, this carbon atom, already made positive by nitro group has little tendency to accommodate the positive charge of the carbocation. Consequently, structures (I) and (V) are unstable and their contribution towards stabilization of the carbocation is almost negligible. Thus, carbocations formed by *ortho* and *para* attacks are virtually resonance hybrids of only two structures while the one formed by *meta* attack is a resonance hybrid of three structures. Therefore, the resonance hybrid carbocation resulting from *meta* attack is more stable than the carbocations resulting from *ortho* and *para* attacks. Consequently, further electrophilic substitution takes place at the *meta* position. Thus, nitro group is *meta* directing.

14.9 PHENOLS

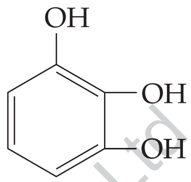
Phenols are compounds containing –OH group attached directly to the benzene ring. If one, two or three –OH groups are attached to the molecule, we obtain *mono*, *di* or *tri* hydric phenols, respectively. Some examples of phenols are given below:



Hydroxybenzene
or Phenol
(*Monohydric*)

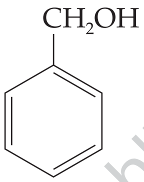


1, 2-Dihydroxybenzene
or Catechol
(*Dihydric*)

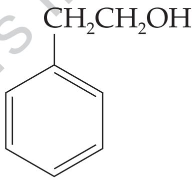


1, 2, 3-Trihydroxybenzene
or Pyrogallol
(*Trihydric*)

Aromatic compounds in which —OH group is not directly attached to benzene ring are called ***aromatic alcohols.*** These may by regarded as aryl derivatives of aliphatic alcohols. We do not keep them in the category of phenols. For example,



Phenyl methanol

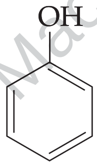


2-Phenyl ethanol

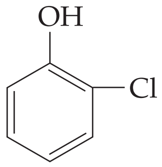
When four or more hydroxyl groups are present, they are called **polyhydric alcohols** or **polyhydric phenols.**

14.10 NOMENCLATURE OF PHENOLS

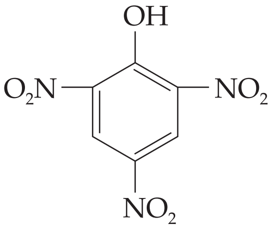
Phenol is the common name for the compound hydroxybenzene.



Phenol

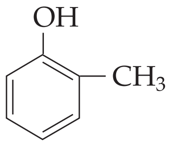


2-Chlorophenol

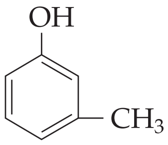


2, 4, 6-Trinitrophenol
(*Picric acid*)

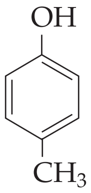
Phenols containing methyl group are known as *cresols.*



2-Methylphenol or
o-Cresol

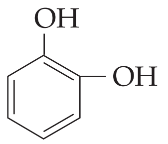


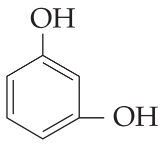
3-Methylphenol or
m-Cresol

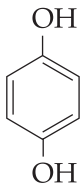


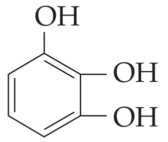
4-Methylphenol or
p-Cresol

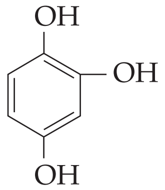
Dihydric and Trihydric Phenols: Common and IUPAC names of a few dihydric and trihydric phenols are given below:

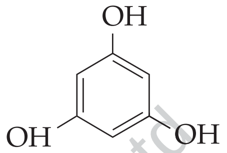

1, 2-Dihydroxybenzene
(Catechol)


1, 3-Dihydroxybenzene
(Resorcinol)


1, 4-Dihydroxybenzene
(Quinol)


1, 2, 3-Trihydroxybenzene
(Pyrogallol)

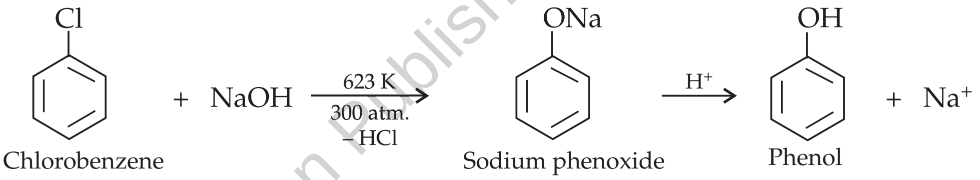

1, 2, 4-Trihydroxybenzene
(Hydroxyquinol)


1, 3, 5-Trihydroxybenzene
(Phloroglucinol)

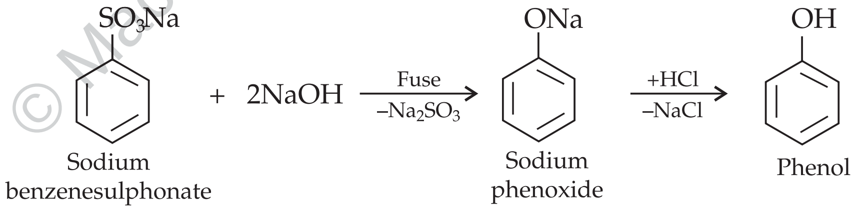
14.11 GENERAL METHODS OF PREPARATION OF PHENOLS

The following methods are used for the preparation of phenols:

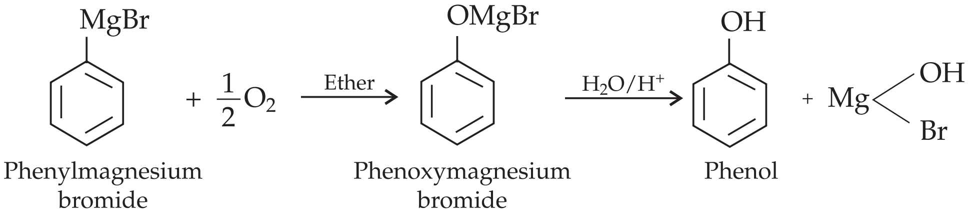
1. **From Aryl Halides (Dow's Process).** Phenol is obtained on a commercial scale by heating chlorobenzene with 10% NaOH solution at about 623 K and under a pressure of 300 atmospheres in the presence of copper catalyst.



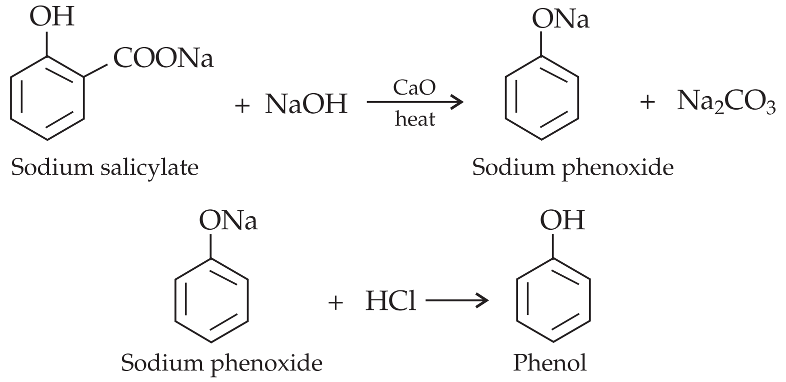
2. **Alkali Fusion of Sulphonates.** Sodium salts of sulphonic acids on fusion with NaOH at 573 K followed by acidification yield phenols.



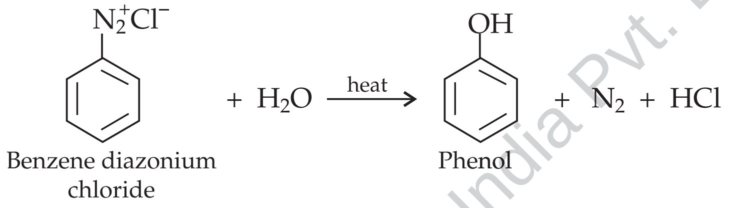
3. **From Grignard Reagent.** Oxygen reacts with phenylmagnesium bromide in ether to form an addition product which on acidification with dilute acid gives phenol.



4. **By Decarboxylation of Sodium Salt of Salicylic Acid.** Phenol can also be obtained by heating sodium salicylate with soda lime which is an equimolar mixture of NaOH and CaO.



5. **From Diazonium Salts (Laboratory Method).** Hydrolysis of diazonium salts with water or dilute acids gives phenols.



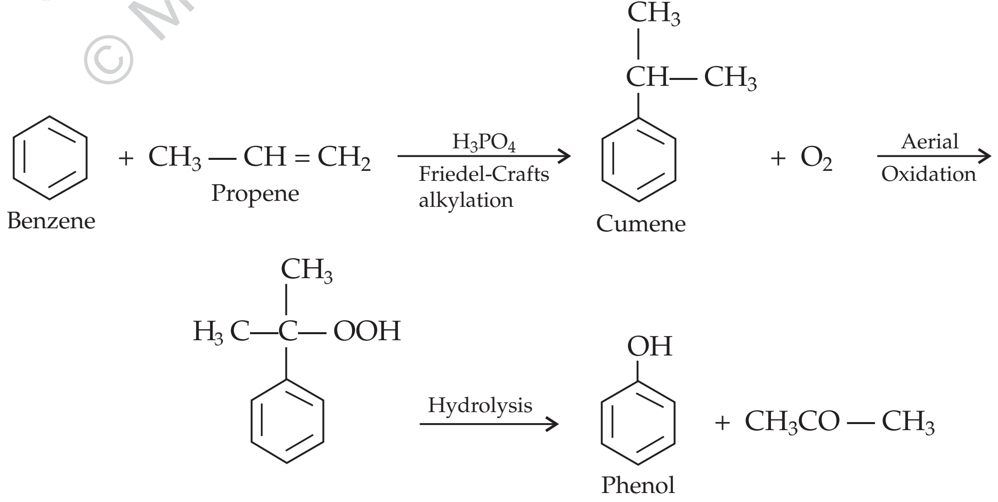
14.12 MANUFACTURE OF PHENOLS

1. **From Aryl Halides (Dow's Process).** This method has been described in the previous section.
2. **From Benzene (Raschig Process).** If we pass vapours of benzene, HCl and air over a catalyst mixture of $CuCl_2$ and $FeCl_3$ at 500 K, chlorobenzene is produced.

$$2C_6H_6 + 2HCl + O_2\text{ (air)} \xrightarrow[\text{500 K}]{CuCl_2+FeCl_3} 2C_6H_5Cl + 2H_2O$$

$$C_6H_5Cl + H_2O\text{ (steam)} \xrightarrow{\text{700 K}} C_6H_5OH + HCl$$

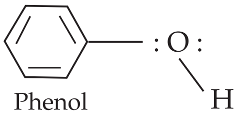
3. **From Cumene.** Friedel-Crafts alkylation of benzene with propene in the presence of phosphoric acid gives cumene. Cumene on aerial oxidation and subsequent hydrolysis gives phenol as shown in the following sequence of reaction.



4. **From Petroleum Oil.** Petroleum oil is a mixture of aliphatic and aromatic hydrocarbons. On cracking of petroleum oil, we obtain simpler and smaller hydrocarbons such as propane, butane, benzene, toluene, etc. It is believed that phenol is formed from the cracking of petroleum oil through the formation of cumene.

14.13 STRUCTURE OF PHENOLS

In phenols, –OH group is attached to carbon of the ring. Since the oxygen atom of the hydroxyl group has two bond pairs and two lone pairs of electrons, therefore, the C — O — H bonds in phenols is not linear.



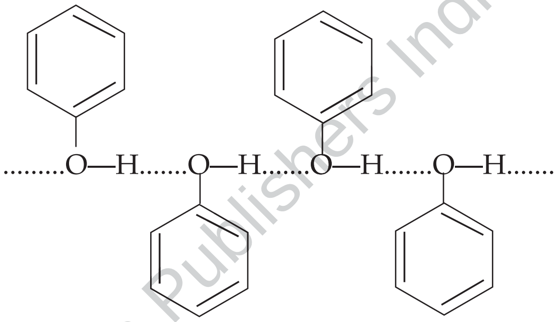
Phenol

14.14 PROPERTIES OF PHENOLS

14.14.1 Physical Properties

(*i*) Phenols are colourless crystalline solids or liquids in pure form. However, they become coloured due to slow oxidation with air.

(*ii*) Phenols have characteristic odours and are sparingly soluble in water but readily soluble in organic solvents.



(*iii*) Phenols boil at higher temperatures than the arenes of comparable molecular masses. For example, b.p. of phenol (molecular mass = 94) is 453 K while that of toluene (molecular mass = 92) is 384 K. Intermolecular hydrogen bonding causes phenols to boil at higher temperature.

14.14.2 Chemical Properties

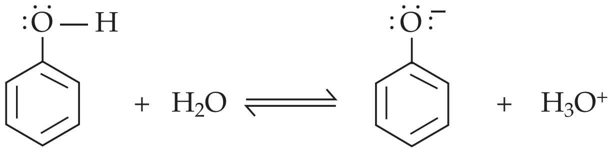
Chemical reactions of phenols have been studied under the following headings:

A. Reactions of phenolic group (—OH group)
B. Reactions of benzene ring
C. Special reactions.

A. REACTIONS DUE TO PHENOLIC (–OH) GROUP

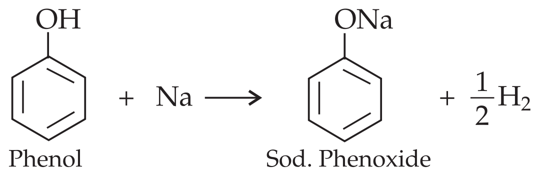
1. Acidic Nature

(*i*) **Phenols turn blue litmus red.** Phenols behave as acids because of the presence of polar O—H group in them. They ionise in aqueous solutions to give H^+ ions according to the following equation:

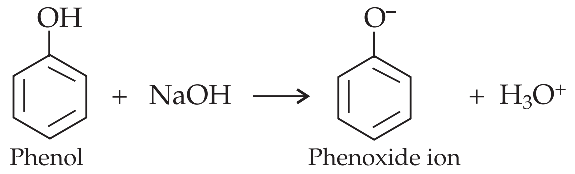


Phenol Phenoxide ion

(*ii*) Reaction with metals. Phenols react with metals such as Na or K to form salt and hydrogen gas is liberated.



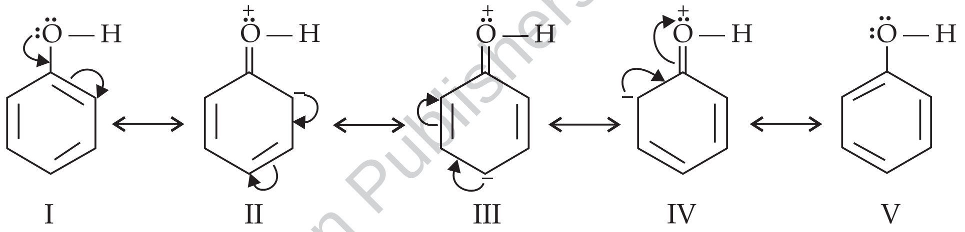
(*iii*) Reaction with alkalies. Phenols dissolve in solutions of alkalies (NaOH or KOH).



Phenols behave as stronger acids than alcohols.

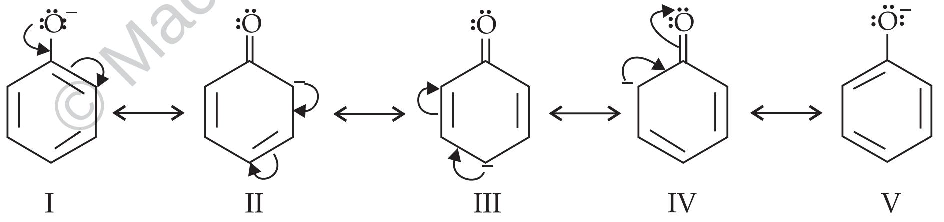
Phenol as well as phenoxide ion both are stabilized by resonance. The various contributing structures of phenol and phenoxide ion are given below:

Phenol



Resonating structures

Phenoxide ion



Resonating structures

We find that phenoxide ion is more stabilized by resonance than phenol. In phenol, three contributing structures (II, III and IV) involve charge separation (positive and negative charges), whereas in case of phenoxide ion, there is no charge separation. Since phenoxide ion is more stabilized than phenol, therefore, the equilibrium in the dissociation of phenols is shifted towards the dissociated form or, we can also say that the position of equilibrium lies well to the left. Hence, phenols furnish a high concentration of H^+ ions and behave as acids.

