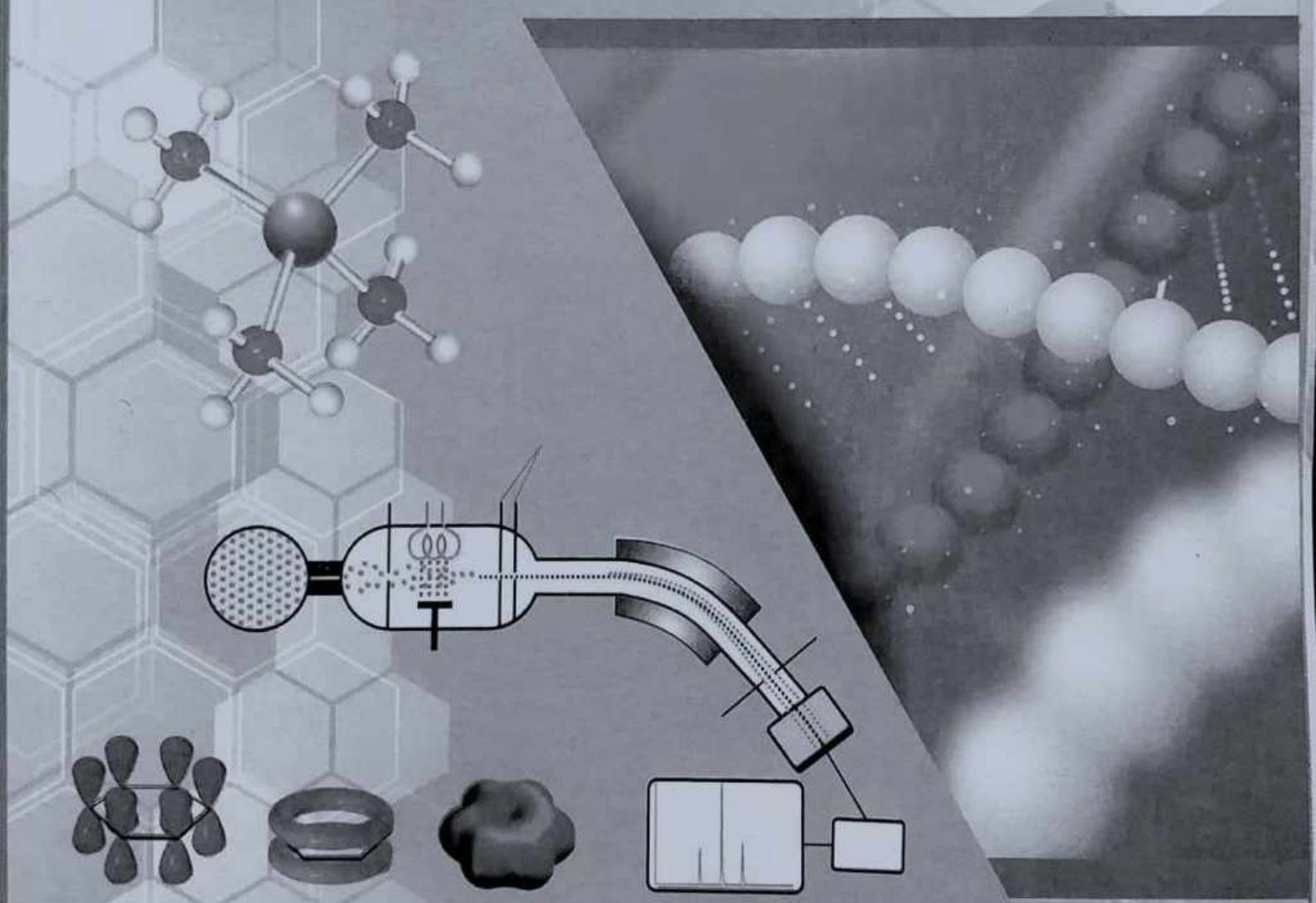
A Textbook of CHEMISTRY XII



Balochistan Textbook Board, Quetta.

بسم الله الرحمن الرحيم

(In the name of ALLAH the most beneficent and the most merciful)

A TEXTBOOK OF
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XII

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CONTENTS

13	s- and p-Block Elements	7
	Introduction	
	13.1 Period 3 (Na to Ar)	
	13.2 Group 1 - Elements	
	13.3 Group 2 - Elements	
	13.4 Group 14(IVA) - Elements	
	13.5 Group 17(VIIA) - Elements: Halogens	
14	d- and f-Block Elements: Transition Elements	54
	Introduction	
	14.1 General Features	
	14.2 Coordination Compounds	
	14.3 Chemistry of Some important Transition Elements	
15	Organic Compounds	88
	Introduction	
	15.1 Sources	
	15.2 Coal as a Source of Organic Compounds	
	15.3 Characteristics of Organic Compounds	
	15.4 Uses of Organic Compounds	
	15.5 New Allotrope of Carbon: Bucky Ball	
	15.6 Functional Groups and Homologous Series	
	15.7 Detection of Elements in Organic Compounds	105
16	Hydrocarbons	
	Introduction	
	16.1 Types of Hydrocarbons	
	16.2 Alkanes and Cycloalkanes	
	16.3 Radical Substitution Reactions	
	16.4 Oxidation of Organic compounds	
	16.5 Alkenes	
	16.6 Isomerism	
	16.7 Alkynes	
	16.8 Benzene and Substituted Benzenes	174
17	Alkyl Halides and Amines	
	Introduction	
	17.1 Alkyl halides	
	17.2 Organometallic Compounds (Grignard' Reagents)	
	17.3 Amines	205
18	Alcohols, Phenols and Ethers	
	Introduction	

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18.1 Alcohols
18.2 Phenols
18.3 Ethers
19 Aldehydes and Ketones 238
Introduction
19.1 Nomenclature
19.2 Physical Properties
19.3 Structure
19.4 Preparations of Aldehydes and Ketones
19.5 Reactivity
19.6 Reactions of Aldehydes and Ketones
20 Carboxylic Acids and their Functional Derivatives 259
Introduction
20.1 Nomenclature
20.2 Physical Properties
20.3 Structure
20.4 Acidity
20.5 Preparations of Carboxylic Acids
20.6 Reactivity
20.7 Reactions of Carboxylic Acids
21 Biochemistry 285
Introduction
21.1 Carbohydrates
21.2 Proteins
21.3 Enzymes
21.4 Lipids
21.5 Nucleic Acids
21.6 Minerals of Biological Significance
22 Industrial Chemistry 312
22.1 Introduction to the Chemical Process Industry and Raw Materials used
22.2 Safety Considerations in Process Industries
22.3 Dyes
22.4 Pesticides
22.5 Petrochemicals
22.6 Synthetic Polymers (PVC and Nylon)
22.7 Cosmetics: Lipsticks, Nail Varnish and Remover, Hair Dyes
22.8 Adhesives