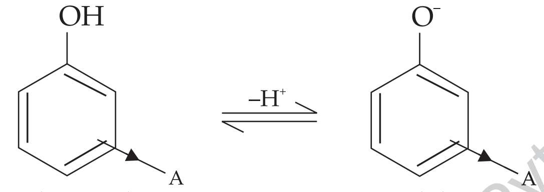
On the contrary, in the case of alcohols, alkoxide ion is not stabilized by resonance and, hence, they are weaker acids than phenols.

$$R-\ddot{\underset{\cdot\cdot}{O}}-H^+ \rightleftharpoons R-\ddot{\underset{\cdot\cdot}{O}}\colon^- + H^+$$

Presence of electron withdrawing groups (NO_2, CHO, COOH, etc.) and electron releasing groups (R, NH_2, etc.) also affects the acidic strength. We have the following generalizations:

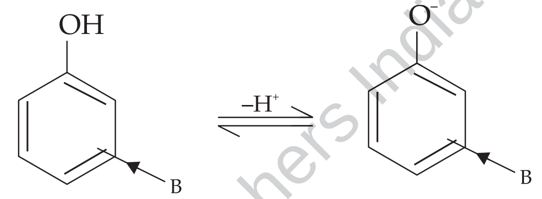
(i) *The electron withdrawing groups* (A) *increase the acidic strength by stabilizing the phenoxide ion by dispersing charge.*

(ii) *The electron releasing groups (B) decrease the acidic strength by destabilizing the phenoxide ion by accumulating the negative charge.*



Acid strength is more

A stabilises the anion

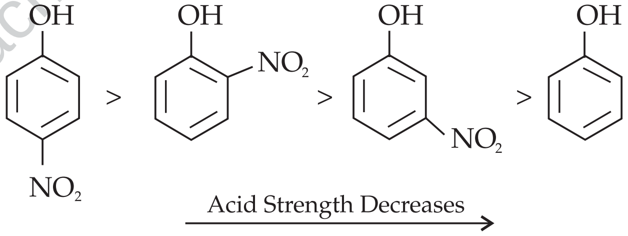


Acid strength is less

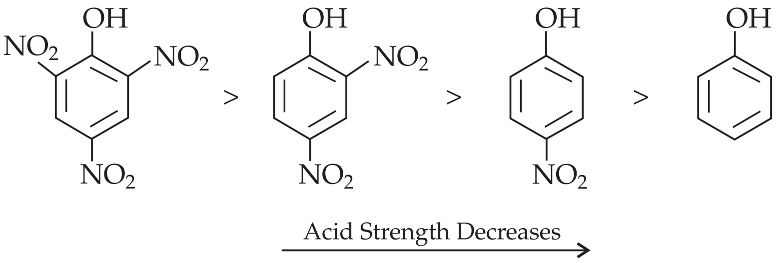
B destabilises the anion

If the anion obtained after release of proton from the phenol can stabilize itself, the phenol will have a strong acid strength.

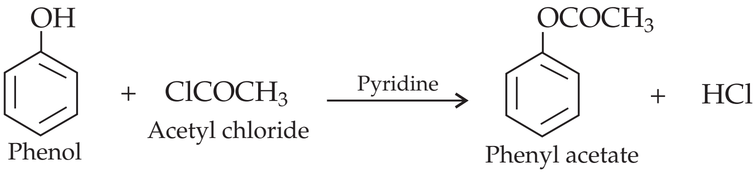
(iii) *The electron releasing or electron attracting effect is generally more pronounced if the substituent is present at the ortho or para position.*

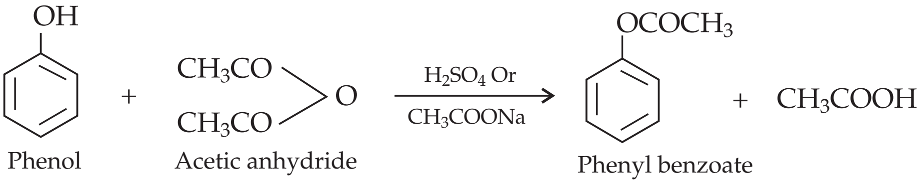


(iv) *The increase in the number of substituents further increases or decreases the acid strength.*

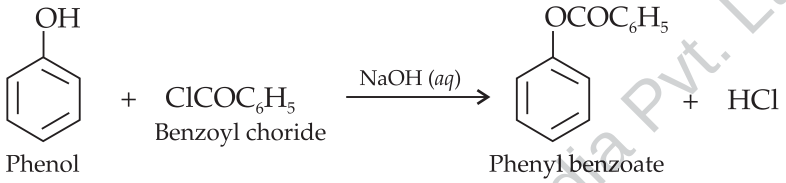


2. **Acylation.** Phenols react with acid chlorides in the presence of pyridine or with acid anhydrides in the presence of mineral acids like H_2SO_4 to form esters. Examples of acetylation are as given below:

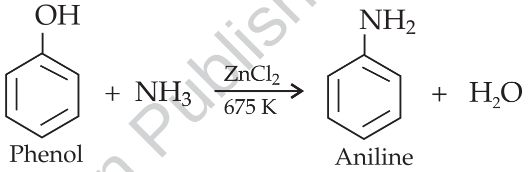




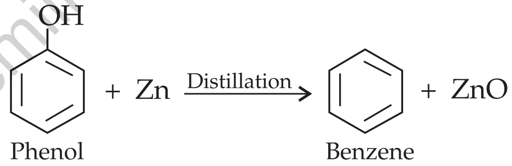
3. **Benzoylation. (Schotten-Baumann reaction)**. Phenols react with benzoyl chloride in the presence of aqueous NaOH to form phenyl benzoate.



4. **Reaction with PCl_5.** Phenols react with PCl_5 to produce triphenyl phosphate as the major product and a small amount of chlorobenzene.
5. **Reaction with Ammonia.** Phenols react with ammonia at 675 K in the presence of anhydrous $ZnCl_2$ to give amino compounds.



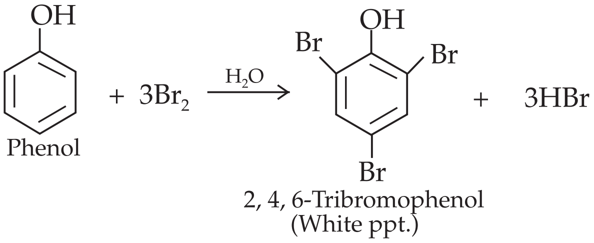
6. **Reaction with Zinc Dust.** On distillation with Zn dust, phenols are reduced to hydrocarbons.



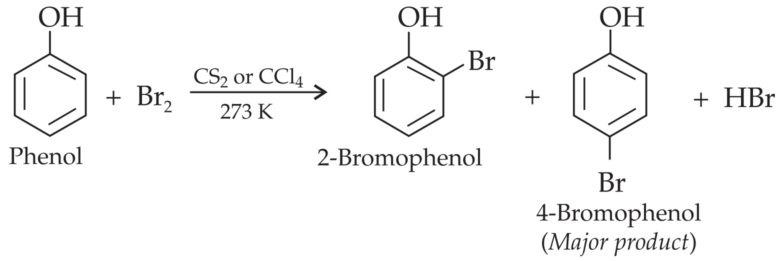
B. ELECTROPHILIC SUBSTITUTION REACTIONS OF RING

Phenolic group is an activating and *ortho-para* directing group. This is because of negative charge or greater electron density on *ortho* and *para* positions with respect to the –OH group as shown by the resonance structures of phenol and phenoxide ion under "phenols behave as stronger acids than alcohols".

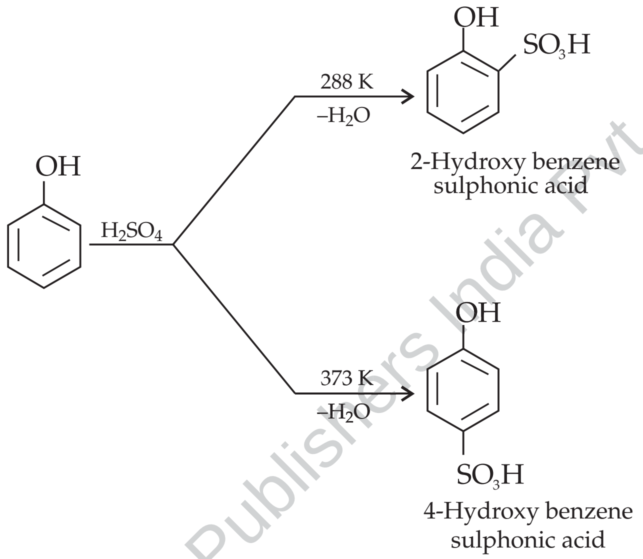
1. **Halogenation.** Phenols readily react with halogens to form polyhalogen substituted compounds. For example, phenol gives white precipitate of 2, 4, 6- Tribromophenol when treated with bromine water.



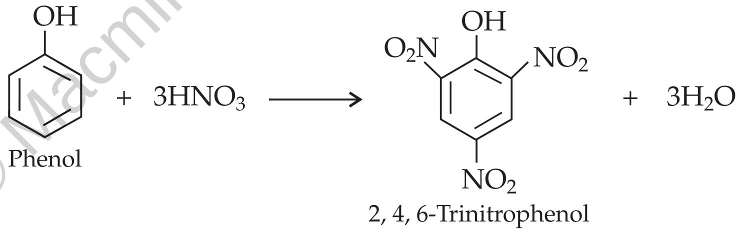
Monobromophenol can be obtained by treating phenol with bromine in the presence of less polar solvents such as a carbon disulphide or carbon tetrachloride keeping low temperature.



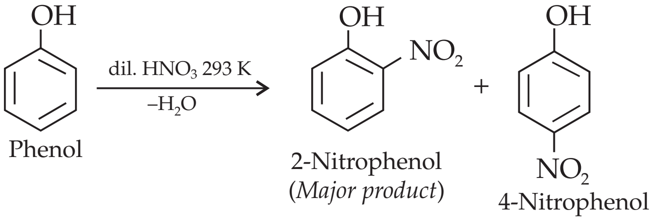
2. **Sulphonation.** Phenols react with conc. H_2SO_4 to give benzene sulphuric acids. Sulphonation takes place mainly at *ortho* position at low temperature and at *para* position at high temperature, as shown below:



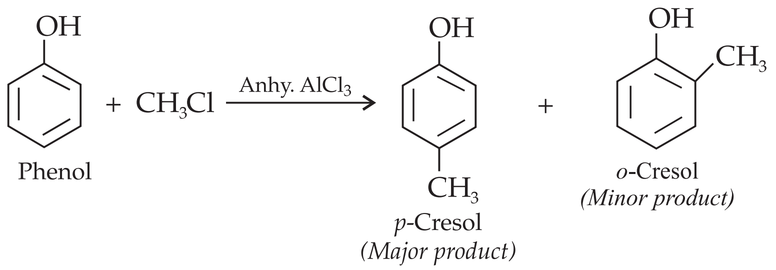
3. **Nitration.** Treatment of phenol with concentrated nitric acid gives 2, 4, 6-trinitrophenol (*picric acid*).



Mononitrophenols can be obtained on treatment with dil. HNO_3 at low temperature (293 K).

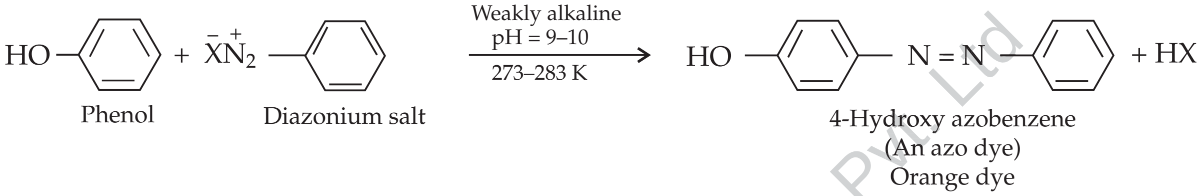


4. **Friedel-Crafts Alkylation.** Phenol reacts with alkyl halides in the presence of anhydrous $AlCl_3$ to form a mixture of *p*- and *o*-cresols. *p*-cresol is the major product.



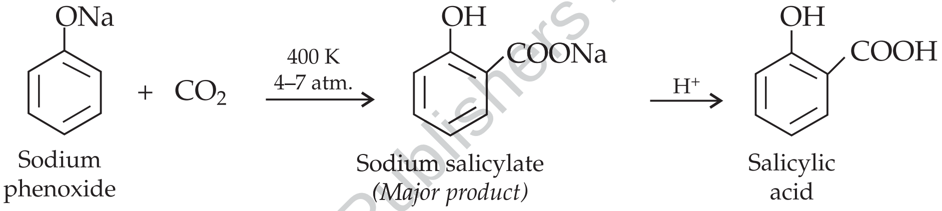
Reaction of $AlCl_3$ with phenol to produce a coordination compound keeps the yield low.

5. **Coupling Reaction.** Phenol reacts with diazonium salts in slightly alkaline medium and at low temperature to form *azo* dyes. **This reaction is used to test the presence of a phenolic group.**



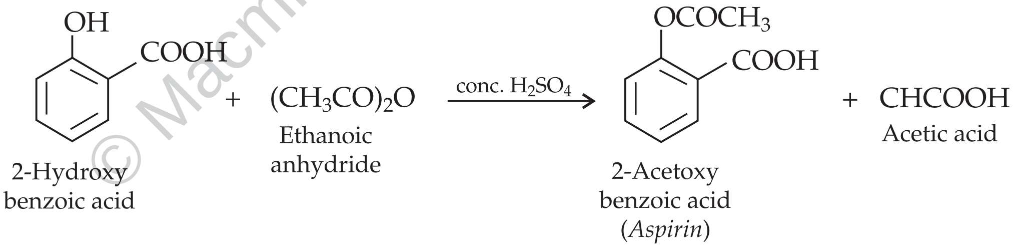
C. SOME SPECIAL REACTIONS OF PHENOLS

1. **Kolbe's Reaction.** When sodium phenoxide, a sodium salt of phenol, is heated with CO_2 at 400 K and a pressure of 4-7 atm, sodium salicylate is formed. This on acidification yields salicylic acid.

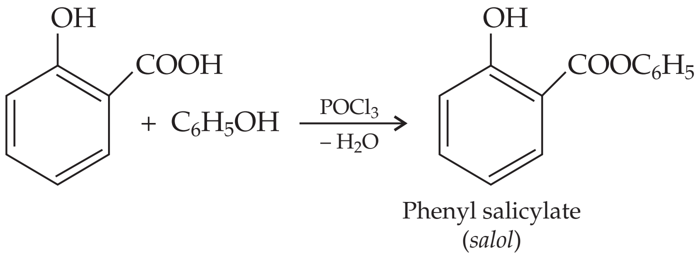


Salicylic acid is a substance of great utility.

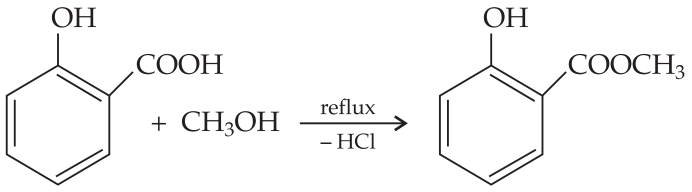
Salicylic acids is the starting material for the manufacture of 2-acetoxybenzoic acid (aspirin), the well known analgesic drug (pain killer).



Aspirin also keeps the blood thin and, thus, keeps off heart ailments. Salicylic acid is employed to prepare *salol, an intestinal antiseptic drug* by heating it with phenol in the presence of phosphorus oxytrichloride.

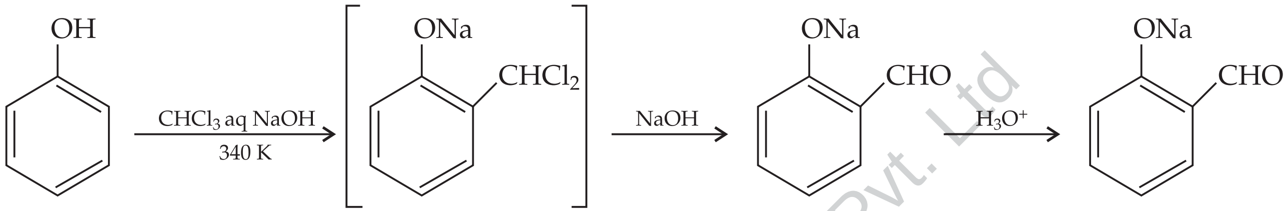


Salicylic acid is used to prepare methyl salicylate, a pleasant smelling liquid, also called as *oil of wintergreen.* It is used in perfumery and as a flavouring agent.