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23 **Environmental Chemistry** 332
Introduction
23.1 Chemistry of the Troposphere
23.2 Chemistry of the Stratosphere: Production and Destruction of Ozone
23.3 Water Pollution and Water Treatment
23.4 Green Chemistry
24 **Analytical Chemistry** 358
Introduction
24.1 Classical Method of Analysis: Combustion Analysis and Determination of Molecular Formula
24.2 Modern Methods of Analysis

References 391
Index 392
Glossary 399

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Chapter 13

s- and p-Block Elements

Major Concepts

13.1 Period 3 (Na to Ar)
13.2 Group 1
13.3 Group 2
13.4 Group 14
13.5 Group 17 (Halogens)

Learning Outcomes:

Students will be able to:

- Recognize the demarcation of the Periodic Table into s-block, p-block, d-block, and f-block. **(Understanding)**
- Describe how physical properties like atomic radius, ionization energy, electronegativity, electrical conductivity, melting and boiling point of elements change within a group and with in a period in the Periodic Table. **(Analyzing)**
- Describe reactions of period 3 elements with water, oxygen and chlorine. **(Applying)**
- Describe physical properties and acid-base behaviour of oxides, chlorides and hydroxides of period 3 elements. **(Applying)**
- Describe reactions of oxides and chlorides of period 3 elements with water. **(Applying)**
- Explain the trends in physical properties and oxidation states in groups I, II, IV and VII of the Periodic Table. **(Analyzing)**
- Describe reactions of Group I elements with water, oxygen and chlorine. **(Applying)**
- Explain effect of heat on nitrates, carbonates and hydrogen carbonates of Group-I elements. **(Applying)**
- Describe reactions of Group II elements with water, oxygen and nitrogen. **(Applying)**
- Discuss the trend in solubility of the hydroxides, sulphates and carbonates of Group-II elements. **(Analyzing)**
- Discuss the trends in thermal stability of the nitrates and carbonates of Group-II elements. **(Analyzing)**
- Differentiate beryllium from other members of its group. **(Analyzing)**
- Describe reactions of Group IV elements with water. **(Applying)**
- Discuss the chlorides and oxides of group IV elements. **(Applying)**
- Explain the relative behaviour of halogens as oxidizing agents and reducing agents. **(Applying)**
- Compare the acidity of hydrogen halides. **(Analyzing)**
- Distinguish between an oxide and a peroxide. **(Understanding)**
- Write representative equations for the formation of oxides and sulphides. **(Applying)**
- Compare the outer most s and p-orbital system of an element with its chemical properties. **(Analyzing)**

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Introduction

The periodic table can be divided into four blocks. These are *s*, *p*, *d* and *f*-blocks. The classification of elements into blocks is based upon the valence orbital of the element involved in bond formation.

i) The elements of group 1, group 2 and period 1 are *s*-block elements. In these elements the last electron enters into *s*-subshell. There are two *s*-block elements in each period because *s*-subshell can accommodate maximum of two electrons. Their general electronic configuration is ns^{1-2} where 'n' represents the valence shell.

ii) The elements of group 13 to 18 except helium are *p*-block elements. In these elements the last electron enters into *p*-subshell. There are six elements of *p*-block in each period because *p*-subshell can hold up at the most six electrons. Their general electronic configuration is $ns^2\ np^{1-6}$.

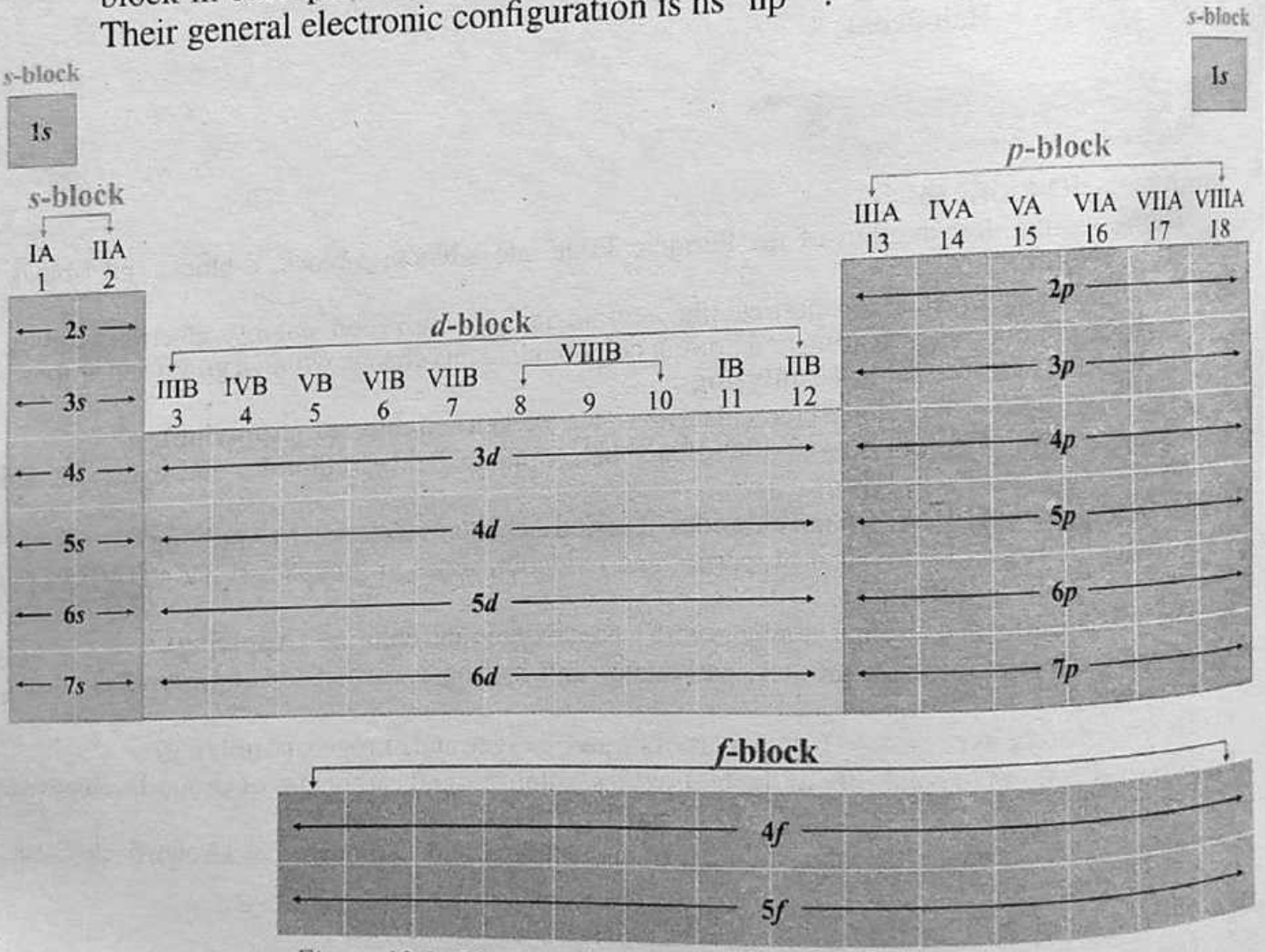


Figure 13.1: Blocks of Elements in the Periodic Table

iii) The elements of group 3 to 12 are *d*-block elements. In these elements the last electron enters into *d*-subshell. There are ten elements of *d*-block in each period because *d*-subshell can accommodate maximum of ten electrons. Their general electronic configuration is $(n-1)d^{1-10}\ ns^{1-2}$. The specific *d*-subshell is one less (n−1) than the period number. The *d*-block elements are also known as transition elements.