Methyl salicylate

2. **Reimer-Tiemann Reaction.** Phenol on treatment with chloroform in the presence of aqueous alkali at 340 K yields *o*-hydroxybenzaldehyde (salicyladehyde) and *p*-hydroxybenzaldehyde. The *ortho* isomer is formed in greater proportion.



o-Hydroxy benzaldehyde
(*Major product*)

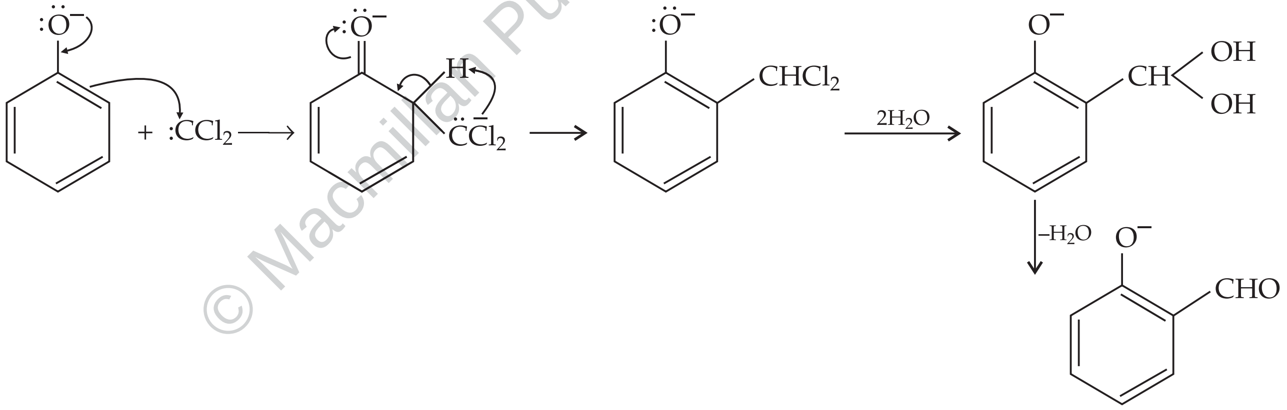
Mechanism of Reimer-Tiemann's reaction

Reimer-Tiemann's reaction is an *electrophilic substitution* reaction. Following steps are involved in the reaction:

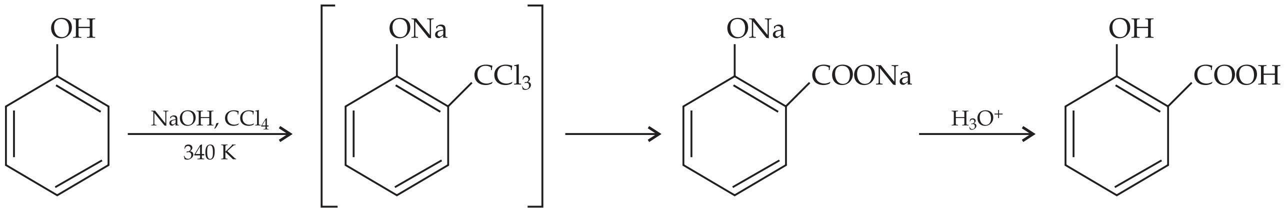
(I) Generation of electrophile

$$CHCl_3 + OH^- \rightleftharpoons H_2O + :\bar{C}Cl_3 \longrightarrow \underset{\substack{\text{Dichlorocarbene}\\\text{(Electrophile)}}}{:CCl_2} + Cl^-$$

(II) Attack of electrophile

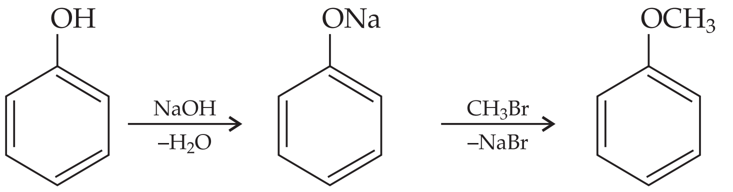


If carbon tetrachloride is used in place of chloroform, salicylic acid is obtained as the major product.



o-Hydroxy benzoic acid
(Salicylic acid)
(*Major product*)

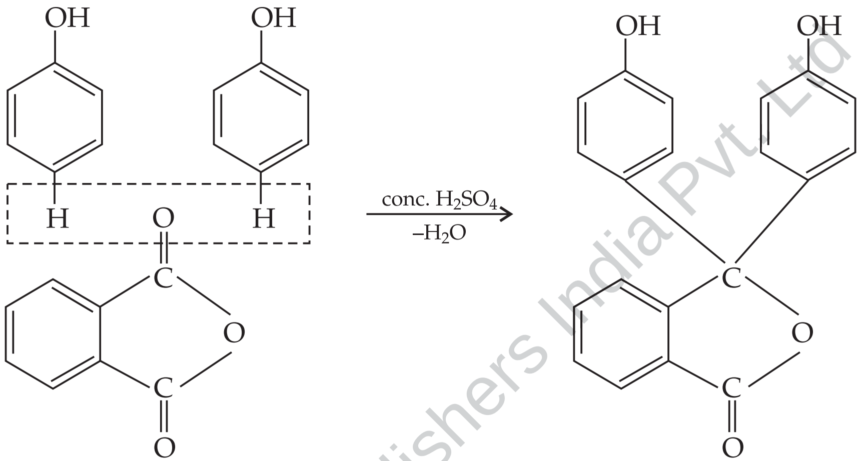
3. **Reaction with Alkyl Halides.** Phenol in the form of sodium phenoxide reacts with alkyl halide to form aromatic ethers (*Williamson's synthesis*).



Sod. phenoxide

Methoxybenzene
(Anisole)

4. **Reaction with Phthalic Anhydride.** Phenol reacts with phthalic anhydride in the presence of conc. H_2SO_4 to form phenolphthalein, a widely used acid-base indicator.



Phthalic anhydride

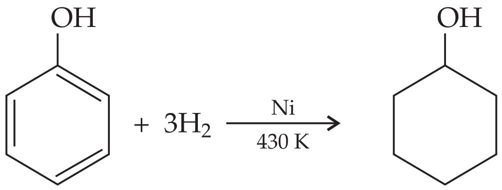
Phenolphthalein

5. **Reaction with Ferric Chloride.** Phenol gives a violet-coloured water soluble complex with ferric chloride. The complex is a coordination compound in which iron is in hexavalent state.

$$6C_6H_5OH \quad + \quad FeCl_3 \longrightarrow [Fe(OC_6H_5)_6]^{3-} \quad + \quad 3H^+ \quad + \quad 3HCl$$

In general all compounds containing enolic group $\left[=\overset{|}{C}-OH\right]$ respond to this test. However, the colours of complexes are different such as green or blue or violet, etc. and depend upon the structure of phenols. **This reaction is used as test to detect phenolic group in the organic compound.**

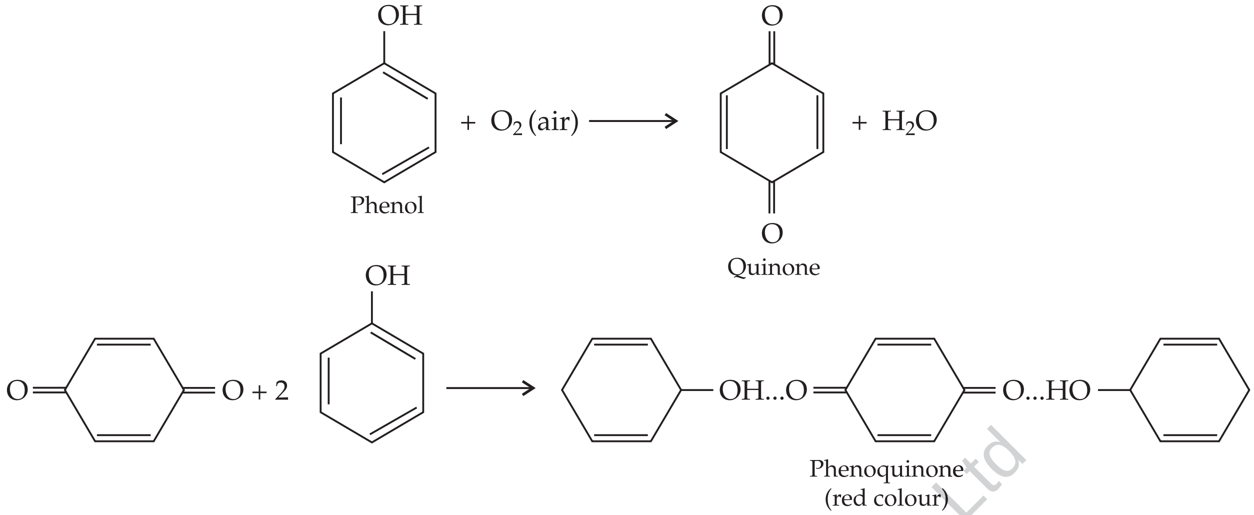
6. **Hydrogenation.** Phenol on hydrogenation at 430 K in the presence of nickel catalyst gives cyclohexanol.



Phenol

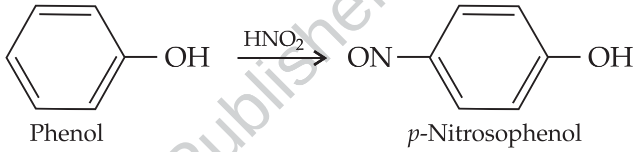
Cyclohexanol

7. **Oxidation.** Phenol gets slowly oxidised on exposure to air and turns pink in colour. Quinone, one of the oxidation products in air forms addition product with phenol having a red colour.

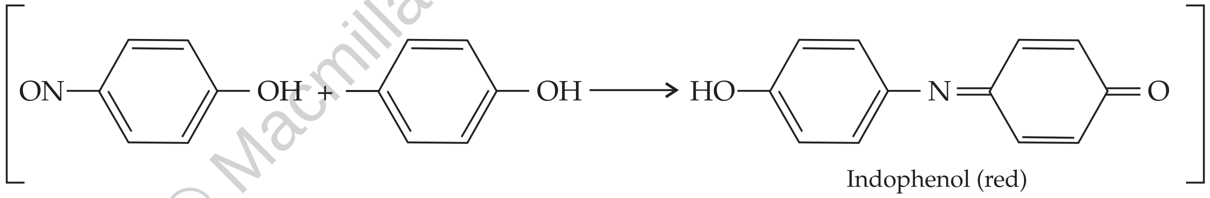


8. **Libermann's Test.** On adding a nitrite to a phenol dissolved in conc. sulphuric acid, red or brown colouration is produced. The colour changes to blue or green by the addition of a strong alkali. **This test can be used to distinguish between phenols and alcohols.**

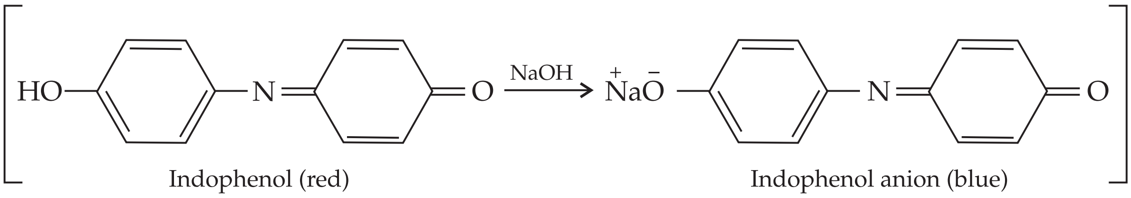
$$\underset{\text{Sodium nitrite}}{2NaNO_2} + H_2SO_4 \longrightarrow \underset{\text{Nitrous acid}}{2HNO_2} + Na_2SO_4$$



p-Nitrosophenol and phenol then react as under:

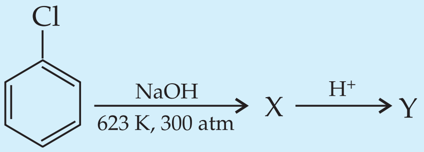


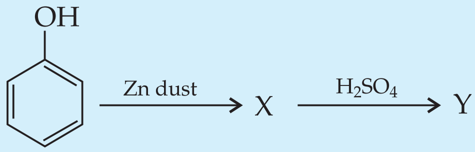
Indophenol (red) on treatment with alkali gives sodium salt of indophenol which is blue in colour.

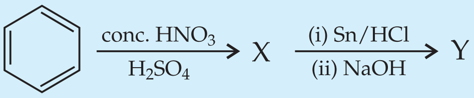


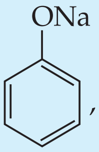
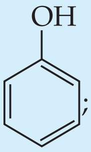
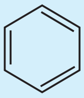
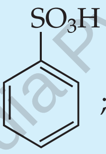
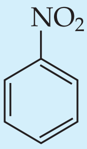
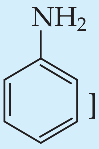
PROBLEMS FOR PRACTICE

1. What is the main product formed when phenol is subjected to Reimer-Tiemann's reaction using CCl_4?
[**Ans.** Salicylic acid]
2. Which is the strongest acid out of ethonol, 2-phenyl ethanol, phenol and 2, 4, 6-trinitrophenol?
[**Ans.** 2,4, 6-Trinitrophenol (due to strong electron withdrawing effect of three nitro groups)]
3. How can you obtain benzene from phenol? [**Ans.** By distilling with zinc]
4. Complete the following equations:

(*i*) 

(*ii*) 

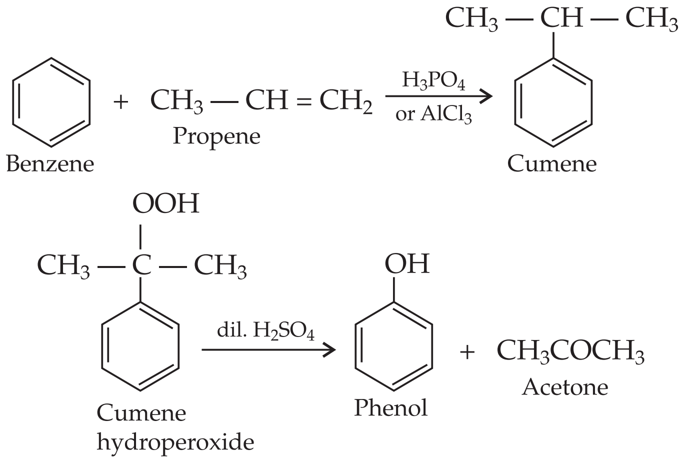
(*iii*) 

[**Ans.** (*i*) X =  , Y =  ; (*ii*) X =  , Y =  ; (*iii*) X =  , Y = ]

5. Which amongst each of the following pairs is more acidic?
   (*i*) phenol or cyclohexanol (*ii*) *p*-nitrophenol or *p*-bromo phenol
   [**Ans.** (*i*) Phenol; (*ii*) *p*-nitro phenol]
6. Arrange the following in the increasing order of acidic strength:
   (*i*) phenol, ethanol, water (*ii*) *p*-nitrophenol, cresol, phenol
   (*iii*) phenol, benzyl alcohol, *o*-nitro-phenol.
   [**Ans.** (*i*) Ethanol, water, phenol; (*ii*) Cresol, phenol, *p*-nitrophenol; (*iii*) Benzyl alcohol, phenol, *o*-nitro phenol]

14.15 COMMERCIAL PREPARATION OF PHENOL

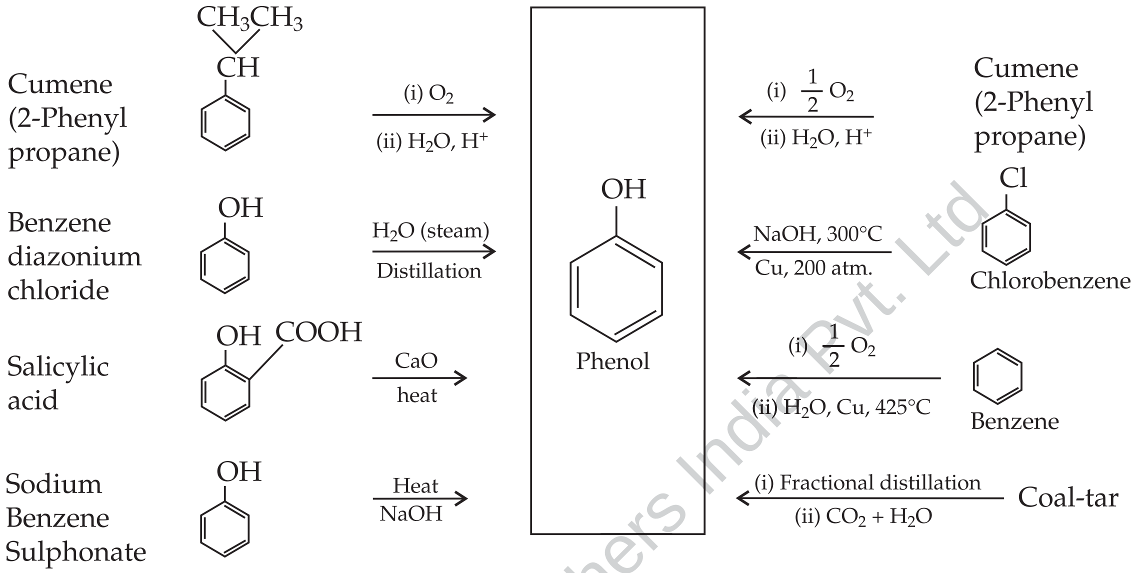
The starting material for the prepartion of phenol on a large scale is cumene (isopropyl benzene). Cumene itself is prepared by Friedel-Crafts alkylation of benzene with propene. Cumene on oxidation by air changes to cumene hydroperoxide, which on treatment with dilute sulphuric acid gives phenol and acetone.



Commercial Uses of Phenol

1. In the manufacture of drugs such as salicylic acid, phenacetin, aspirin, salol, etc.
2. As powerful antiseptic in soaps, lotions, etc.
3. For the manufacture of bakelite by polymerising with formaldehyde.
4. For the manufacture of cyclohexanol used as solvent for rubber.
5. For the manufacture of phenolphthalein and picric acid.
6. As a preservative for ink.

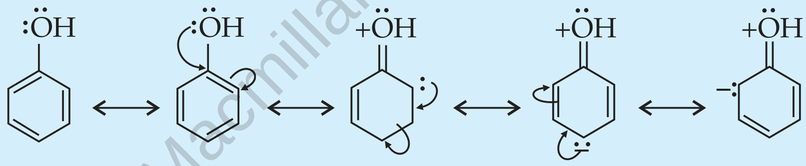
Preparation of Phenol



MISCELLANEOUS SOLVED QUESTIONS

1. *Explain how does the – OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?*

Solution. Resonating structures of phenol:



It is clear from the resonating structures of phenol that due to presence of –OH group electron density is increased at *o*– and *p*- positions in phenol. Therefore, further electrophilic substitution in phenol is activated.