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iv) Lanthanides and actinides are *f*-block elements. In these elements the last electron enters into *f*-subshell. There are fourteen *f*-block elements in each period because *f*-subshell can hold up at the most fourteen electrons. Their general electronic configuration is $(n-2)f^{1-14}$ $(n-1)d^{0 \text{ or } 1}$ ns^2. The specific *f*-subshell is two less (n–2) than the period number. In most of the periodic tables, the *f*-block elements are placed below the periodic table to save the space.

Groups and Periods of Elements in the Periodic Table

The vertical columns of elements in the periodic table are called groups or families. There are two systems for numbering the groups: the older system and the newer IUPAC system. According to latest IUPAC system, the modern periodic table has 18 groups of the elements. Elements in the same group of periodic table show similar properties because they have same number of valence electrons.

The horizontal rows of elements in the periodic table are called periods. The modern periodic table has seven periods. The first period is the shortest period and has only two elements: the hydrogen and helium. The second and third periods contain 8 elements each and are called short periods. The fourth and fifth periods contain 18 elements each and are called long periods. The sixth and seventh periods contain 32 elements each and are called the longest periods.

13.1 Period 3 Elements (Na to Ar)

Period 3 consists of eight elements *viz.* sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), chlorine (Cl) and argon (Ar).

13.1.1 Physical and Atomic Properties of the Elements

The properties of elements tend to change from left to right across a period or from top to bottom down a group. The properties that change across a period or down the group with the rise of atomic number are called periodic properties. These properties are also known as atomic properties. These properties are based upon the electronic configurations (valence shell electronic configurations) of atoms of the elements. Some of the atomic properties are atomic radius, ionization energy, electronegativity, electrical conductivity, melting and boiling points.

13.1.1.1 Electronic Structure

Across the period 3 of the periodic table, from Na to Ar, each element has one more proton and one more electron than the one preceding it.

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Table 13.1: Electronic Configuration of Atoms of the Period 3 Elements

Element	Symbol	Atomic Number	Complete Electronic Configuration	Valence Shell Electronic Configuration
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$	$3s^1$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$	$3s^2$
Aluminium	Al	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	$3s^2 3p^1$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	$3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$	$3s^2 3p^3$
Sulphur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$	$3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$	$3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	$3s^2 3p^6$

Electronic configurations of atoms play an important role in knowing the physical and chemical properties of the elements and their compounds.

13.1.1.2 Trends in Atomic Radius

The average distance between the centre of nucleus and the outermost electronic shell of an atom is called atomic radius. The units used to measure atomic radius are nanometre ($1nm = 10^{-9}$ m), angstrom ($1A° = 10^{-10}$ m), and picometre ($1pm = 10^{-12}$ m).

Table 13.2: The Atomic Radius of Atoms of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic Radius (pm)	190	145	118	111	98	88	79	71

The atomic radius generally decreases from Na to Ar across the period. This is due to increase in the nuclear charge that pulls the electrons closer to the nucleus. The number of core electrons remains the same across the period. Because of this, the shielding effect remains almost constant for the elements.

13.1.1.3 Trends in Ionization Energy

Ionization energy is the minimum amount of energy required to remove an electron from the isolated gaseous atom or ion in its ground state. The value of ionization energy shows how tightly the electron is bound to the nucleus of an atom. The higher the value of ionization energy, the more difficult it is to remove the electron. For example, 496 kJ/mol energy is required to remove an electron from a gaseous sodium atom.

$$Na \longrightarrow Na^+ + 1e^- \qquad IE = 496\ kJ/mol$$

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Table 13.3: First Ionization Energy of Atoms of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
IE (kJ/mol)	496	738	578	786	1012	1000	1251	1520

The minimum amount of energy needed to remove the first electron from an isolated gaseous atom is called first ionization energy. For example, the first ionization energy of magnesium is:

$$Mg \longrightarrow Mg^{+} + 1e^{-} \qquad IE_1 = 738\ kJ/mol$$

The minimum amount of energy needed to remove the second most loosely bound electron is called second ionization energy. For example, the second ionization energy of magnesium is:

$$Mg^{+} \longrightarrow Mg^{++} + 1e^{-} \qquad IE_2 = 1451\ kJ/mol$$

The amount of energy needed to remove the third electron is the third ionization energy and so on. For example, the third ionization energy of magnesium is:

$$Mg^{++} \longrightarrow Mg^{+++} + 1e^{-} \qquad IE_3 = 7730\ kJ/mol$$

Ionization energy values increase with the removal of each electron because the repulsion among the remaining electrons decreases. As a result of this, the force of attraction between nucleus and valence electron increases.

Ionization energy values increase in the following order:

$1^{st}\ IE < 2^{nd}\ IE < 3^{rd}\ IE < \ldots$

Ionization energy depends upon:

i) Atomic radius
ii) Nuclear charge
iii) Shielding effect
iv) Electronic configuration of Elements

The ionization energy generally increases from sodium (Na) to argon (Ar) across the period. This is either due to increase in the nuclear charge or decrease in the atomic radius along the period. The metals (Na, Mg and Al) have small values of ionization energies while non-metals (P, S, Cl and Ar) have high values of ionization energies. The high values of ionization energies of non-metals are due to their smaller size. The high ionization energy of argon is due to its stable electronic configuration.

13.1.1.4 Trends in Electronegativity

Electronegativity is the relative tendency (ability or power) of an atom in a molecule to attract a shared pair (bond pair) of electrons towards itself. Electronegativity has no unit. Elements with low electronegativity values are metals and have tendency to lose electrons. Elements with high electronegativity values are non-metals and have tendency to gain electrons.

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Table 13.4: The Electronegativity of Atoms of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Electronegativity	0.93	1.31	1.81	2.02	2.19	2.58	3.16	–

The electronegativity of argon is not included in the table because the compounds of argon are rare.

Electronegativity increases from sodium to chlorine due to increase in nuclear charge. The shielding effect remains constant along the period.

13.1.1.5 Trends in Electrical Conductivity

Electrical Conductivity is the ability of a material to carry an electric current. The electrical conductivity is due to loose electrons in a material. Sodium, magnesium and aluminium are good conductors, silicon is semiconductor while the rest of the elements of period 3 are non-conductors.

Table 13.5: Electrical Conductivity of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Electrical Conductivity	Good	Good	Good	Poor	None	None	None	None

Electrical conductivity increases from sodium to aluminium. This rise is due to the increasing number of delocalized electrons in the metallic solid. Silicon has giant covalent structure similar to that of diamond and has few delocalized electrons. Because of this, it is a semiconductor. The elements from phosphorus to argon are non-conductors because their electrons are tightly bound to the nucleus and are not free to move.

13.1.1.6 Trends in Melting and Boiling Points

The melting and boiling points of period 3 elements increase from left to right up to the silicon and then gradually decrease.

Table 13.6: Melting and Boiling Points of the Period 3 Elements

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Melting Point (°C)	98	650	660	1420	600	119	–102	–189
Boiling Point (°C)	883	1100	2400	2480	1000	444	–34	–186

Melting and boiling points of elements depend upon the number of valence electrons or bond strength. The sodium, magnesium and aluminium have strong metallic bonds while silicon has strong covalent bonds. The sodium, magnesium and aluminium contain one, two and three valence electrons respectively. Hence, sodium provides one, magnesium two and aluminium three electrons for metallic bonds. Silicon, a semimetal, has four valence electrons and forms four covalent bonds with other silicon atoms.

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The other elements of period 3 (P, S, Cl and Ar) are non-metals and have low melting and boiling points. This is because, they form simple molecules and their molecules are held together by London dispersion forces which are very weak attractive forces. The small amount of energy is required to overcome these attractive forces.

The melting and boiling points of sulphur are higher than other three non-metals (P, Cl and Ar). This is because; the size of sulphur (S_8) molecule is larger than other three non-metals (P_4, Cl_2 and Ar). The strength of London forces depend upon the size of molecules. The larger the size of molecules, the stronger is the London forces. Consequently, the melting and boiling points decrease in the following order:

$$S_8 > P_4 > Cl_2 > Ar$$

13.1.2 Reactions of Period 3 Elements with Water, Oxygen, and Chlorine

13.1.2.1 Reactions of Period 3 Elements with Water

Reaction of Sodium with Water

Sodium reacts with cold water violently to produce hydrogen gas and a colourless solution of sodium hydroxide. The reaction is exothermic.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

Reaction of Magnesium with Water

Magnesium reacts with cold water gently to produce magnesium hydroxide.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

Magnesium burns in steam with white flame to produce magnesium oxide and hydrogen gas.

$$Mg + H_2O \longrightarrow MgO + H_2$$

Reaction of Aluminium with Water

Finely divided aluminium reacts with steam to give aluminium oxide and hydrogen gas. This reaction is relatively slow due to the formation of aluminium oxide layer on the surface of metal.

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$$

Reaction of Silicon with Water

Silicon does not react with water in its elemental form at room temperature. It reacts with water at extremely high temperature producing silicon dioxide and hydrogen gas. The inertness of silicon is due to a protective layer of silicon dioxide on its surface.

$$Si + 2H_2O \longrightarrow SiO_2 + 2H_2$$

Reactions of Phosphorus, Sulphur and Argon with Water

Phosphorus, sulphur and argon do not react with water.

$P_4 + H_2O \longrightarrow$ No Reaction

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$S + H_2O \longrightarrow$ No Reaction

$Ar + H_2O \longrightarrow$ No Reaction

Reaction of Chlorine with Water

Chlorine reacts with water to produce mixture of hydrochloric acid and hypochlorous acid. This reaction is reversible.

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

The HOCl, in the presence of sunlight, is slowly decomposed into hydrochloric acid and oxygen gas.

$$2HOCl \longrightarrow 2HCl + O_2$$

The equation that shows the overall change is as:

$$2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2$$

13.1.2.2 Reactions of Period 3 Elements with Oxygen

Reaction of Sodium with Oxygen

Sodium burns with a yellow flame to give a mixture of sodium oxide and sodium peroxide.

$$4Na + O_2 \longrightarrow 2Na_2O$$

$$2Na + O_2 \longrightarrow Na_2O_2$$

Reaction of Magnesium with Oxygen

Magnesium burns in oxygen with a brilliant white flame to form magnesium oxide.

$$2Mg + O_2 \longrightarrow 2MgO$$

Reaction of Aluminium with Oxygen

Finely divided aluminium burns in oxygen with a brilliant white flame to produce white alumina (aluminium oxide).

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

Reaction of Silicon with Oxygen

Silicon burns in oxygen with a bright yellow flame at high temperature and produces silicon dioxide .

$$Si + O_2 \xrightarrow{400\text{–}1000^\circ C} SiO_2$$

Reaction of Phosphorus with Oxygen

Phosphorus burns in oxygen with a white flame and produces white smoke. The smoke contains phosphorus (III) oxide and phosphorus (V) oxide.

$$P_4 + 3O_2 \longrightarrow P_4O_6$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

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Reaction of Sulphur with Oxygen

Sulphur burns in oxygen with a brilliant blue flame and gives sulphur dioxide gas.

$$S + O_2 \longrightarrow SO_2$$

Reaction of Chlorine with Oxygen

Chlorine does not react with oxygen directly.

$$Cl_2 + O_2 \longrightarrow \text{No Reaction}$$

Reaction of Argon with Oxygen

Argon does not react with oxygen.

$$Ar + O_2 \longrightarrow \text{No Reaction}$$

13.1.2.3 Reactions of Period 3 Elements with Chlorine

Reaction of Sodium with Chlorine

Sodium burns in the presence of chlorine with bright yellow or orange flame and forms sodium chloride.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

Reaction of Magnesium with Chlorine

Magnesium burns in chlorine with intense white flame and forms magnesium chloride.

$$Mg + Cl_2 \longrightarrow MgCl_2$$

Reaction of Aluminium with Chlorine

Aluminium readily combines with chlorine on heating to form aluminium chloride.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

Reaction of Silicon with Chlorine

Silicon reacts with chlorine on heating to form liquid silicon tetrachloride.

$$Si + 2Cl_2 \longrightarrow SiCl_4$$

Reaction of Phosphorus with Chlorine

When dry chlorine gas is passed over molten white phosphorus, a mixture of two chlorides (phosphorus trichloride and phosphorus pentachloride) is obtained. The phosphorus gives phosphorus trichloride with limited supply of chlorine and phosphorus pentachloride with excess chlorine.

$$P_4 + \underset{\text{Limited}}{6Cl_2} \longrightarrow 4PCl_3$$

$$P_4 + \underset{\text{Excess}}{10Cl_2} \longrightarrow 4PCl_5$$

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Reaction of Sulphur with Chlorine

Sulphur reacts with chlorine on heating to form disulphur dichloride liquid.

$$2S + Cl_2 \longrightarrow S_2Cl_2$$

Reaction of Argon with Chlorine

Argon does not react with chlorine.

$$Ar + Cl_2 \longrightarrow \text{No Reaction}$$

13.1.3 Physical Properties of the Oxides of Period 3 Elements

Oxides are the binary compounds (compounds composed of only two elements) of oxygen with other elements. There may be oxides of all the elements except fluorine.