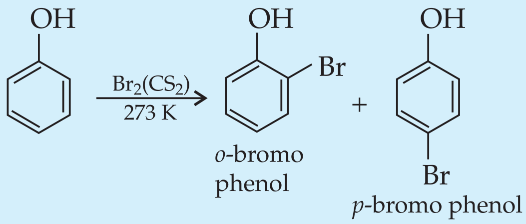
2. *Give equations for the following reactions:*

(*i*) *Bromine in CS_2 with phenol.*

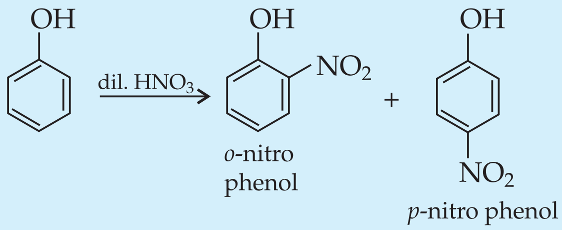
(*ii*) *Action of dil. HNO_3 with phenol.*

Solution.

(*i*)



(*ii*)



QUICK SCAN (FOR REVISION)

1. **Arenes** are mixed aliphatic-aromatic compounds. An alkyl, alkenyl or alkynyl group attached to a benzene ring constitutes an arene.
2. **Benzene** is obtained on industrial scale from coal-tar and petroleum.
3. **Laboratory methods** of preparation of benzene are: decarboxylation of benzoic acid or phthalic acid with soda lime, distillation of phenol with zinc dust, hydrolysis of benzene sulphonic acid with steam and reduction of benzene diazonium chloride with alkaline sodium stannate.
4. Benzene gives substitution reactions like halogenation in the presence of Fe and in the absence of sunlight, nitration with nitric acid in the presence of sulphuric acid, sulphonation, Friedel-Crafts alkylation and Friedel-Crafts acylation.
5. Under **drastic conditions, addition** of hydrogen, chlorine and ozone can be carried out on benzene.
6. According to **Kekule,** six carbon atoms of benzene are linked to each other by alternate double and single bonds to form a hexagonal ring.
7. According to **molecular orbital theory,** each carbon atom in benzene is sp^2 hybridised and, thus, forms three σ-bonds, two with adjacent carbon atoms and one with hydrogen atom. There are electron clouds of π-electrons above and below the plane of benzene.
8. Electrophilic substitution reaction in benzene ring takes place through an **electrophile.**
9. The **electrophiles** in halogenation, nitration and sulphonation are halogenium ion, nitronium ion and sulphonium ion respectively.
10. Groups which direct the incoming group at *ortho* or *para* positions with respect to them are called *o-p* **directing groups.** Examples are —NH$_2$, —CH$_3$, NHR, etc.
11. Groups which direct the incoming group at *meta* position are called *meta*-**directing groups.** Examples are NO$_2$, —SO$_3$H, —COOH, etc.
12. **Nuclear halogen** compounds are the compounds in which the halogen is directly attached to the benzene ring.
13. **Side-chain halogen** compounds are the compounds in which the halogen is attached to the side-chain of the ring.
14. Nuclear halogen compounds can be prepared by **direct halogenation** of benzene in the presence of a halogen carrier like Fe or FeCl$_3$ in the absence of light.
15. **Halogen derivatives** of benzene are **less** reactive than their aliphatic counterparts towards nucleophilic substitution reactions.
16. Hydrolysis of benzenediazonium salts with boiling dil. H$_2$SO$_4$ gives phenols.
17. Sodium salts of aromatic sulphonic acids on fusion with NaOH at 573-623 K followed by acidification with dil. H$_2$SO$_4$ give phenols.
18. Decarboxylation of sodium salt of salicylic acid with sodalime followed by acidification with dil. HCl gives phenol.
19. When O$_2$ is bubbled through an ethereal solution of C$_6$H$_5$MgBr, it gives C$_6$H$_5$OMgBr which upon treatment with dil. HCl gives phenol.
20. Commercially, phenol can be prepared from cumene (isopropyl benzene) obtained by F.C. alkylation of benzene with propene in the presence of H$_3$PO$_4$. Aerial oxidation of cumene gives cumene hydroperoxide which upon treatment with dil. H$_2$SO$_4$ gives phenol along with acetone.
21. Phenols are stronger acids than alcohols because phenoxide ion is stabilized by resonance but alkoxide is not. Phenols turn blue litmus red and dissolve in alkalies to form phenoxides. They are, however, less acidic than carbonic acid and, hence, do not decompose NaHCO$_3$ to evolve CO$_2$ gas.
22. Phenols being weaker nucleophiles than alcohols do not directly react with carboxylic acids to form esters.
23. Phenols react with dimethyl sulphate or diethyl sulphate in the presence of NaOH to form the corresponding phenolic ethers.
24. Phenols but not alcohols on distillation with zinc dust give the corresponding aromatic hydrocarbons.
25. Because of the presence of strongly activating OH group, phenols readily undergo *electrophilic substitution reactions* because of the presence of activating phenolic group, as given below:
    (*i*) *With* Br$_2$ *water,* phenol gives 2, 4, 6-tribromophenol.
    (*ii*) *With* Br$_2$ *in* CS$_2$ *at 273 K,* a mixture of *p*-bromophenol (major) and *o*-bromophenol (minor) is obtained.
    (*iii*) *With dil. HNO*$_3$ *at 293 K,* phenol gives a mixture of *o*-nitrophenol (*major*) and *p*-nitrophenol *(minor).*
    (*iv*) *With conc. HNO*$_3$ *in* presence of conc. H$_2$SO$_4$, phenol gives a poor yield of picric acid.

(*v*) *With conc.* H_2SO_4 *at 288-293 K*, phenol gives *o*-hydroxy benzene sulphonic acid as the main product but at 373 K, it gives *p*-hydroxy benzene sulphonic acid as the main product.

26. Phenol coupled with diazonium salts in slightly alkaline medium at 273 - 278 K to form orange—coloured **azo dyes.**

27. Salicylic acid reacts with phenol in the presence of $POCl_3$ to form phenyl salicylate *(salol)* which is used as an internal *antiseptic.*

28. Phenol condenses with phthalic anhydride in the presence of conc. H_2SO_4 to form phenolphthalein which is widely used as an indicator in **acid-alkali titrations.**

29. Phenol reacts with $CHCl_3$ in the presence of NaOH at 340 K to form salicylaldehyde as the major product along with a small amount of *p*-hydroxy-benzaldehyde — **Reimer-Tiemann's reaction.** If CCl_4 is used in place of $CHCl_3$ salicylic acid is the main product.

EXERCISES

Very Short Answer Type Questions

1. Classify the following groups as *ortho, para* or *meta*-directing when present on the benzene nucleus:
   (*i*) —CH_3 (*ii*) NH_2
   (*iii*) —NO_2 (*iv*) —SO_3H
2. Classify the following groups as activating or deactivating groups with respect to further electrophilic substitution in the benzene ring:
   (*i*) —Cl (*ii*) —CN
   (*iii*) —NO_2 (*iv*) —NH_2
3. Complete the following equation:

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3}$$

4. What is the directive influence of phenolic group?
5. How will you know whether a given OH group is phenolic in nature?
6. How much bromine (in moles) is needed to produce 2, 4, 6- tribromophenol from 1 mole of phenol?
7. Why boiling points of phenols are higher than those of the corresponding aromatic hydrocarbons and alkyl halides?
8. Phenol is heated with choloform and NaOH at 340 K. What is the product formed? Also, give the name of the reaction involved.
9. How is cumene prepared from benzene?
10. Name the phenol with molecular formula C_7H_8O which on treatment with Br_2 water readily gives a precipitate of $C_7H_5OBr_3$.
11. Phenol reacts with benzoyl chloride in the presence of NaOH. What is the product formed? What is the name of this reaction?
12. Why is common phenol more acidic than ethyl alcohol?

Short Answer Type Questions

1. Explain the mechanism of nitration of benzene.
2. Write molecular orbital structure of benzene.
3. What are phenols? How do they differ structurally from aromatic alcohols?
4. How is phenol obtained commercially?
5. How is phenol prepared from:
   (*i*) Benzene
   (*ii*) Chlorobenzene
   (*iii*) Benzenediazonium chloride
   (*iv*) Sodium benzenesulphonate?
6. Why is phenol acidic in nature but methanol is not?
7. Write the resonance structures of phenol (which are similar to that of chlorobenzene) and explain why phenol is more acidic than ethanol. Explain whether *p*-nitrophenol should be more or less acidic than phenol.
8. Account for the acidic character of phenol.
9. Alkanols and phenols both contain —OH groups. How do you explain that alkanols are neutral while phenols are acidic?
10. Explain why phenol is more acidic than ethanol.
11. How does phenol react with the following:
    (*i*) Acetyl chloride
    (*ii*) Bromine in water
    (*iii*) Chloroform in the presence of NaOH?
12. Show with the help of chemical equations what happens when phenol is warmed with CCl_4 in the presence of aqueous NaOH.
13. How can phenol be converted into (*i*) benzene (*ii*) salicylic acid (*iii*) picric acid (*iv*) phenolphthalein (*v*) aspirin?
14. How is phenol converted into salicylaldehyde and salicylic acid?
15. How will you convert phenol into:
    (*i*) *p*-hydroxyazobenzene
    (*ii*) phenyl benzoate?

16. Write the structure of main product in the
    (*i*) action of excess of bromine on phenol
    (*ii*) action of conc. nitric acid on phenol.
17. How is anisole prepared from phenol?

Long Answer Type Questions

1. Write the following chemical properties of benzene:
    (*i*) Substitution reactions (*ii*) Oxidation reactions.
2. Write the mechanism of halogenation of benzene. What is the evidence in support of this mechanism?
3. What are *o-p* directing and *m*-directing groups? Write the electronic interpretation of the *o-p* directing influence of amino group.
4. How is phenol obtained from benzenesulphonic acid and how can it be converted into: (*a*) benzene, (*b*) salicylaldehyde, (*c*) phenolphthalein, and (*d*) phenyl benzoate?
5. How is phenol obtained commercially from benzene and propene?

ANSWERS TO SELECTED QUESTIONS

Very Short Answer Type Questions

1. *ortho-para* directing: —CH_3, —NH_2 *meta*-directing: —NO_2, —SO_3H
2. —NH_2 group is activating. —Cl, —CN and —NO_2 groups are deactivating.
3. $C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5 + HCl$
4. *o, p*-directing
5. Phenolic OH group gives blue or violet colouration with neutral $FeCl_3$ while alcoholic OH group does not.
6. Three
7. Intermolecular H-bonding
8. Salicylaldehyde; Reimer-Tiemann's reaction.
9. By Friedel-Crafts reaction of benzene with propene in presence of H_3PO_4 followed by aerial oxidation and subsequent hydrolysis with a mineral acid.
10. *m*-Cresol
11. Phenyl benzoate. Schotten-Baumann reaction.
12. Phenoxide ion left after the removal of a proton is stabilized by resonance whereas alkoxide ion (left after the removal of a porton from alcohol) is not.

COMPETITION FILE

SUBJECTIVE PROBLEMS

Problem 1. *Answer the following:*

(*a*) *Why benzene cannot be iodated with iodine directly?*

(*b*) *Why fluoroarenes cannot be prepared by direct reaction of fluorine?*

(*c*) *How benzene can be iodated?*

(*d*) *Why iodation of an arene occurs with ICl?*

(*e*) *Why nitrobenzene and not benzene is a suitable solvent for Friedel-Crafts alkylation of bromobenzene?*

Ans.

(*a*) Iodation with iodine is slow and somewhat reversible.

$$C_6H_6 + I_2 \rightleftharpoons C_6H_6 + HI$$

(*b*) Fluroine is too reactive in nature. Both addition and polysubstitution occur.

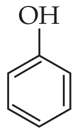
(*c*) The presence of I^- makes the reaction reversible. Iodation can occur smoothly if an oxidising agent such as HNO_3, HIO_3 or H_2O_2, etc. is present which can convert I^- to I_2.

(*d*) ICl is more reactive than iodine. The aromatic ring can displace Cl^- more easily from $I^{\delta+}Cl^{\delta-}$ than it can displace I^- from the nonpolar I_2.

(*e*) Benzene is more reactive than bromobenzene in Friedel-Crafts reaction and alkylates more rapidly than bromobenzene. Nitrobenzene may be used as a solvent because it does not undergo Friedel-Crafts reaction owing to deactivating effect of NO_2 group.

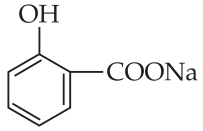
Problem 2. *An organic compound (A) has 76.6% C and 6.38% H. Its vapour density is 47. It gives characteristic colour with $FeCl_3$ solution. (A) when treated with CO_2 and NaOH at 140°C under pressure gives (B) which on being acidified gives (C). (C) reacts with acetyl chloride to give (D) which is a well-known pain killer. Identify (A), (B), (C) and (D) and explain the reactions involved.*

Ans. (A) =



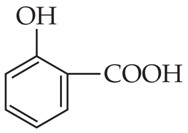
Phenol

(B) =



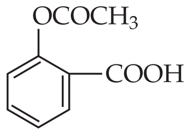
Sod. salicyate

(C) =



Salicylate acid

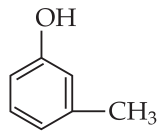
(D) =



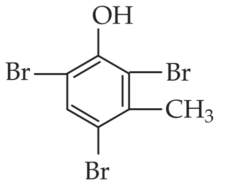
Aspirin (pain killer)

Problem 3. *An organic compound (A), C_7H_8O, is insoluble in aqueous $NaHCO_3$ but is soluble in NaOH. (A) on treatment with bromine water rapidly forms compound (B), $C_7H_8OBr_3$. (i) Give structures for (A) and (B), (ii) What will be (A) if it does not dissolve in NaOH but shows reactions given above? Give your answer with proper reasoning.*

Ans. A =

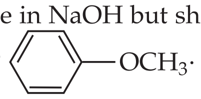


m-cresol (A)



2, 4, 6-tribromo-3-methylphenol

If A does not dissolve in NaOH but shows the above reactions it would be



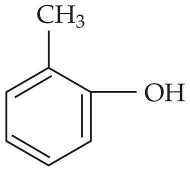
OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

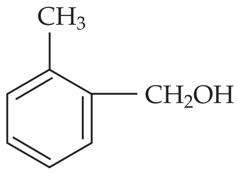
Choose the correct answer:

1. In Friedel-Crafts reaction, besides $AlCl_3$ what are the reactants?
   (*a*) $C_6H_6 + CH_3$ (*b*) $C_6H_6 + NH_3$
   (*c*) $C_6H_6 + NH_2$ (*d*) $C_6H_6 + CH_3\,Cl$
2. Aromatic hydrocarbon shows mostly
   (*a*) addition electrophilic
   (*b*) addition nucleophilic
   (*c*) substitution electrophilic
   (*d*) substitution nucleophilic
3. Which one of these is not compatible with arenes?
   (*a*) Greater stability (*b*) Resonance
   (*c*) Delocalisation of π-electron
   (*d*) Electrophilic addition
4. The *ortho*/*para* directing group among the following is
   (*a*) COOH (*b*) CN
   (*c*) $COCH_3$ (*d*) $NHCOCH_3$
5. The reaction of aromatic acyl chloride and phenol in the presence of a base NaOH or pyridine is called
   (*a*) Kolbe's reaction
   (*b*) Perkin's reaction
   (*c*) Sandmeyer's reaction
   (*d*) Schotten-Baumann reaction
6. Benzene diazoniun chloride on reaction with phenol in weakly basic medium gives
   (*a*) diphenyl ether (*b*) *p*-Hydroxyazobenzene
   (*c*) chlorobenzene (*d*) benzene
7. Consider the following reaction:
   Phenol $\xrightarrow{\text{Zn dust}}$ X $\xrightarrow[\text{anhyd. AlCl}_3]{CH_3Cl}$ Y $\xrightarrow{\text{alkaline KMnO}_4}$ Z,
   the product Z is
   (*a*) benzaldehyde (*b*) benzoic acid
   (*c*) benzene (*d*) toluene
8. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is
   (*a*) benzoic acid (*b*) salicylaldehyde
   (*c*) salicylic acid (*d*) phthalic acid
9. Which is most reactive towards electrophilic reagent?

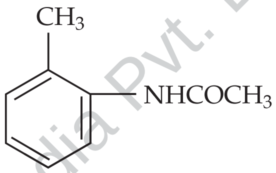
(*a*)



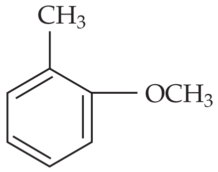
(*b*)



(*c*)

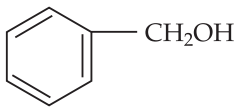


(*d*)

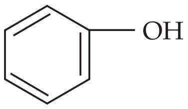


10. Which of the following compounds has the most acidic nature?

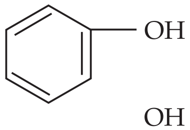
(*a*)



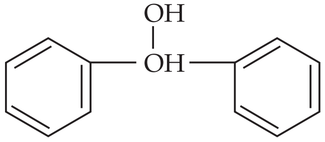
(*b*)



(*c*)



(*d*)



(B) Fill in the Blanks

Fill in the blank spaces:

1. Phenol forms coloured complexes with neutral ___________ .
2. Phenol on treatment with bromine water gives _______ but with bromine in CS_2, it mainly gives __________ .
3. Benzyl alcohol and phenol can be distinguished by using _______ reagent.
4. The acidity of phenol is due to the _______ of its anion.
5. Phenol is acidic because of resonance stabilization of its conjugate base, namely _______.
6. Amongst the three isomers of nitrophenols, the one that is least soluble in water is _______.

7. Formation of phenol from chlorobenzene is an example of ______ aromatic substitution.

(C) True/False Statements

Write T for true and F for false statements:

1. Arenes are pure aromatic compounds.
2. *n*-heptane can be converted to benzene by passing the vapour over Cr_2O_3.
3. Continued decarboxylation of phthalic acid produces benzoic acid.
4. When benzene vapours mixed with air are passed over heated vanadium pentoxide catalyst, maleic anhydride is obtained.
5. Groups such as —COOH and —CN are *o-p* directing, whereas groups such as —OH, —NH_2 are *meta* directing.
6. Phenols from coloured complexes with neutral ferric chloride.
7. Phenol is a weaker acid than carbonic acid.
8. An electron-donating substituent in benzene orients the incoming electrophile to the *meta*-position.
9. Diphenyl ether cannot be prepared by dehydration of phenol with conc. sulphuric acid.

(D) Assertion-Reason Type Question

In the following questions, two statements are given, one labelled as ***Assertion A*** *and the other as* ***Reason R.*** *Examine the two statements carefully and mark the correct choice out of (a), (b), (c) and (d) according to the instructions below:*

If both **A** and **R** are correct and **R** is the correct explanation of **A**, mark *(a)*

If both **A** and **R** are correct but **R** is not the explanation of **A,** mark *(b)*

If **A** is correct but **R** is wrong, mark *(c)*

If **A** is wrong but **R** is correct, mark *(d)*

1. Assertion A : Phenol is more reactive than benzene towards electrophilic substitution reaction.

Reason R : In case of phenol, the intermediate carbocation is more resonance stabilised.

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring
   - (*a*) deactivates the ring by inductive effect
   - (*b*) deactivates the ring by resonance
   - (*c*) increases the charge density at *ortho* and *para* position relative to *meta* position by resonance
   - (*d*) directs the incoming electrophile to *meta* position by increasing the charge density relative to *ortho* and *para* position
2. In an electrophilic substitution reaction of nitrobenzene, the presence of nitro group
   - (*a*) deactivates the ring by inductive effect
   - (*b*) activates the ring by inductive effect
   - (*c*) decreases the charge density at *ortho* and *para* position of the ring relative to *meta* position by resonance
   - (*d*) increases the charge density at *meta* position relative to the *ortho* and *para* positions of the ring by resonance
3. Phenol is less acidic than
   - (*a*) ethanol
   - (*b*) *o*-nitrophenol
   - (*c*) *o*-methylphenol
   - (*d*) *o*-methoxyphenol
4. Which of the following is most acidic?
   - (*a*) Benzyl alcohol
   - (*b*) Cyclohexanol
   - (*c*) Phenol
   - (*d*) *m*-Chlorophenol
5. Phenol can be distinguished from ethanol by the reactions with
   - (*a*) Br_2/water
   - (*b*) Na
   - (*c*) Neutral $FeCl_3$
   - (*d*) All the above

II. Assertion-Reason Type Questions

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the following choices.

(*i*) Both A and R are correct and R is the correct explanation of A.

(*ii*) Both A and R are correct but R is not the correct explanation of A.

(*iii*) Both A and R are not correct.

(*iv*) A is not correct but R is correct.

1. **Assertion (A) :** Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.

   Reason (R) : The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2^+.

2. **Assertion (A) :** Phenol forms 2, 4, 6-tribromophenol on treatment with Br_2 in carbon disulphide at 273 K.

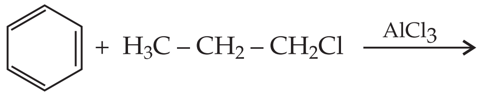
   Reason (R) : Bromine polarises in carbon disulphide.

3. **Assertion (A) :** Phenols give *o*- and *p*-nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.

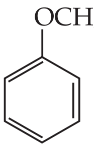
   Reason (R) : —OH group in phenol is *o*-, *p*-directing.

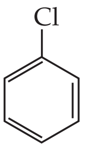
III. Short Answer Type Questions

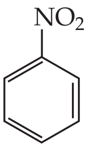
1. What will be the product obtained as a result of the following reaction and why?



2. How will you convert benzene into
   (*i*) *p*–nitrobromobenzene
   (*ii*) *m*–nitrobromobenzene?
3. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile. Give reason.

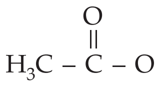






4. Despite their -I effect, halogens are *o*- and *p*-directing in haloarenes. Explain.
5. Nucleophiles and electrophiles are reaction intermediates having electron rich and electron deficient centres respectively. Hence, they tend to attack electron deficient and electron rich centres respectively. Classify the following species as electrophiles and nucleophiles.

   (*a*) H_3CO^-

   (*b*)

$H_3C-\overset{\overset{\Large O}{\|}}{C}-O$

   (*c*) $\dot{Cl}$

   (*d*) $Cl_2C:$

   (*e*) $(H_3C)_3C^+$

   (*f*) Br^-

   (*g*) H_3COH

   (*h*) R-NH-R
6. When phenol is treated with bromine water, white precipitate is obtained. Give the structure and the name of the compound formed.
7. Explain why is OH group in phenols more strongly held as compared to OH group in alcohols.
8. Explain why nucleophilic substitution reactions are not very common in phenols.
9. Write steps to carry out the conversion of phenol to aspirin.
10. Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?

IV. Long Answer Type Questions

1. (*a*) Name the starting material used in the industrial preparation of phenol.
   (*b*) Write complete reaction for the bromination of phenol in aqueous and non-aqueous medium.
   (*c*) Why Lewis acid is not required in bromination of phenol? Explain
2. How can phenol be converted to aspirin?

ANSWERS

(A) Multiple Choice Questions

1. (*d*) 2. (*c*) 3. (*d*) 4. (*d*) 5. (*d*) 6. (*b*) 7. (*b*)
8. (*c*) 9. (*a*) 10. (*b*)

(B) Fill in the Blanks

1. $FeCl_3$
2. 2, 4, 6-tribromophenol, 4-bromophenol
3. neutral $FeCl_3$
4. resonance stabilization
5. phenoxide ion
6. *o*-nitrophenol, due to intermolecular hydrogen bonding
7. nucleophilic

(C) True/False Statements

1. F 2. F 3. F 4. T 5. F 6. T 7. T
8. F, *o*-and *p*-positions 9. T

(D) Assertion-Reason Type Question

1. (*c*)

Some Additional Questions

I. Multiple Choice Questions

1. (*a*), (*c*) 2. (*a*), (*c*) 3. (*b*) 4. (*d*) 5. (*a*), (*c*)

II. Assertion-Reason Type Questions

1. (*i*) 2. (*ii*) 3. (*iv*)

III. Short Answer Type Questions

1. Propyl chloride forms less stable $CH_3 — CH_2 — CH_2^{\oplus}$ carbocation with anhydrous $AlCl_3$ which rearranges to a more stable $CH_3 — \overset{\oplus}{C}H — CH_3$ carbocation and gives isopropylbenzene as the product of the reaction.

3. The +R effect of $—OCH_3$ > $—Cl$ and $—NO_2$ has a – R effect. Relative reactivity of the substituted benzene rings is as follows:

$$C_6H_5—OCH_3 > C_6H_5—Cl > C_6H_5–NO_2$$

4. Halogens attached to benzene rings exert –I and +R effect. +R effect dominates –I effect and increases the electron density at *ortho* and *para* positions of the benzene ring with respect to halogens.

15

CHAPTER

Green Chemistry

LEARNING OBJECTIVES

- Explain what is green chemistry.
- List the pollutants that causes atmospheric pollution.
- Design a greenhouse to explain greenhouse effect.
- Explain global warming, its causes and consequences.
- Explain the chemistry of origin of the ozone layer in the upper layers of the atmosphere.
- List the chemicals causing depletion of ozone layer.

15.1 INTRODUCTION

Contamination of any part of the environment is called **pollution** and the substances which cause pollution are called pollutants. When the concentration of a substance already present in the nature or of a new substance increases to a undesirable proportion causing harm to the environment, the substance is said to be a **pollutant**. For example, nitrate is added to the soil in order to increase plant growth, but an excessive concentration of nitrate present in drinking water can be toxic.

15.1.1 Green Chemistry: A New Route to Protect Environment

The branch of chemistry that deals with processes and products that reduce or eliminate the use and generation of hazardous substances is called **green chemistry.**

Green chemistry simply utilises the information that is available to the scientific community regarding the toxicity and other hazards posed by certain chemicals in order to fully evaluate the negative as well as positive impact of chemistry by design.

Chemists all over the world are using their creative and innovative skills to develop new processes, synthetic methods, analytical tools, reaction conditions, etc. Some developments have been reported as mentioned below:

(*i*) For the manufacturing of polystyrene, CFC was used which is a blowing agent, which is the main cause of ozone layer depletion. But now, new technique has been developed using CO_2 as blowing agent.

(*ii*) Instead of using synthetic materials for packing, green chemistry plans to use environment-friendly recyclable safely disposable materials.

(*iii*) Use of biotechnological alternatives.

15.2 ATMOSPHERIC POLLUTION

The atmosphere surrounding us may be divided into four regions:

(*i*) Troposphere
(*ii*) Stratosphere
(*iii*) Mesosphere
(*iv*) Thermosphere

The lowest region is called **troposphere**, which extends upto the height of ~10 km from the sea level. Above the troposphere, between 10 and 50 km above the sea level, lies the **stratosphere**. It contains nitrogen, oxygen and ozone. **Mesosphere** lies above stratosphere up to the height of 90 km from the sea level. It contains O_2^+ and NO^+. **Thermosphere** is beyond 90 km and upto 500 km from the sea level.

Atmospheric pollution is generally studied under troposphere and stratosphere pollution.

15.2.1 Tropospheric Pollution

Gases such as carbon monoxide, oxides of nitrogen, oxides of sulphur, hydrogen sulphide and many volatile organic compounds, suspended particulate matters are continuously released into the atmosphere due to human and natural activities. These chemical substances cause pollution.

15.3 AIR POLLUTION

Most air pollution is the result of burning things – fuels or just waste matter. Petrol is a good example. It is made of hydrocarbons, which are compounds of hydrogen and carbon. If it burns in plenty of air, the main products are carbon dioxide and water vapour. But in a car engine, there is not enough air. Incomplete combustion of petrol releases harmful products into the atmosphere.

The main harmful products are:

(*i*) **Carbon monoxide.** It is poisonous because it binds to haemoglobin much more strongly than oxygen. The presence of CO, therefore reduces the amount of haemoglobin available in the blood for transport of oxygen to the body cells, thereby reducing O_2 level and impairing the normal metabolism of the body. High level concentration of CO in the blood can cause mental impairment, laboured respiration, muscular weakness, dizziness and even death. High level of CO (100 ppm or more) will affect the plants causing leaf drop, reduction in leaf size and premature ageing, etc.

(*ii*) **Carbon dioxide.** In a balanced ecosystem, CO_2 released into the atmosphere is removed regularly by the green plants. Forests account for about 70% of all photosynthesis occurring at any time but with the extent of deforestation that has taken place, there is an increase in the concentration of CO_2 in the atmosphere.

CO_2 causes mild narcotic effects, stimulation of the respiratory centre and leads to asphyxiation. The increased concentration of CO_2 also causes greenhouse effect which leads to global warming.

(*iii*) **Nitrogen oxides.** In automobiles, nitrogen oxides are formed because the air in the engine gets so hot that nitrogen and oxygen present in the air react together. Nitric oxide is also formed as a result of lightning taking place in the atmosphere.

$$N_2\,(g) + O_2\,(g) \xrightarrow{1483\text{ K}} 2NO\,(g)$$

NO gas thus formed combines with oxygen instantly to give NO_2.

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

Rate of formation of NO_2 is faster when NO reacts with O_3 (ozone) in the stratosphere.

$$NO\,(g) + O_3\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$$

Harmful effects:

- (*a*) NO_2 results in respiratory problems in human beings and leads to bronchitis.
- (*b*) High concentration of NO_2 is harmful to plants resulting in the leaf spotting and suppresses the vegetative growth.

(*iv*) **Oxides of sulphur.** SO_2, SO_3 and vapours of sulphuric acid act as major pollutants for air. SO_2 forms because petrol contains a little sulphur.

Even low concentration of SO_2 causes respiratory diseases *e.g.*, asthma, bronchitis, emphysema in human beings. SO_2 causes irritation to eyes. In presence of particulate matter, SO_2 gets oxidised rapidly to SO_3.

$$2SO_2\ (g) + O_2\ (g) \rightarrow 2SO_3\ (g)$$

Oxidation of SO_2 to SO_3 can also be affected by O_3 (ozone) and H_2O_2 (hydrogen peroxide).

$$SO_2\ (g) + O_3\ (g) \rightarrow SO_3\ (g) + O_2\ (g)$$

$$SO_2\ (g) + H_2O_2\ (l) \rightarrow H_2SO_4\ (aq)$$

Harmful effects: It is extremely harmful to both plants and animals.

- (*a*) It is a major source of irritation for eyes and respiratory track and leads to bronchitis and lung cancer.
- (*b*) Increased concentration of oxides of sulphur (SO_2) kills leaf tissues, it deteriorates and weakens building materials. The gas released from Mathura refinery is a constant threat to Taj Mahal at Agra.
- (*c*) It also accelerates the corrosion of metals such as Cu, Zn, Fe, etc.

(*v*) **Hydrocarbons.** Incomplete combustion of fossil fuel in industry and thermal power plants and the exhaust of automobiles releases unburnt hydrocarbons causing pollution.

Harmful effects:

- (*a*) CH_4 is a greenhouse gas having 20 times more capacity of taking heat compared to CO_2.
- (*b*) They produce a foul smell.
- (*c*) Can cause liver damage and cancer.
- (*d*) Derivatives of hydrocarbons *e.g.* CF_2Cl_2 (used for refrigeration) when enters the upper atmosphere decomposes in presence of U.V. light to produce Cl_2 or free radicals which cause the decomposition of O_3 and leads to ozone layer depletion.

(*vi*) **Acid rain.** Rainwater is usually slightly acidic (pH 5.6 – 6.0) in nature due to the presence of CO_2 in the atmosphere. But acid rain describes any form of precipitation that has elevated level of hydrogen ions (low pH). This is caused due to the presence of sulphur dioxide and nitrogen oxide.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$$

$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$$

Harmful effects:

- (*a*) Corrosion of monuments and structures: H_2SO_4 and HNO_3 react with marble ($CaCO_3$).

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O$$

- (*b*) Articles made up of metals slowly lose their metallic lustre.
- (*c*) Acid rain has caused elimination of aquatic life.
- (*d*) It damages leaves of trees and plants and retards the growth of forests.

15.3.1 Particulates in Atmospheric Pollution

Particulates are the tiny solid or liquid particles suspended in air. These particles are usually invisible to the naked eye. The particulate matter is in the range of 0.001 to 10 nm. The particulates include soot, cement, dust, fly ash, hydrocarbons, soil dust, pulverised coal, mineral particles, etc. There are four types of non-viable particulates present in the atmosphere:

(*i*) **Mists.** Mists are produced by particles of spray liquids and the condensation of vapours in air. They arise because of chemical reactions and condensation of vapours.

(*ii*) **Smoke.** It denotes small sooty particles produced by combustion of organic matter. Oil smoke, carbon smoke and tobacco smoke are common examples.

(*iii*) **Fumes.** Fumes, condensed vapours, fumes of metals are the well-known particulates of this type. These are released into the atmosphere by the various metal finishing processes.

(*iv*) **Dust.** It consists of fine particles produced during grinding of solid materials. These include the particles of coal, cement, limestone, fly ash, silica dust, etc.

The particles smaller than 5 microns penetrate into the lungs. A number of them are carcinogenic. Inhalation of small particles irritate the lungs and exposure to such particles for a long period of time causes 'scarring' or fibrosis of lung lining. This is termed as **"Pneumoconiosis".**

Suspended particles in the atmosphere reduce the visibility and concentration of the sun rays reaching the earth and thereby lowering the temperature of the earth. This contributes to fog.

Smog: Smog is a mixture of smoke, dust particles and small drops of fog. It is a major air pollutant in big cities. Smogs are of two types:

(*i*) Chemical smog

(*ii*) Photochemical smog

(*i*) **Chemical smog.** It occurs in cool humid climate and is a result of build up of SO_2 and particulate matter from fuel combustion. This was observed in London in 1962 causing death of many people.

(*ii*) **Photochemical smog.** This type of smog is formed by the combination of smoke, dust and fog with an air pollutant in the atmosphere as a result of photochemical reactions. It develops in cities in which the atmosphere is loaded with large quantities of automobile exhausts. Photochemical smog is chemically oxidising because it has high concentration of oxidising agents. It is characterized by brown hazy irritating fumes.