The relationship between the physical properties of oxides of period 3 elements and their structures is discussed here in this topic. Argon does not form an oxide because it has complete outermost shell.

13.1.3.1 Structure of Oxides

The oxides of sodium, magnesium and aluminium consist of giant structure of metal ions and oxide ions. Silicon dioxide has giant covalent structure. The oxides of phosphorus, sulphur and chlorine consist of molecules.

Table 13.7: The Structure of Oxides of Period 3 Elements

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_3	Cl_2O
				P_4O_{10}	SO_2	Cl_2O_7
Giant ionic	Giant ionic	Giant ionic with covalent character	Giant covalent	Molecular Covalent	Molecular Covalent	Molecular Covalent

Na_2O, MgO, Al_2O_3 and SiO_2 have strong attractive forces (Intra molecular forces) in all directions. Hence, they have regular arrangement of particles (atoms or ions) and have giant structures because the arrangement is repeated many times with large number of particles throughout the substance. The oxides of non-metals (phosphorus, sulphur and chlorine) consist of molecules and have weak intermolecular forces (London Forces). Hence, they have simple structures and the arrangement of their atoms is not repeated.

13.1.3.2 Nature of Oxides

Sodium and magnesium oxides are ionic. The aluminium oxide is mostly ionic and has a significant covalent character. Silicon dioxide has a covalent character. The oxides of silicon phosphorus, sulphur and chlorine have covalent characters.

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Table 13.8: The Ionic Character of Oxides of Period 3 Elements

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6	SO_3	Cl_2O
					P_4O_{10}	SO_2	Cl_2O_7
Character	Ionic	Ionic	Mostly Ionic	Covalent	Covalent	Covalent	Covalent
ΔEN	2.51	2.13	1.83	1.54	1.25	0.86	0.44

The ionic character of period 3 elements decreases while covalent character increases along the period due to decrease in the electronegativity difference. The elements form ionic bonds when the electronegativity difference between two elements is large. The elements form covalent bonds when the electronegativity difference between two elements is small.

13.1.3.3 Melting and Boiling Points of Oxides

The oxides of sodium, magnesium and aluminium have high melting and boiling points because they are ionic and a lot of energy is required to break the strong attractive forces between the ions (cations and anions).

The melting and boiling points of silicon dioxide are also high because a large amount of energy is required to break very strong silicon-oxygen covalent bond. It is concluded that the oxides of metals (Na_2O, MgO and Al_2O_3) and silicon (SiO_2) have giant ionic and covalent structures, hence they have high melting and boiling points.

Table 13.9: Melting and Boiling Points of Oxides of Period 3 Elements

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	P_4O_6	SO_3	SO_2	Cl_2O_7	Cl_2O
Melting Point (°C)	1275	2852	2040	1610	340	24	17	-72	-92	-120.6
Boiling Point (°C)	1950	3600	2977	2230	360	173	45	-10	82	2.2

The oxides of phosphorus (P_4O_6 and P_4O_{10}), sulphur (SO_2 and SO_3) and chlorine (Cl_2O and Cl_2O_7) are simple molecular covalent. The melting and boiling points of these oxides are much lower than those of metal oxides or silicon dioxide. Because they consist of molecules and have intermolecular forces (dipole-dipole forces or London dispersion forces). The strength of these forces depends either on the polarity of molecules or on the size of molecules.

13.1.3.4 Electrical conductivity

The oxides of metals (Na_2O, MgO and Al_2O_3) do not conduct electricity in the solid state due to absence of mobile electrons or free ions. They conduct electricity in the molten state because of the movement of ions.

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Silicon dioxide does not conduct electricity either as a liquid or solid. This is due to absence of mobile electrons or ions in the SiO_2.

Table 13.10: The Electrical Conductivity of Oxides of Period 3 Elements

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6 / P_4O_{10}	SO_3 / SO_2	Cl_2O / Cl_2O_7
In the Solid State	None	None	None	None	None	None	None
In the Molten State	High	High	High	Very Low	None	None	None

The oxides of non-metals (P_4O_6, P_4O_{10}, SO_2, SO_3, Cl_2O and Cl_2O_7) do not conduct electricity either as a gas, liquid or solid. Because they consist of molecules and none of them have free electrons or ions.

13.1.4 Acid-Base Behaviour of the Oxides of Period 3 Elements

The ionic character of period 3 elements decreases while covalent character increases along the period due to decrease in the electronegativity difference. The elements form ionic bonds when the electronegativity difference between two elements is large, while they form covalent bonds when the electronegativity difference between two elements is small.

Sodium and magnesium oxides are ionic and contain O^{2-} ion. Oxide ion is a strongly basic ion that reacts with water to form hydroxide ions.

$$O^{2-} + H_2O \longrightarrow 2OH^-$$

Al_2O_3 has both ionic and covalent characters and is amphoteric. It reacts with both acids and bases to form salts.

SiO_2 has a covalent character. It does not contain oxide ion. It is weakly acidic. It reacts with strong bases to form salts.

Oxides of non-metals have covalent characters and are acidic in nature. They form acidic solutions when dissolved in water.

Table 13.11: The Acid-Base Behaviour of Oxides of Period 3 Elements

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Character	Strongly Basic	Weakly Basic	Amphoteric	Weakly Acidic	Acidic	Strongly Acidic	Very Strongly Acidic
ΔEN	2.51	2.13	1.83	1.54	1.25	0.86	0.44

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13.1.4.1 Trends in Acid-Base Behaviour

The basic character of oxides of period 3 elements decreases while acidic character increases along the period due to decrease in the electronegativity difference (ΔEN).

13.1.4.2 Reactions of Oxides with Water, Acids and Bases

Reactions of Oxides with Water

Sodium oxide reacts readily with water to form basic solution. The pH of solution is around 14.

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Magnesium oxide reacts with water to form basic solution. The reaction is slow and some magnesium hydroxide is formed in the reaction. The pH of solution is around 9.

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

Aluminium oxide is insoluble in water and does not react with water.

$$Al_2O_3 + H_2O \longrightarrow \text{No Reaction}$$

Silicon dioxide does not react with water because it has a giant covalent structure and is completely insoluble in water.

$$SiO_2 + H_2O \longrightarrow \text{No Reaction}$$

The oxides of non-metals (phosphorus, sulphur, and chlorine) react with water to form acidic solutions.