The chemistry of formation of photochemical smog centres around nitric oxide. At high temperature, in petrol and diesel engines of automobiles, N_2 and O_2 react to form a small quantity of NO which enters into the atmosphere with exhaust gases. This NO is oxidised to NO_2 which in turn absorbs energy from sunlight and breaks up into nitric oxide and free oxygen atom.

$$NO_2\,(g) \xrightarrow{h\nu} NO\,(g) + O\,(g)$$

Atomic oxygen is very active and combines with O_2 to form ozone (O_3).

$$O\,(g) + O_2\,(g) \rightarrow O_3\,(g)$$

O_3 thus formed reacts rapidly with NO (*g*) to give NO_2 (*g*).

$$NO\,(g) + O_3\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$$

Both NO_2 and O_2 are strong oxidising agents and can react with unburnt hydrocarbons in the polluted air to produce formaldehyde, peroxyacetyl nitrate (PAN), and acrolein.

$$3CH_4\,(g) + 2O_3\,(g) \rightarrow 3HCHO + 3H_2O$$

Harmful effects:

(*i*) Peroxyacetyl nitrate (PAN), O_3 and acrolein cause eye-burn and are harmful to respiratory system.

(*ii*) Photochemical smog affects plant growth.

15.3.2 Control of Photochemical Smog

If we control the primary precursors of photochemical smog, such as NO_2 and hydrocarbons, the secondary precursors such as ozone and peroxyacyle nitrates (PAN) of the photochemical smog will automatically be reduced. For this purpose,

(*i*) We use catalytic convertors in automobiles which prevent the release of NO_2 and hydrocarbons to the atmosphere.

(*ii*) We plant Pinus, Juniperus, Quercus and Pyrus which are capable of metabolising nitrous oxide and can help in this matter.

15.3.3 A Simple Experiment to Detect Air Pollutants

We can detect carbon and root particles, dust particles and pollens in the atmosphere by performing a simple experiment given below and we don't need any sophisticated instruments to do this. Steps involved to carry out the experiment are given below:

1. Take a plastic box of about 500 ml capacity with an airtight lid.
2. Remove the lid and cut a hole of about 2″ diameter in the centre of the lid.
3. Replace the lid on the plastic box and press it tight on the box.
4. Cut a filter paper of 3″ diameter and place it above the hole of the lid.
5. Place a heavy steel washer of suitable diameter over the filter paper such that it keeps the filter paper in place.
6. Insert an iron tube near the bottom of the box by first making a hole of about $\frac{1}{2}''$ diameter. Apply quick fix or araldite around the outer wall of the box and the tube so that it becomes airtight.
7. Connect the iron tube to the vacuum pump with the help of a rubber tubing. Switch on the vacuum pump and keep it running for a few hours.
8. Vacuum pump will suck out the air from the box and air from the atmosphere will enter the box through the filter paper disc. Any impurities in the atmosphere will be retained by the filter paper. If the impurities are those of smoke or carbon particles, they will leave a grey colour on the filter paper. If the impurities are those of pollen, they will leave a yellow colour. The intensity of the colour on the filter paper will tell about the concentration of pollutants in the atmosphere.

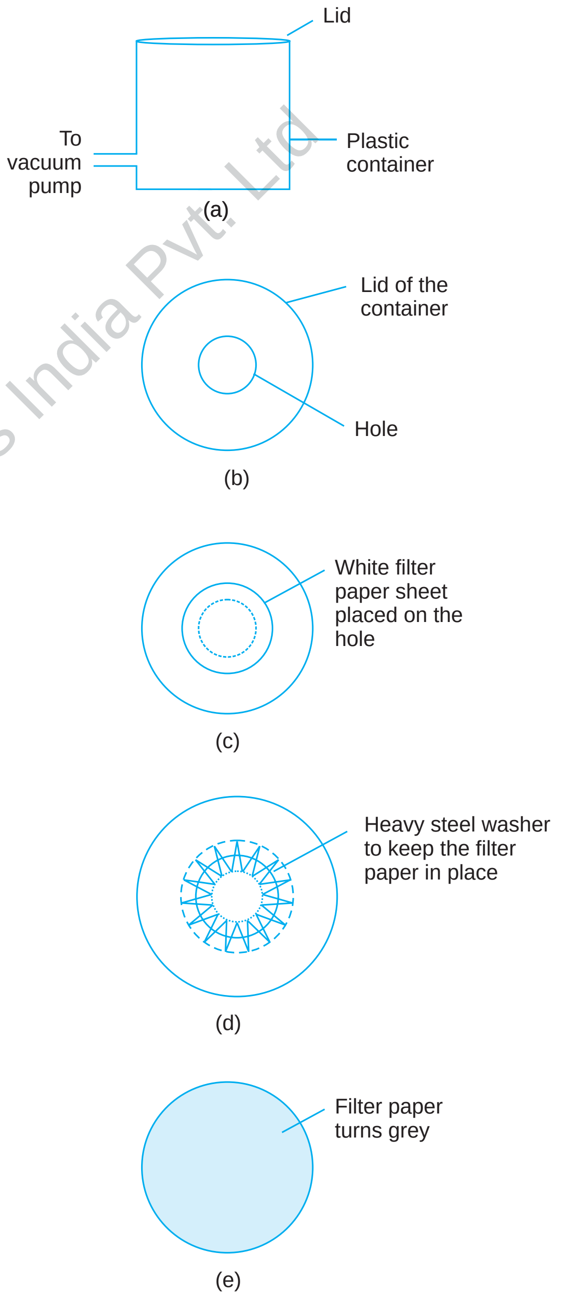


Fig. 15.1: *(a) to (e) Detection of air pollutants*

15.4 OZONE LAYER

The layer of earth's atmosphere that surrounds us is called the troposphere. It extends up to 10 km from the earth's surface. The next higher layer stratosphere extends 10–50 km above the earth's surface. A layer of ozone (O_3) is found between 15 and 35 km in the stratosphere.

Maximum concentration of ozone occurs at a distance of 25 km. Now what is the role of this ozone layer around the earth in the stratosphere.

It absorbs high frequency, low wavelength, ultraviolet radiations coming from the sun and does not let them reach the earth. The high energy ultraviolet rays are injurious to human and animal life. These rays cause skin cancer.

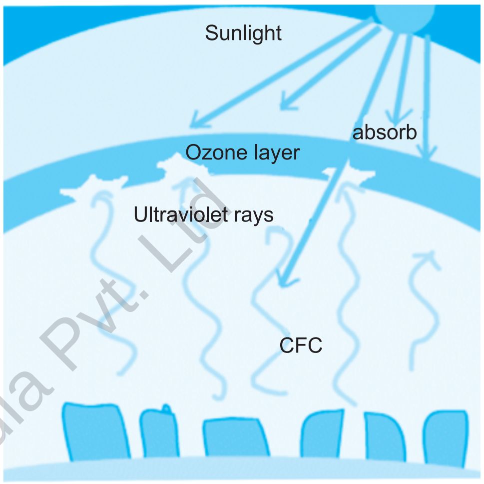


Fig. 15.2: *Ozone layer depletion*

15.4.1 Ozone Hole (Ozone Layer Depletion)

In 1985, scientists discovered that ozone layer was thinning over antarctica. The thinning of ozone layer is termed as **ozone hole**. Since then it continues to get thinner and thinner it may be thinning at other places also. It poses a serious environmental problem because a thin ozone layer cannot completely absorb the ultraviolet rays. If the ultraviolet rays reach the earth, they are sure to cause havoc to human and animal health in the form of skin cancer, cataracts and weak immune system. Increased UV radiation can also lead to reduction in the crop yield and could also affect adversely the marine life. Thus, decrease in the concentration of ozone in the ozone layer is referred to as **depletion of ozone layer**. It may be understood that literally the hole is not formed in the layer, it is just the thinning of the ozone layer.

15.4.2 Causes of Ozone Hole (Ozone Layer Depletion)

Major culprits in the formation of the ozone hole are chlorofluorocarbons (CFC's) which are used in the refrigerators and airconditioners. Chlorofluorocarbons are also used in aerosols and as organic solvents.

Jet planes and space rockets fired from the earth for various purposes also contribute to the destruction of ozone layer. The jet planes flying at high altitude give out emissions at higher temperatures sufficient to promote combination of atmospheric oxygen and nitrogen to form nitric oxide (NO).

$$N_2 + O_2 \xrightarrow[\text{Temperature}]{\text{High}} 2NO$$

These oxides also destroy the ozone layer. When chlorofluorocarbons reach the stratosphere, the UV rays from the sun cause them to break releasing chlorine atoms which react with ozone, causing the chemical cycle of ozone destruction. One chlorine atom can destroy 1 lakh ozone molecules. Ozone depletion is not limited to south pole (antarctica). It is a global phenomenon. With the depletion of ozone in the stratosphere, more UV rays will reach the earth and cause more destruction. Besides chlorofluorocarbons (CFCs), methane and N_2O gases are also responsible for ozone layer depletion as they also react with ozone producing oxygen. Oxygen has no capability to absorb UV rays.

Reactions which explain the destruction of ozone layer by chlorofluorocarbons are given as under:

$$\mathrm{CF_2Cl_2}\,(g) \xrightarrow{\text{UV}} \dot{\mathrm{C}}\mathrm{l}\,(g) + \dot{\mathrm{C}}\mathrm{F_2Cl}\,(g)$$

$$\dot{\mathrm{C}}\mathrm{l}\,(g) + \mathrm{O_3}\,(g) \longrightarrow \mathrm{Cl}\dot{\mathrm{O}}\,(g) + \mathrm{O_2}\,(g)$$

$$\mathrm{Cl}\dot{\mathrm{O}}\,(g) + \mathrm{O}\,(g) \longrightarrow \dot{\mathrm{C}}\mathrm{l}\,(g) + \mathrm{O_2}$$

Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals which cause the breakdown of zone.

15.4.3 Effects of Ozone Layer Depletion

It has been reported that 5% depletion of ozone layer causes 10% increase in UV radiations reaching the earth. Some effects of ozone layer depletion are given below:

1. It causes skin cancer, cataract and malfunctioning of the immune system.
2. It causes damage to the nucleic acids in the living organisms.
3. UV radiations retard the process of photosynthesis in plants and phytoplanktons affecting the whole food chain.

15.4.4 How to Stop Ozone Layer Depletion?

In 1987, the Montreal Protocol was signed asking member countries to reduce the use of CFCs and other ozone depleting substances. The treaty was amended to ban production of CFC after 1995 by the developed countries and later by the developing countries. 165 countries signed the treaty. With effect from Ist January, 1996, only the existing stock and recycled CFCs are used in countries like USA.

It is mandatory that the refrigerants from unserviceable refrigerators and airconditioners should not be released into the atmosphere unlike as it was done earlier. These gases should be rather recycled.

There is simply no way we could create ozone fast enough in large quantities and release it to the stratosphere. The only way to check ozone depletion is to remove excess chlorine and bromine from the stratosphere. And to achieve that, we have to stop making CFCs.

Vienna Meet of 1995 and Kyoto Protocol of 1997 further highlighted the need to pay more attention to the preservation of environment by stopping the manufacture of harmful substances. Substitutes for CFCs have been identified. It has been found that hydrofluorocarbons (HFC's) and hydrochlorofluoro carbons (HCFCs) are less stable compounds than chlorofluorocarbons and therefore less likely to reach the stratosphere and cause the decomposition of ozone.

Scientists at Indian Institute of Chemical Technology, Hyderabad have developed a process for the manufacture of HFCs that can be used as refrigerants as efficiently as CFCs.

15.5 BIOFUELS

With the economic advancement, our energy, requirement has increased. We require energy for heating, lighting, air-conditioning of homes and establishments, running automobiles, etc. We are totally dependent on fossil fuels like coal and petroleum for our needs. Deforestation is taking place at a fast rate in our mad rush for firewood. Firewood on burning produces carbon dioxide. Similarly, exhausts of automobiles also throw a lot of carbon dioxide into the atmosphere.

Thus, we are in a very piquant situation. On one hand, the fossil fuels are getting exhausted. On the other hand, the fuels that we are using are causing a lot of pollution. We therefore require alternative fuels that are non-polluting. Biotechnology can be used to overcome these problems. Large scale generation of biomass is to be created where solar energy gets trapped as chemical energy to produce organic matter.

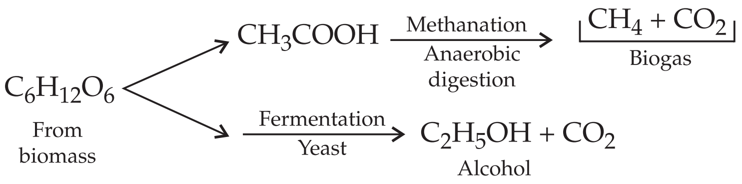
$$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyll}]{\text{Solar energy}} (CH_2O)_6 + 6O_2 + 6H_2O$$

In this age of energy crisis and atmospheric pollution, biomass holds promise of a good renewable energy source. Due to the process of recycling, no new CO_2 is released to the atmosphere.

Large scale propagation of fast growing fuel wood trees like eucalyptus, acacia, populus, leucaena and albizia is possible through tissue culture. Quantum of biomass obtainable is encouraging. However, we require proper technology to convert biomass into gaseous or liquid fuels.

Anaerobic digestion of biomass containing cellulose, sugar, etc., can be carried out to obtain methane as a fuel. Alternatively, fermentation of biomass can be done to obtain alcohol, a fuel in the liquid form.

The conversion reactions are explained as under:



Anaerobic digestion of the biomass first gives acetic acid, which on further degradation gives out methane and carbon dioxide. Bacteria desulphovibrio convert the biomass into acid which is further converted into methane by the bacteria methanococcus and methanothrix.

15.5.1 Biodiesel

It is a new ray of hope to cope with the energy crisis and the almost disappearing fossil fuels. *Jatropha* is a fast growing plant which has high seed yield and is usually not eaten by animals. On crushing, the seeds give an oil, which on trans-esterification gives diesel. The other plants in this category are: *neem, karanji, mahua, hirda, marwa and rohitak*.

Progressive farmers are beginning to discover the market for this. And this could be the biggest source of biofuel with a little push from oil companies and customers in future. Although the price will be high in the initial years, it will progressively fall going forward.

15.6 BIOPESTICIDES AND BIOFERTILIZERS

Biopesticides

In the last few decades, use of chemical and synthetic pesticides has increased in agricultural practices. Although it brought about the *Green Revolution* where the production of foodgrains increased substantially, but it also brought along problems of environmental pollution. Many of these pesticides are non-biodegradable and toxic, causing loss of soil fertility and health problem.

In recent years, a number of biopesticides, which have been developed, are being used increasingly in agriculture. Perhaps the oldest plant-derived pesticide is *pyrethrin* comprising six structurally similar esters. The main source of obtaining this compound is *chrysanthemum cinerariaefolium* (a member of sunflower family). Neem has insecticidal properties. A number of neem products are now available in the market. Efforts are being made towards genetic improvement of neem tree to have better yield of *azadirachtin* alkaloids. The most successful biocontrol agent is *bacillus thuringiensis* which is a spore forming bacterium. The active component here is a crystalline protein which is highly toxic to pests of crop plants. The toxin contained in it causes paralysis of the insect larva leading to death.

Biofertilizers

Fertilizers increase the concentration of salt in the soil beyond desired limits. Increased salt concentration reduces fertility and therefore chemical fertilizers should be used in the minimum possible quantities. To escape the ill-effects of chemical fertilizers, manure (compost) should be used to provide nutrition to the plants. Manures are obtained by anaerobic decomposition of the animal and plant waste. Living organism which help in the fertilization of soil are called *biofertilizers.* Biofertilizers should be used in place of chemical fertilizers to maintain and increase the fertility of the soil.

Use of leguminous species (pea family) as a means of enriching soil fertility is well known due to their ability to fix atmospheric nitrogen with the help of bacterium *rhizobium* in their root nodules. A number of other microbes including bacterial species and cyanobacteria (blue green algae) act as nitrogen-fixers. Two well known blue-green algae are anabaena and nostoc which occur in free living conditions in the soil. The biological mechanism of conversion of atmospheric nitrogen to ammonia is influenced by the enzyme *nitrogenase.*

MISCELLANEOUS SOLVED QUESTIONS

1. *Define 'environmental chemistry'.*

Ans. The branch of science which deals with the chemical phenomenon occurring in the environment is called environmental chemistry.

2. *Carbon monoxide gas is more dangerous than carbon dioxide gas. Why?*

Ans. CO is more dangerous than CO_2 because of its ability to block the delivery of oxygen to the organs and tissues. It also binds to haemoglobin to form carboxyhaemoglobin, which is about 300 times, more stable than the oxygen-haemoglobin complex. In blood, when the concentration of carboxyhaemoglobin reaches about 3–4 per cent, the oxygen carrying capacity of blood is greatly reduced. This oxygen deficiency results into headache, weak eyesight, nervousness and cardiovascular disorder.

3. *List gases which are responsible for greenhouse effect.*

Ans. The gases responsible for greenhouse effect are CO_2, CH_4, O_3, N_2O, H_2O Chlorofluorocarbon compounds (CFCs).

4. *What is smog? How is classical smog different from photochemical smogs?*

Ans. Smog is a mixture of smoke, dust particles and small drops of fog.

Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and SO_2. It is a reducing mixture.

Photochemical smog occurs in warm, dry and sunny climate. It results from the action of sunlight on unsaturated hydrocarbons and oxides of nitrogen produced by automobiles and factories. It is an oxidising mixture.

5. *What do you mean by ozone hole? What are its consequences?*

Ans. The decomposition products of CFCs destroy the ozone layer present in the stratosphere in presence of UV radiations.

$$CF_2Cl_2\,(g) \xrightarrow{h\nu} \dot{Cl}\,(g) + CF_2\dot{Cl}\,(g)$$

A highly reactive chlorine atom is produced. This reacts with O_3 to form chlorine monoxide.

$$Cl\,(g) + O_3\,(g) \rightarrow Cl\dot{O}\,(g) + O_2\,(g)$$

Reaction with atomic oxygen produces more chlorine atoms.

$$Cl\dot{O}\,(g) + O\,(g) \rightarrow \dot{Cl}\,(g) + O_2\,(g)$$

These chlorine atoms are free to react with more O_3 and thus destroy them. This is called **ozone hole**.

The depletion of ozone layer in the stratosphere has resulted in increased human cataracts, skin cancer, reduction of planktons in ocean waters, depletion of plants and crops. It has also increased evaporation of surface water and decreased the moisture content of the soil.

6. *What are pesticides and herbicides? Explain, giving examples.*

Ans. Pesticides are substances that are used to kill or block the reproductive processes of unwanted organisms, *e.g.*, DDT, BHC. Herbicides are chemicals used to destroy weeds. $NaClO_3$ and Na_3AsO_3 (Sod. arsenate) are examples of herbicides.

QUICK SCAN (FOR REVISION)

1. **Environmental chemistry** is the study of the origin, transport, reactions, effects and fates of chemical species. Some of the chemical species released into the environment are harmful and cause **pollution**.
2. Pollutants may be defined as a substance present in environment in greater proportion than its natural abundance and resulting in harmful effects leading to pollution.
3. Green chemistry deals with the processes and products that reduce or eliminate the use and generation of hazardous substances.
4. **Troposphere** is the lowest region of the atmosphere (~ 10 km) whereas stratosphere extends above troposphere upto 50 km above the sea level. Oxides of sulphur, nitrogen, carbon, halogens along with particulate matters cause **tropospheric pollution**. The gaseous pollutants come down to the earth in the form of acid rain. Most of the solar energy (75%) reaching earth is absorbed by the earth surface and rest is radiated back to atmosphere. These gases mentioned above trap heat which results into **global warming**. Many human activities are producing

chemicals which are responsible for the **depletion of ozone layer**, in the atmosphere leading to the formation of **ozone hole**.

5. A plant absorbs carbon dioxide, which is naturally found in the Earth's atmosphere.
6. The plant uses the carbon dioxide in order to grow by the process of photosynthesis.
7. Acid rain contains traces of acids such as H_2SO_4, HNO_3, H_2CO_3 dissolved in water. Its pH is generally less than 5.6. It damages monuments and structures made of firm marble, corrodes articles made from metals, destroys plants and trees, and is also harmful to the aquatic life in lakes and rivers.
8. London smog consists of droplets of H_2SO_4 deposited on the particulates suspended in the atmosphere.
9. With the industrial revolution in the late 1700's, humans began emitting more fossil fuels from coal, oil, and gas to run their cars, trucks, and factories.
10. There is more carbon dioxide in the atmosphere today than at any point in the last 800,000 years.
11. Ozone prevents the harmful ultra violet (U.V.) radiations of sun from reaching the surface of earth. If ozone layer from the region gets completely depleted, then these harmful radiations will have direct access to all living species, both plants and animals. These will cause havoc and increase our misery.
12. Ozone hole caused by the depletion of ozone layer, exposes living beings, both plants and animals to the harmful U.V. radiations leading to many diseases.

EXERCISES

Very Short Answer Type Questions

1. Is carbon dioxide in the atmosphere really increasing?
2. What are air pollutants?
3. What are the two sources of SO_2 in air?
4. What are the harmful effects of acid rain?
5. What is the utility of ozone layer?
6. What is photochemical smog?
7. Name two highly toxic compounds of mercury.
8. How does SO_2 cause pollution?
9. Why is the use of CFCs discouraged?

Short Answer Type Questions

1. Give some harmful effects of depletion of ozone layer.
2. What is the ozone hole?
3. Acid rain is known to contain some acids. Name these acids and their sources.
4. Ozone is a toxic gas and is a strong oxidising agent even then its presence in the stratosphere is very important. Explain what would happen if ozone from this region is completely removed.
5. Dissolved oxygen in water is very important for aquatic life. What processes are responsible for the reduction of dissolved oxygen in water?
6. On the basis of chemical reactions involved, explain how do chlorofluorocarbons cause thinning of ozone layer in stratosphere.
7. What could be the harmful effects of improper management of industrial and domestic solid waste in a city?
8. What are biodegradable and non-biodegradable pollutants?
9. A factory was started near a village. Suddenly villagers started feeling the presence of irritating vapours in the village and cases of headache, chest pain, cough, dryness of throat and breathing problems increased. Villagers blamed the emissions from the chimney of the factory for such problems. Explain what could have happened. Give chemical reactions to support your explanation.
10. Oxidation of sulphur dioxide into sulphur trioxide in the absence of a catalyst is a slow process but this oxidation occurs easily in the atmosphere. Explain how does this happen. Give chemical reactions for the conversion of SO_2 into SO_3.
11. From where does ozone come in the photochemical smog?
12. How is ozone produced in stratosphere?
13. Ozone is a gas heavier than air. Why does ozone layer not settle down near the earth?
14. Some years ago formation of polar stratospheric clouds was reported over Antarctica. Why were these formed? What happens when such clouds break up by warmth of sunlight?

Long Answer Type Questions

1. What are smogs? Distinguish between chemical and photochemical smog.
2. Explain giving reasons "the presence of CO reduces the amount of haemoglobin available in the blood for carrying oxygen to the body cells."
3. Define environmental pollution. What are its causes?
4. Write short notes on:
   (*a*) Smog
   (*b*) Biofuels
   (*c*) Depletion of ozone layer
5. For dry cleaning, in the place of tetrachloroethane, liquefied carbon dioxide with suitable detergent is an alternative solvent. What type of harm to the environment will be prevented by stopping use of tetrachloroethane? Will use of liquefied carbon dioxide with detergent be completely safe from the point of view of pollution? Explain.
6. Explain the following:
   (*i*) Biodiesel
   (*ii*) Biopesticides
   (*iii*) Biofertilizers

COMPETITION FILE

OBJECTIVE QUESTIONS

(A) Multiple Choice Questions

Choose the correct answer:

1. Acid rain is due to the formation of oxides of
   (*a*) sulphur (*b*) nitrogen
   (*c*) none of these (*d*) (*a*) and (*b*) both
2. Which oxide of nitrogen is not a common pollutant?
   (*a*) NO_2 (*b*) N_2O_5
   (*c*) NO (*d*) N_2O
3. Besides CO_2, the other greenhouse gas is
   (*a*) CH_4 (*b*) N_2
   (*c*) Ar (*d*) O_2
4. The major air pollutant is
   (*a*) CO (*b*) oxides of nitrogen
   (*c*) oxides of sulphur (*d*) all of these
5. The gas which reacts with haemoglobin in blood is
   (*a*) CO (*b*) SO_2
   (*c*) CO_2 (*d*) NO
6. Ozone is present in
   (*a*) troposphere (*b*) stratosphere
   (*c*) mesosphere (*d*) thermosphere
7. The gas that protects us from U.V. radiations is
   (*a*) CO_2 (*b*) O_2
   (*c*) O_3 (*d*) N_2
8. Which of the following does not increase the amount of CO_2 in atmosphere?
   (*a*) Decay of animals (*b*) Breathing
   (*c*) Photosynthesis (*d*) Burning of petrol
9. Which of the following species is most toxic?
   (*a*) CH_3Hg^+ (*b*) $HgCl_2$
   (*c*) Hg_2Cl_2 (*d*) Hg-metal
10. Which of the following particulates is most toxic?
   (*a*) Fly ash
   (*b*) Soot
   (*c*) Inorganic compounds
   (*d*) Smog
11. Increased concentration of CO_2 in atmosphere is responsible for
   (*a*) greenhouse effect
   (*b*) acid rain
   (*c*) lack of photosynthesis
   (*d*) death of aquatic life
12. The major air pollutant is
   (*a*) CO (*b*) oxides of nitrogen
   (*c*) soot (*d*) oxides of sulphur
13. The region closest to the earth surface is
   (*a*) stratosphere (*b*) mesosphere
   (*c*) thermosphere (*d*) troposphere
14. Major cause of ozone layer depletion is the release of
   (*a*) freon into the atmosphere
   (*b*) CO gas into the atmosphere
   (*c*) unburnt carbon
   (*d*) smog
15. The normal pH value of rainwater is
   (*a*) 7.0 (*b*) 6.0
   (*c*) 5.6 (*d*) 5.0

16. The gas that does not cause acid rain is
    (*a*) CO_2 (*b*) SO_2
    (*c*) NO_2 (*d*) N_2

17. Carbon monoxide acts as
    (*a*) hypnotic (*b*) narcotic
    (*c*) antiseptic (*d*) insecticide

18. CCl_4 and freons
    (*a*) are green compounds because they are green coloured
    (*b*) deplete ozone concentration
    (*c*) cause increase in ozone concentration
    (*d*) have no effect on ozone concentration

19. Which one of the following statements regarding photochemical smog is not correct?
    (*a*) Carbon monoxide does not play any role in photochemical smog formation.
    (*b*) Photochemical smog is an oxidising agent in character.
    (*c*) Photochemical smog is formed through photochemical reaction involving solar energy.
    (*d*) Photochemical smog does not cause irritation in eyes and throat.

20. What is D.D.T. among the following?
    (*a*) A fertilizer
    (*b*) Biodegradable pollutant
    (*c*) Non-biodegradable pollutant
    (*d*) Greenhouse gas

21. The gas emitted by supersonic jet planes that slowly depletes the concentration of ozone layer is
    (*a*) CO (*b*) NO
    (*c*) SO_2 (*d*) O_2
    (*e*) HF

22. How does the concentration of carbon dioxide in the atmosphere affect climate?
    (*a*) As carbon dioxide concentration increases, temperature decreases.
    (*b*) As carbon dioxide concentration increases, temperature increases.
    (*c*) Carbon dioxide concentration has no effect on climate.
    (*d*) As carbon dioxide concentration increases, temperature becomes more random.

23. Which of the following processes does NOT add carbon to the atmosphere?
    (*a*) volcanic eruptions
    (*b*) respiration
    (*c*) weathering of limestone
    (*d*) none of these

24. Although direct measurements of atmospheric carbon dioxide have only been taken consistently since 1950, scientists have been able to retrieve data from the past 500,000 years. They have been able to do this by looking at
    (*a*) ice cores from ice sheets
    (*b*) sediment cores from the ocean
    (*c*) tree rings
    (*d*) all of the choices

25. Carbon dioxide (CO_2) in the air enters a tree via the process of
    (*a*) respiration (*b*) ingestion (eating)
    (*c*) photosynthesis (*d*) decomposition

26. Carbon is a common component of
    (*a*) limestone (*b*) all organisms
    (*c*) volcanic gases (*d*) all of the choices

27. Photosynthesis is the process by which plants
    (*a*) release CO_2 to the atmosphere
    (*b*) turn CO_2 into sugars
    (*c*) turn sugars into energy
    (*d*) none of the choices

28. Respiration is the process by which ______________ is consumed and ______________ is produced.
    (*a*) carbon dioxide, oxygen
    (*b*) carbon dioxide, energy
    (*c*) oxygen, carbon dioxide
    (*d*) energy, carbon dioxide

SOME ADDITIONAL QUESTIONS

I. Multiple Choice Questions

Choose one or more than one correct answer(s):

1. Which of the following gases is not a greenhouse gas?
    (*a*) CO (*b*) O_3
    (*c*) CH_4 (*d*) H_2O vapour

2. Photochemical smog occurs in warm, dry and sunny climate. One of the following is not amongst the components of photochemical smog, identify it.
    (*a*) NO_2 (*b*) O_3
    (*c*) SO_2
    (*d*) Unsaturated hydrocarbon

3. Which of the following statements is **not** true about classical smog?
   - (*a*) Its main components are produced by the action of sunlight on emissions of automobiles and factories.
   - (*b*) Produced in cold and humid climate.
   - (*c*) It contains compounds of reducing nature.
   - (*d*) It contains smoke, fog and sulphur dioxide.

4. Which of the following statements about photochemical smog is not correct?
   - (*a*) It has a high concentration of oxidising agents.
   - (*b*) It has a low concentration of oxidising agents.
   - (*c*) It can be controlled by controlling the release of NO_2, hydrocarbons, ozone, etc.
   - (*d*) Plantation of some plants like pinus helps in controlling photochemical smog.

5. The gaseous envelope around the earth is known as atmosphere. The lowest layer of this is extended upto 10 km from sea level, this layer is ______.
   - (*a*) stratosphere
   - (*b*) troposphere
   - (*c*) mesosphere
   - (*d*) hydrosphere

6. Dinitrogen and dioxygen are the main constituents of air but these do not react with each other to form oxides of nitrogen because ______.
   - (*a*) the reaction is endothermic and requires very high temperature.
   - (*b*) the reaction can be initiated only in presence of a catalyst.
   - (*c*) oxides of nitrogen are unstable.
   - (*d*) N_2 and O_2 are unreactive.

7. The pollutants which come directly into the air from sources are called primary pollutants. Primary pollutants are sometimes converted into secondary pollutants. Which of the following belongs to secondary air pollutants?
   - (*a*) CO
   - (*b*) Hydrocarbon
   - (*c*) Peroxyacetyl nitrate (PAN)
   - (*d*) NO

8. Which of the following statements is correct?
   - (*a*) Ozone hole is a hole formed in the stratosphere from which ozone oozes out.
   - (*b*) Ozone hole is a hole formed in the troposphere from which ozone oozes out.
   - (*c*) Ozone hole is thinning of ozone layer of stratosphere at some places.
   - (*d*) Ozone hole means vanishing of ozone layer around the earth completely.

9. The consequences of global warming may be ———.
   - (*a*) increase in average temperature of the earth
   - (*b*) melting of Himalayan Glaciers,
   - (*c*) increased biochemical oxygen demand,
   - (*d*) eutrophication.

II. Matching Type Questions

In the following questions more than one option of Column I and Column II may match.

1. Match the terms given in Column I with the compounds given in Column II.

Column I	Column II
(*i*) Acid rain	(*a*) $CHCl_2–CHF_2$
(*ii*) Photochemical smog	(*b*) CO
(*iii*) Combination with haemoglobin	(*c*) CO_2
(*iv*) Depletion of ozone layer	(*d*) SO_2
	(*e*) Unsaturated hydrocarbons

2. Match the pollutant(s) in Column I with the effect(s) in Column II.

Column I	Column II
(*i*) Oxides of sulphur	(*a*) Global warming
(*ii*) Nitrogen dioxide	(*b*) Damage to kidney
(*iii*) Carbon dioxide	(*c*) 'Blue baby' syndrome
(*iv*) Nitrate in drinking water	(*d*) Respiratory diseases
(*v*) Lead	(*e*) Red haze in traffic and congested areas

3. Match the activity given in Column I with the type of pollution created by it given in Column II.

Column I (Activity)	Column II (Effect)
(*i*) Releasing gases to the atmosphere after burning waste material containing sulphur.	(*a*) Water pollution
(*ii*) Using carbamates as pesticides.	(*b*) Photochemical smog, damage to plant life, corrosion to building material, induce breathing problems, water pollution.

(*iii*) Using synthetic detergents for washing clothes.	(*c*) Damaging ozone layer.
(*iv*) Releasing gases produced by automobiles and factories in the atmosphere.	(*d*) May cause nerve diseases in human.
(*v*) Using chlorofluorocarbon compounds for cleaning computer parts.	(*e*) Classical smog, acid rain, water pollution, induce breathing problems, damage to buildings, corrosion of metals.

4. Match the pollutants given in Column I with their effects given in Column II.

Column I	**Column II**
(*i*) Phosphate fertilisers in water	(*a*) BOD level of water increases
(*ii*) Methane in air	(*b*) Acid rain
(*iii*) Synthetic detergents in water	(*c*) Global warming
(*iv*) Nitrogen oxides in air	(*d*) Eutrophication

III. Assertion-Reason Type Questions

(In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below in each question.)

1. ***Assertion (A):*** Greenhouse effect was observed in houses used to grow plants and these are made of green glass.

   Reason (R): Greenhouse name has been given because glass houses are made of green glass.

   (*i*) Both A and R are correct and R is the correct explanation of A.

   (*ii*) Both A and R are correct but R is not the correct explanation of A.

   (*iii*) Both A and R are not correct.

   (*iv*) A is not correct but R is correct.

2. ***Assertion (A):*** Photochemical smog is oxidising in nature.

   Reason (R): Photochemical smog contains NO_2 and O_3, which are formed during the sequence of reactions.

   (*i*) Both A and R are correct and R is the correct explanation of A.

   (*ii*) Both A and R are correct but R is not the correct explanation of A.

   (*iii*) Both A and R are not correct.

   (*iv*) A is not correct but R is correct.

3. ***Assertion (A):*** Carbon dioxide is one of the important greenhouse gases.

   Reason (R): It is largely produced by respiratory function of animals and plants.

   (*i*) Both A and R are correct and R is the correct explanation of A.

   (*ii*) Both A and R are correct but R is not the correct explanation of A.

   (*iii*) Both A and R are not correct.