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3 \quad \text{(Phosphorous acid)}$$

$$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4 \quad \text{(Phosphoric acid)}$$

$$SO_2 + H_2O \longrightarrow H_2SO_3 \quad \text{(Sulphurous acid)}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \quad \text{(Sulphuric acid)}$$

$$Cl_2O + H_2O \longrightarrow 2HClO \quad \text{(Hypochlorous acid)}$$

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4 \quad \text{(Perchloric acid)}$$

Reactions of Oxides with Acids

Sodium oxide reacts with dilute hydrochloric acid to form aqueous solution of sodium chloride.

$$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$$

Magnesium oxide reacts with warm dilute hydrochloric acid to form aqueous solution of magnesium chloride.

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$$

Aluminium oxide reacts with hot dilute hydrochloric acid to form aqueous solution of aluminium chloride.

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$$

In this reaction aluminium oxide acts as a base.

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Silicon dioxide is a stable compound and does not react with most of the acids at normal conditions. It reacts only with hydrofluoric acid (HF).

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

Tetrafluorosilane (SiF_4) reacts further with HF to produce hexafluorosilicic acid.

$$SiF_4 + 2HF \longrightarrow H_2[SiF_6]$$

Reactions of Oxides with Bases

Aluminium oxide reacts with hot concentrated sodium hydroxide to form a colourless solution of sodium tetrahydroxoaluminate.

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$$

In this reaction aluminium oxide acts as an acid.

Silicon dioxide slowly reacts with hot concentrated sodium hydroxide to form colourless solution of sodium silicate and water.

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

Phosphorus trioxide reacts directly with sodium hydroxide to produce two series of salts (sodium dihydrogenphosphite and sodium hydrogenphosphite).

$$4NaOH + P_4O_6 + 2H_2O \longrightarrow 4NaH_2PO_3$$

$$8NaOH + P_4O_6 \longrightarrow 4Na_2HPO_3 + 2H_2O$$

Phosphorus pentaoxide reacts directly with sodium hydroxide to produce three series of salts (sodium dihydrogen phosphate, sodium hydrogen phosphate and sodium phosphate).

$$4NaOH + P_4O_{10} + 2H_2O \longrightarrow 4NaH_2PO_4$$

$$8NaOH + P_4O_{10} \longrightarrow 4Na_2HPO_4 + 2H_2O$$

$$12NaOH + P_4O_{10} \longrightarrow 4Na_3PO_4 + 6H_2O$$

Sulphur dioxide reacts directly with sodium hydroxide solution to produce sodium sulphite.

$$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$$

When SO_2 is in excess then sodium bisulphite is formed.

$$SO_2 + NaOH \longrightarrow NaHSO_3$$

Sulphur trioxide reacts directly with sodium hydroxide solution to produce sodium sulphate.

$$SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$$

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Dichlorine monoxide reacts with solution of sodium hydroxide to produce sodium hypochlorite.

$$Cl_2O + 2NaOH \longrightarrow 2NaClO + H_2O$$

Dichlorine heptoxide reacts with solution of sodium hydroxide to produce sodium perchlorate.

$$Cl_2O_7 + 2NaOH \longrightarrow 2NaClO_4 + H_2O$$

13.1.5 Chlorides of the Period 3 Elements

The binary compounds of chlorine with period 3 elements are called chlorides of the period 3 elements. The formulae of the chlorides of period 3 elements are given in the table.

Table 13.12: Chlorides of Period 3 Elements

Formula of Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3 PCl_5	SCl_2
Oxidation Number	+1	+2	+3	+4	+3 +5	+2

The oxidation number of the element in its chloride is equal to the number of chlorine atoms attached to the element.

13.1.5.1 Nature and Structure of Chlorides

NaCl and $MgCl_2$ are white ionic compounds and consist of giant structures. They composed of oppositely charged ions that held together by strong electrostatic forces.

$AlCl_3$ is white covalent compound. It has a layered lattice at room temperature. It turns to dimeric gas (Al_2Cl_6) on heating to about 180°C and then has a simple molecular structure.

Table 13.13: Chlorides of Period 3 Elements

Formula of Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3 PCl_5	SCl_2
Structure	Ionic	Ionic	Covalent	Molecular covalent	Molecular covalent	Molecular covalent

$SiCl_4$ and PCl_3 are colourless covalent compounds. They are found in the liquid states. They have simple molecular structures. Their molecules are held together by weak van der Waal's forces.

PCl_5 is a white ionic compound in the solid state and has an ionic lattice of $[PCl_6]^-[PCl_4]^+$. However, it has a simple molecular structure in the gaseous state.

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SCl_2 is a cherry red liquid. It is a covalent compound and has a simple molecular structure.

13.1.5.2 Melting and Boiling Points of Chlorides

Sodium chloride and magnesium chloride have high melting and boiling points because they need a large amount of energy to break the strong electrostatic attractions between their ions.

Aluminium chloride and silicon tetrachloride have low melting and boiling points because they need small amount of energy to break weak van der Waal's forces between their molecules.

Table 13.14: Melting and Boiling Points of Chlorides

Formula of Chloride	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	PCl_5	SCl_2
Melting Point (°C)	801	714	192.6	−68.74	−93.6	160.5	−121
Boiling Point (°C)	1413	1412	180	57.65	76.1	166.8	59

Phosphorus trichloride (PCl_3) has low melting and boiling points due to presence of weak intermolecular forces between their molecules.

Phosphorus pentachloride (PCl_5) has higher melting and boiling points than phosphorus trichloride because they have different structures. The forces of attractions that hold solid lattice of PCl_3 together are weak van der Waal's forces and that hold solid lattice of PCl_5 together are strong ionic bonds.

SCl_2 has low melting and boiling points because their molecules are held together by weak intermolecular forces.

13.1.5.3 Electrical Conductivity of Chlorides

The chlorides of the period 3 elements on the left such as NaCl and $MgCl_2$ are ionic. They do not conduct electricity in the solid because their ions are locked in place and not able to move. They can only conduct electricity when they are either melted or dissolved in polar solvents such as water because in molten state or in solution form their ions are free to move.

Note that aluminium chloride is covalent not ionic as would normally be expected from a metal and a non-metal binary compound. It does not conduct electricity either in solid state or in liquid state.

The chlorides of the elements on the right of the period such as $SiCl_4$, PCl_3, PCl_5, and SCl_2 are covalent in nature. They do not conduct electricity either in solid or molten state because they do not have any ions or any mobile electrons.

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13.1.5.4 Solubility of Chlorides in Water

NaCl does not react with water. It dissolves in water to form a neutral solution (pH ≈7) of metal cations and chloride ions.

$$NaCl \xrightarrow{Water} Na^+ + Cl^-$$

$MgCl_2$ also does not react with water. It dissolves in water to form slightly acidic solution (pH ≈ 6.5) of metal cations and chloride ions.

$$MgCl_2 \xrightarrow{Water} Mg^{++} + 2Cl^-$$

The covalent chlorides (Al_2Cl_6, $SiCl_4$, PCl_3 and PCl_5) are hydrolysed by water to form acidic solutions.

$$Al_2Cl_6 + 6H_2O \xrightarrow{Water} 2Al(OH)_3 + 6HCl \quad (pH \approx 3)$$

$$SiCl_4 + 2H_2O \xrightarrow{Water} SiO_2 + 4HCl \quad (pH \approx 2)$$

$$PCl_3 + 3H_2O \xrightarrow{Water} H_3PO_3 + 3HCl \quad (pH \approx 2)$$

$$PCl_5 + 4H_2O \xrightarrow{Water} H_3PO_4 + 5HCl \quad (pH \approx 2)$$

Keep in Mind

Ionic chlorides generally give neutral solutions and covalent chlorides generally give acidic solutions in water.

13.1.6 Hydroxides of Period 3 Elements

The hydroxides of sodium and magnesium viz. NaOH and $Mg(OH)_2$ are basic. They are white hygroscopic crystalline solids. Sodium hydroxide is highly soluble in water and magnesium hydroxide is slightly soluble in water. Sodium hydroxide reacts with dil. HCl to produce colourless solution of sodium chloride.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Magnesium hydroxide reacts with dil. HCl to produce colourless solution of magnesium chloride.

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

The hydroxide of aluminium viz. $Al(OH)_3$ is amphoteric. It can react both as an acid and as a base. Aluminium hydroxide reacts with dil. HCl to produce colourless solution of aluminium chloride.

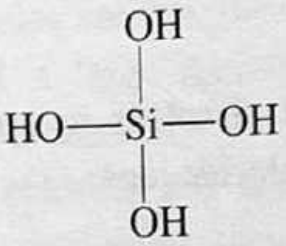
$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

Aluminium hydroxide reacts with the solution of sodium hydroxide to produce colourless solution of sodium tetrahydroxoaluminate (III).

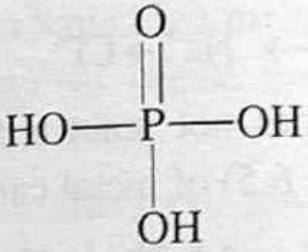
$$Al(OH)_3 + NaOH \longrightarrow Na[Al(OH)_4]$$

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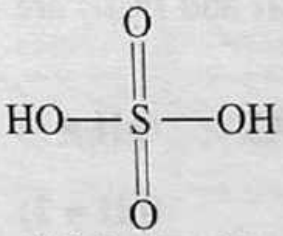
The hydroxides of Si, P, S and Cl are $Si(OH)_4$, H_3PO_4, H_2SO_4, and $HClO_4$. They are all acidic. Their acidity ranges from the very weak silicic acid to the very strong perchloric acid.



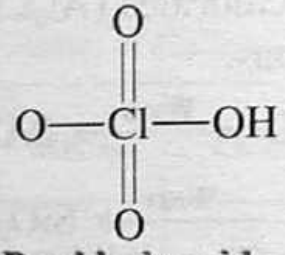
Orthosilicic acid



Phosphoric acid



Sulphuric acid



Perchloric acid

The —OH groups of these hydroxides are covalently bonded to the atoms of period 3 elements.

13.2 Group 1 Elements

The elements of group 1 (IA) include lithium, sodium, potassium, rubidium, cesium and francium, and are known as alkali metals. The word alkali has been taken from an Arabic word meaning "ashes". Because many compounds of alkali metals particularly sodium and potassium were isolated from the ashes of wood by early chemists. These are the most active metals in the periodic table. They have to be stored in oil (kerosene) to prevent their reaction with oxygen and water in the air. They are not found in the elemental state; they found only in combined states. Alkali metals are soft enough to be cut with a knife. They have silvery appearance. This can only be seen when they are freshly cut. They are good conductors of electricity.

Table 13.15: Electronic Configuration of Alkali Metals

Name	Symbol	Atomic number	Electronic configuration	Valence shell electronic configuration
Lithium	Li	3	$1s^2 2s^1$	$2s^1$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s^1$	$3s^1$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$4s^1$
Rubidium	Rb	37	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$	$5s^1$
Cesium	Cs	55	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$	$6s^1$
Francium	Fr	87	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^1$	$7s^1$

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Their valence shell electronic configuration is "ns^1". They are excellent reducing agents. They form monovalent positive ions (M^+) by losing one valence electron and attain the stable electronic configuration of noble gases. They show oxidation state of +1.

13.2.1 Atomic and Physical Properties of the Group 1 Elements

The trends in some atomic and physical properties of the group 1 elements are discussed below:

13.2.1.1 Trends in Atomic Radius

The atomic radius of alkali metals increases as we move down the group. This is due to increase in number of shells and shielding effect.

Table 13.16: Atomic Radius of Group 1 Elements

Element	Li	Na	K	Rb	Cs	Fr
Atomic Radius (pm)	152	186	227	248	265	348 By (van der Waal's)

Francium has the largest atomic radius of any other neutral element but it is an extremely unstable element and little is known about its properties. The credit is, therefore, goes to cesium.

13.2.1.2 Trends in First Ionization Energy

Alkali metals have one electron in the valence shell (ns^1). This ns^1 electron is loosely bound to the nucleus and this electron can be detached easily. They have, therefore, the lowest first ionization energies of all the elements in the periodic table. Thus, they are the powerful reducing agents.

Table 13.17: Ionization Energies of Group 1 Elements

Element	Li	Na	K	Rb	Cs
Ionization Energy (kJ/mol)	520.3	495.8	418.9	403.0	375.7

The ionization energy of alkali metals decreases down the group. This is due to increase in atomic size.

13.2.1.3 Trends in Electronegativity

Alkali metals have greater tendency to lose their valence electrons and are highly electropositive. Because of this, they have very low electronegativity values.

Table 13.18: Electronegativity Values of Group 1 Elements

Element	Li	Na	K	Rb	Cs
Electronegativity Values	0.98	0.93	0.82	0.82	0.79

The values of electronegativity decrease down the group due to increase in atomic size.

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13.2.1.4 Trends in Melting and Boiling Points

They have very low melting and boiling points. This is due to the presence of weak metallic bonds of the alkali metals in the solid state.

Table 13.19: Melting and Boiling Points of Group 1 Elements

Element	Li	Na	K	Rb	Cs
Melting Point (°C)	180.5	97.8	63.7	38.9	28.7
Boiling Point (°C)	1330	892	760	688	670

The melting and boiling points of alkali metals decrease as we go down the group. This is due to increase in atomic size. As the size of atoms get larger, the attraction between the metal cations and the negatively charged electronic cloud becomes weaker and thus the melting and boiling points decrease.

13.2.1.5 Trends in Density

Mass per unit volume (m/V) is called density. It means how much mass a substance has in a unit volume. Alkali metals have low densities due to large atomic volumes.