   (*iv*) A is not correct but R is correct.

4. ***Assertion (A):*** Ozone is destroyed by solar radiation in upper stratosphere.

   Reason (R): Thinning of the ozone layer allows excessive UV radiations to reach the surface of earth.

   (*i*) Both A and R are correct and R is the correct explanation of A.

   (*ii*) Both A and R are correct but R is not the correct explanation of A.

   (*iii*) Both A and R are not correct.

   (*iv*) A is not correct but R is correct.

ANSWERS

(A) Multiple Choice Questions

1. (*d*)	2. (*d*)	3. (*a*)	4. (*d*)	5. (*a*)	6. (*b*)	7. (*c*)	8. (*c*)
9. (*a*)	10. (*b*)	11. (*a*)	12. (*a*)	13. (*d*)	14. (*a*)	15. (*c*)	16. (*d*)
17. (*b*)	18. (*b*)	19. (*d*)	20. (*c*)	21. (*b*)	22. (*b*)	23. (*d*)	24. (*d*)
25. (*c*)	26. (*d*)	27. (*b*)	28. (*c*)				

Some Additional Questions

I. Multiple Choice Questions

1. (*a*) 2. (*c*) 3. (*a*) 4. (*b*) 5. (*b*) 6. (*a*) 7. (*c*) 8. (*c*)
9. (*a*), (*b*)

II. Matching Type Questions

1. (*i*) → (*c*), (*d*) (*ii*) → (*e*), (*d*) (*iii*) → (*b*) (*iv*) → (*a*)
2. (*i*) → (*d*) (*ii*) → (*e*) (*iii*) → (*a*) (*iv*) → (*c*) (*v*) → (*b*)
3. (*i*) → (*e*) (*ii*) → (*d*) (*iii*) → (*a*) (*iv*) → (*b*) (*v*) → (*c*)
4. (*i*) → (*a*), (*d*) (*ii*) → (*c*) (*iii*) → (*a*) (*iv*) → (*b*)

III. Assertion-Reason Type Questions

1. (*iii*) 2. (*i*) 3. (*ii*) 4. (*iv*)

SPECIMEN QUESTION PAPER

Chemistry Class XI

Time: 3 Hours **Total Marks:** 100

Section A (40 Marks)

Compulsory: Attempt **all** *questions.*

Question 1

(A) *Each question in this section is provided with four possible options. Choose the most appropriate option.*

[$1 \times 15 = 15$]

(*i*) The set representing the correct order of first ionization potential is

(*a*) K > Na > Li (*b*) Be > Mg > Ca

(*c*) B > C > N (*d*) Ge > Si > C

(*ii*) Which of the following elements will gain one electron more readily in comparison to other elements of their group?

(*a*) S (*g*) (*b*) Na (*g*)

(*c*) O (*g*) (*d*) Cl (*g*)

(*iii*) In which of the following substances will hydrogen bond be strongest?

(*a*) HCl (*b*) H_2O

(*c*) HI (*d*) H_2S

(*iv*) In which of the following compounds, an element exhibits two oxidation states?

(*a*) NH_2OH (*b*) NH_4NO_3

(*c*) N_2H_4 (*d*) N_3H

(*v*) Metals form basic hydroxides. Which of the following metal hydroxides is the least basic in nature?

(*a*) $Mg(OH)_2$ (*b*) $Ca(OH)_2$

(*c*) $Sr(OH)_2$ (*d*) $Ba(OH)_2$

(*vi*) Hydrochloric acid decomposes

(*a*) salts of stronger bases (*b*) salts of weaker bases

(*c*) salts of stronger acids (*d*) salts of weaker acids

(*vii*) Rate law cannot be determined from a balanced equation if

(*a*) a reverse reaction is involved (*b*) it is an elementary reaction

(*c*) it is a sequence of elementary reactions (*d*) any of the reactants is in excess

(*viii*) For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by

(*a*) adding a suitable catalyst

(*b*) adding an inert gas

(*c*) decreasing the volume of the container

(*d*) increasing the amount of $CO(g)$

(*ix*) 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution is

(*a*) 759.00 torr	(*b*) 7.60 torr
(*c*) 76.00 torr	(*d*) 752.40 torr

(*x*) Which of the following has a molecular weight of 92?

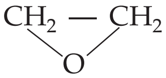
(*a*) Toluene	(*b*) Benzene
(*c*) Ethylene	(*d*) Propene

(*xi*) Anti-Markownikoff's addition of HBr is not observed in

(*a*) propene	(*b*) butene-1
(*c*) butene-2	(*d*) pentene-2

(*xii*) Which of the following has the highest nucleophilicity?

(*a*) F^-	(*b*) OH^-
(*c*) CH_3^-	(*d*) NH_2^-

(*xiii*) Reaction of  $CH_2 - CH_2$ (O bridging) with RMgX leads to the formation of

(*a*) RCHORR	(*b*) $RCHOHCH_3$
(*c*)  R_2CHCH_2OH	(*d*) RCH_2CH_2OH

(*xiv*) The reaction of aromatic acyl chloride and phenol in the presence of a base NaOH or pyridine is called

(*a*) Kolbe's reaction	(*b*) Perkin's reaction
(*c*) Sandmeyer's reaction	(*d*) Schotten-Baumann's reaction

(*xv*) The gaseous envelope around the earth is known as atmosphere. The lower layer of this, extended up to 10 km from the sea level is known as

(*a*) stratosphere	(*b*) troposphere
(*c*) mesosphere	(*d*) hydrosphere

(B) *Fill in the blanks by writing suitable word(s).* [½ × 10 = 5]

(*i*) The modern atomic mass unit is based on the mass of ________________.

(*ii*) The electronic configuration of He is $1s^2$ and that of oxygen is ________________.

(*iii*) Electron affinity of fluorine is ________________ than that of chlorine.

(*iv*) *f*-block elements are called ________________ elements.

(*v*) CCl_4 is a covalent compound and will not give ________________ with $AgNO_3$ solution.

(*vi*) Bond angle in water molecule is 104.5° instead of 109°–28′ because of ________________ repulsion.

(*vii*) Ca^{2+} has a smaller ionic radius than K^+ because it has ________________ .

(*viii*) Alkaline earth metals cannot be prepared by the ________________ of their aqueous solutions.

(*ix*) If the rate of a reaction is found to be proportional to $[A]^\alpha$ $[B]^\beta$, then $\alpha + \beta$ represents the ________________ of the reaction.

(*x*) The rate of a chemical reaction almost doubles for every ________________ rise in temperature.

(C) *Match each item under Column A with the most appropriate item in Column B. Rewrite the correct matching pairs in the answer sheet provided.* [½ × 10 = 5]

Column A	Column B
(*i*) Electrophile	(*a*) A cold alkaline solution of $KMnO_4$
(*ii*) Wohler synthesis	(*b*) Self-linking of carbon atoms
(*iii*) Commercial preparation of phenol	(*c*) Palladium supported over $BaSO_4$
(*iv*) Arrhenius	(*d*) Nitronium ion and sulphonium ion
(*v*) Baeyer's reagent	(*e*) Law of mass action
(*vi*) Azeotropes	(*f*) Aerial oxidation of cumene followed by the treatment with dil H_2SO_4
(*vii*) Lindlar's catalyst	(*g*) Lowering of vapour pressure
(*viii*) Guldberg and Waage	(*h*) Theory of ionisation
(*ix*) Catenation	(*i*) Constant-boiling mixtures
(*x*) Raoult's law	(*j*) Preparation of urea

(D) *Correct the following statements.* [1 × 5 = 5]

(*i*) Effect of temperature on equilibrium constant is given by van't Hoff equation, viz.,

$$\log \frac{(K_p)_2}{(K_p)_1} = \frac{\Delta H}{2.303 R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

(*ii*) If intermolecular forces of attraction increase on mixing of two liquids, the solution shows positive deviation. For example, chloroform + acetone.

(*iii*) Organic compounds being polar are usually insoluble in water.

(*iv*) Oxidative ozonolysis of alkenes gives a mixture of two aldehydes or one aldehyde and one ketone depending upon the structure of the alkene.

(*v*) If an alkyl halide can undergo dehydrohalogenation in two different ways, then the less highly substituted alkene is the major product.

(E) *Answer the following questions.* [1 × 10 = 10]

(*i*) Draw the shapes of 2s and 2p_x orbitals. Indicate the nodal plane in the case of 2p_x orbital.

(*ii*) All transition elements are *d*-block elements, but all *d*-block elements are not transition elements. Explain?

(*iii*) Among alkali metals, which element do you expect to be least electronegative and why?

(*iv*) Explain why PCl_5 is trigonal bipyramidal whereas IF_5 is a squre pyramidal.

(*v*) Covalent bonds are directional bonds while non-ionic bonds are non-directional. Give reason.

(*vi*) In a reaction, if the concentration of the reactant A is tripled, the rate of reaction becomes twenty seven times. What is the order of the reaction?

(*vii*) What is meant by equilibrium constant of a reaction? Write an expression for the equilibrium constant for the synthesis of ammonia.

(*viii*) Explain why vapour pressure of a solvent is lowered by the addition of a non-volatile solute.

(*ix*) Give four main reasons to justify why organic chemistry is studied as a separate branch of chemistry.

(*x*) How can iodoethane be converted into ethane and butane, respectively?

Section B (60 Marks)

Attempt any **six** *questions.*

Question 2

(*a*) An atom having atomic mass number 13 has 7 neutrons. What is the atomic number of the atom? [2]

(*b*) Show the distribution of electrons in an oxygen atom (atomic number 8) using orbital diagram. [3]

(*c*) First member of each group of representative elements (i.e., *s* and *p*-block elements) shows anomalous behaviour. Illustrate with two examples. [2]

(*d*) How would you explain the fact that first ionization enthalpy of sodium is lower than that of magnesium but its second ionisation enthalpy is higher than that of magnesium? [3]

Question 3

(*a*) The density of ice is smaller than that of water. Explain. [2]

(*b*) Draw the structure of sulphur hexafluoride molecule. Mention the hybridisation of central atom and the shape of the molecule. [4]

(*c*) Name the species which are oxidised or reduced in the following reactions:

(*i*) $Zn\ (s) + PbCl_2\ (aq) \longrightarrow Pb\ (s) + ZnCl_2\ (aq)$

(*ii*) $2Fe^{3+}\ (aq) + 2I^-\ (aq) \longrightarrow I_2\ (aq) + 2Fe^{2+}\ (aq)$ [2]

(*d*) Lime water turns milky on passing CO_2, but milkiness disappears on passing excess of CO_2. Give reason. [2]

Question 4

(*a*) Write the electronic configurations of F, Cl, Br and I. Explain the trend in their physical properties under the following headings:

(*i*) Melting and boiling points

(*ii*) Oxidation states [3]

(*b*) With the help of suitable diagrams, explain the two types of non-ideal solutions. [4]

(*c*) Differentiate between molarity and molality. [2]

(*d*) Explain the term azeotrope. [1]

Question 5

(*a*) Why is molecularity applicable only for elementary reactions and order is applicable for elementary as well as complex reactions. [3]

(*b*) Explain the difference between the instantaneous rate of a reaction and the average rate of a reaction. [2]

(*c*) State Le-chatelier's principle. Discuss its application in the manufacture of NH_3 by Haber's process. [5]

Question 6

(*a*) Write structural formulae for compounds named as:

- (*i*) 1-Bromoheptane
- (*ii*) 5-Bromoheptanoic acid [2]

(*b*) Name one compound of each of the following classes, write its formula and state its one important use:

(*i*) Aldehyde (*ii*) Alcohol (*iii*) Carboxylic acid [3]

(*c*) Write the structures and names of products obtained in the reactions of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane. [2]

(*d*) Alkynes on reduction with sodium in liquid ammonia form *trans* alkenes. Will the butene thus formed on reduction of 2-butyne show geometrical isomerism? [3]

Question 7

(*a*) Write down the structure and IUPAC name for neopentyl bromide. Why is the solubility of haloalkanes in water very low? [2]

(*b*) Preparation of alcohols from alkenes involves the electrophilic attack on alkene carbon atom. Explain its mechanism. [2]

(*c*) Write the resonance structure of phenol and explain why phenol is more acidic than alcohol. Explain whether *p*-nitrophenol should be more or less acidic than phenol. [4]

(*d*) Write the causes of global warming. [2]

Question 8

(*a*) Describe the contribution of Rutherford's model in establishing a picture of the atom. [2]

(*b*) Draw a labelled diagram of mass spectrometer. [3]

(*c*) Define covalent radius and van der Waal's radius. Which of the two is greater? [3]

(*d*) Which one of the following pairs of elements would have a higher electron affinity? Explain.

(*i*) N or O (*ii*) F or Cl [2]

APPENDIX-1

Table I. Basic and Derived S.I. Units and Conversion Factors

Quantity	*S.I. Unit*	*Other Unit*	*Conversion Factor*
Length	Metre (m)	Angstrom	1 Å = 10^{-10} m = 10^{-8} cm = 10^{-1} nm
Mass	kilogram (kg)	Pound	1 lb = 0.45359237 kg
Time	Second (s)	Hour	1 hour = 3600 s, 1 min = 60 s
* Force	Newton (N)	Dyne	1 dyne = 10^{-5} N
*Energy	Joule (J)	Calorie	1 cal. = 4.184 J
		Erg	1 erg = 10^{-7} J
*Pressure	Pascal (Pa)	Atmosphere	1 atm. = 101325 Pa
		Bar	1 bar = 10^{-5} Pa
		mm Hg	1 mm Hg = 133.322 Pa
		lb/in^2	1 lb/in^2 = 6898.8 Pa
*Volume	Cubic metre (m^3)	Litre	1 L = 1 dm^3 = 10^{-3} m^3
		Cubic inch	1 in^3 = 1.638 × 10^{-8} m^3
*Temperature	Kelvin (K)	Celsius	1°C = 1 K
		Fahrenheit	1 °F = 5K/9
* Derived Unit			

Table II. Prefix in Metric System

Prefix	*Symbol*	*Factor*
pico	p	1 picometre (pm) = 1 × 10^{-12} m
nano	n	1 nanometre (nm) = 1 × 10^{-9} m
micro	µ	1 microgram (µg) = 1 × 10^{-6} g
milli	m	1 milligram (mg) = 1 × 10^{-3} g
centi	c	1 centimetre (cm) = 1 × 10^{-2} m
deci	d	1 decimetre (dm) = 1 × 10^{-1} m
kilo	k	1 kilometre (km) = 1 × 10^{3} m
mega	M	1 megametre (Mm) = 1 × 10^{6} m
giga	G	1 gigametre (Gm) = 1 × 10^{9} m

APPENDIX-2

Table III. Important Ores

Type of Ore		*Name of the Ore*	*Formula*	*Chief metal present*
Oxide	1.	Haematite	Fe_2O_3	Fe
	2.	Cuprite	Cu_2O	Cu
	3.	Bauxite	$Al_2O_3.2H_2O$	Al
	4.	Magnetite	Fe_3O_4	Fe
	5.	Pyrolusite	MnO_2	Mn
	6.	Cassiterite or tinstone	SnO_2	Sn
	7.	Zincite	ZnO	Zn
	8.	Pitch blende	U_3O_8	U
Sulphide	1.	Iron pyrites	FeS_2	Fe
	2.	Copper pyrites	$CuFeS_2$	Cu
	3.	Galena	PbS	Pb
	4.	Cinnabar	HgS	Hg
	5.	Zinc blende	ZnS	Zn
	6.	Silver glance or Argentite	Ag_2S	Ag
	7.	Copper glance	Cu_2S	Cu
Carbonate	1.	Magnesite	$MgCO_3$	Cu
	2.	Dolomite	$CaCO_3.MgCO_3$	Mg
	3.	Siderite	$FeCO_3$	Fe
	4.	Malachite	$Cu(OH)_2.CuCO_3$	Cu
	5.	Lime stone	$CaCO_3$	Ca
	6.	Calamine	$ZnCO_3$	Zn
Halide	1.	Common salt or rock salt	$NaCl$	Na
	2.	Carnallite	$KMgCl_2 \cdot 6H_2O$	Mg
	3.	Horn silver	$AgCl$	Ag
	4.	Silivine	KCl	K
	5.	Fluorospar	CaF_2	Ca
	6.	Cryolite	Na_3AlF_6	Al
Sulphate	1.	Epsom salt	$MgSO_4.7H_2O$	Mg
	2.	Gypsum	$CaSO_4.2H_2O$	Ca
	3.	Barytes	$BaSO_4$	Ba
	4.	Anglesite	$PbSO_4$	Pb
	5.	Anhydrite	$CaSO_4$	Ca
Silicate	1.	Asbestos	$CaMg_3Si_4O_{12}$	Mg
	2.	Feldspar	$KAlSi_3O_8$	Al
	3.	Mica	$(K_2O.3Al_2O_36SiO_2.2H_2O)$	Al
Nitrate	1.	Chile salt petre	$NaNO_3$	Na
	2.	Bengal salt petre	KNO_3	K
Phosphate	1.	Phosphorite	$Ca_3(PO_4)_2$	Ca

LOGARITHMS

											Mean Differences								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

(Contd.)

LOGARITHMS

											Mean Differences								
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9217	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9360	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9916	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

											Mean Differences								
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1798	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7

(Contd.)

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Differences								
											1	2	3	4	5	6	7	8	9
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8616	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9793	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20