Table 13.20: The Densities and Atomic Volumes of Group 1 Elements

Element	Li	Na	K	Rb	Cs
Atomic Volumes (cm^3/mol)	12.97	23.68	45.36	55.80	69.95
Density (g/cm^3)	0.54	0.97	0.86	1.53	1.90

Lithium, sodium and potassium are the only metals, which are less dense than water ($1 g/cm^3$). When they are added to water, they float on the surface of water. Density of group 1 elements generally increases down the group. This is due to increase in atomic masses. The potassium, however, is less dense than sodium. This is due to an abnormal increase in the atomic volume of potassium.

13.2.2 Trends in Reactivity with Water

Alkali metals react with water to produce hydroxide and liberate hydrogen gas. The hydroxides of group 1 elements are water soluble, thus they dissolve in water and form an alkaline solution of metal hydroxide.

Metal (M) + Water (H_2O) ⟶ Metal hydroxide (MOH) + Hydrogen (H_2)

The reactivity of group 1 elements increases down the group. Lithium is the least reactive and caesium is the most reactive.

The equations for the reactions of alkali metals with water are:

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$
$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$
$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

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13.2.3 Reactions of Alkali Metals with Oxygen

Alkali metals react with oxygen or air quickly and thus becomes tarnished (dull) due to the formation of a film of oxides on their surfaces. The alkali metals are, therefore, stored in kerosene or paraffin oil to ensure safety and purity.

13.2.3.1 Formation of Oxides

Lithium reacts with oxygen to form mainly normal oxide, Li_2O (and some peroxide).

$$4Li + O_2 \longrightarrow 2Li_2O \quad \textbf{(Lithium monoxide)}$$

$$2Li + O_2 \longrightarrow Li_2O_2 \quad \textbf{(Lithium peroxide)}$$

Sodium reacts with oxygen to give mainly peroxide, Na_2O_2 (and some normal oxide).

$$4Na + O_2 \longrightarrow 2Na_2O \quad \textbf{(Sodium monoxide)}$$

$$2Na + O_2 \longrightarrow Na_2O_2 \quad \textbf{(Sodium peroxide)}$$

Potassium, rubidium and cesium react with oxygen to give KO_2, RbO_2 and CsO_2 respectively.

$$K + O_2 \longrightarrow KO_2 \quad \textbf{(Potassium super oxide)}$$

$$Rb + O_2 \longrightarrow RbO_2 \quad \textbf{(Rubidium super oxide)}$$

$$Cs + O_2 \longrightarrow CsO_2 \quad \textbf{(Cesium super oxide)}$$

Keep in Mind

The binary compounds of oxygen are called oxides. They are mainly of three types: normal oxides, peroxides and superoxides. The main difference between normal oxide, peroxide and superoxide is that the oxidation state of oxygen of normal oxide is -2, peroxide is -1 and that of superoxide is $-\frac{1}{2}$. Examples of normal oxides are Na_2O and CO_2, peroxides are Na_2O_2 and K_2O_2 while those of superoxides are KO_2 and RbO_2.

13.2.3.2 Reactions of Oxides with Water

The normal oxides of alkali metals react with water to produce metal hydroxides.

$$Li_2O + H_2O \longrightarrow 2LiOH$$

$$Na_2O + H_2O \longrightarrow 2NaOH$$

The peroxides of alkali metals react with water to produce metal hydroxides and hydrogen peroxides.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

The super oxides of alkali metals react with water to produce metal hydroxides and hydrogen peroxides with the liberation of oxygen gas.

$$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$$

$$2RbO_2 + 2H_2O \longrightarrow 2RbOH + H_2O_2 + O_2$$

13.2.3.3 Reactions of Oxides with Dilute Acids

The normal oxides react with dilute acids to produce salt and water.

$$Li_2O + 2HCl \longrightarrow 2LiCl + H_2O$$

$$Na_2O + 2HCl \longrightarrow 2NaCl + H_2O$$

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The peroxides are strong oxidizing agents. They combine with dilute acids to produce salt and hydrogen peroxide.

$$Na_2O_2 + 2HCl \longrightarrow 2NaCl + H_2O_2$$

The super oxides are also strong oxidizing agents. They combine with dilute acids to produce salt, hydrogen peroxides and oxygen gas.

$$2KO_2 + 2HCl \longrightarrow 2KCl + H_2O_2 + O_2$$

13.2.4 Reactions of Alkali Metals with Halogens

Alkali metals react directly with halogens to produce their respective metal halides.

$$2M + X_2 \longrightarrow 2MX$$

Where,

'M' represents Li, Na, K, Rb or Cs and 'X_2' represents F_2, Cl_2, Br_2 or I_2.

For example; when sodium reacts with chlorine, then sodium chloride is formed.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

The halides of alkali metals are white crystalline solids and are readily soluble in water. They are good conductors of electricity in the molten state or in solution form.

13.2.5 Effect of Heat on Nitrates, Carbonates and Bicarbonates

13.2.5.1 Effect of Heat on Nitrates

The nitrates of alkali metals are highly stable toward heat. They decompose into nitrites and oxygen gas on strong heating except lithium nitrate. Lithium nitrate decomposes more readily into oxide, nitrogen peroxide and oxygen gas.

$$4LiNO_3 \xrightarrow{Heat} 2Li_2O + 4NO_2 + O_2$$

$$2NaNO_3 \xrightarrow{Heat} 2NaNO_2 + O_2$$

The thermal stability of nitrates increases down the group due to increase in the polarizing power of positive ions.

13.2.5.2 Effect of Heat on Carbonates

The carbonates of alkali metals are highly stable toward heat. The lithium carbonate is significantly less stable towards heat and decomposes more readily. The carbonates of other alkali metals do not decompose even at higher temperature.

$$2Li_2CO_3 \xrightarrow{Heat} 2Li_2O + 2CO_2$$

The thermal stability of carbonates increases down the group due to increase in he polarizing power of positive ions.

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13.2.5.3 Effect of Heat on Bicarbonates

The bicarbonates of alkali metals are stable toward heat but are not much stable. However, they decompose on heating to produce carbonates, carbon dioxide and water vapours.

$$2NaHCO_3 \xrightarrow{Heat} Na_2CO_3 + CO_2 + H_2O$$

The thermal stability of bicarbonates increases down the group due to increase in the polarizing power of positive ions.

13.2.6 Flame Tests: Origin of the Flames

Various metals give very attractive coloured flames when burnt in air. The colours of flames are the result of electrons moving from higher energy levels to lower energy levels in metal atoms. The alkali metals give characteristic coloured flames when a sample of an alkali metal or its salt is heated in the Bunsen burner. The colour of the emitted light (flames) can be used to identify the alkali metals. This process is known as flame test. Since the amount of energy released during the returning of electron to the ground state is different in different atoms, hence, different colours are imparted by the atoms to the flame.

Table 13.21: Alkali metals and their Flame Colours

Elements	Lithium	Sodium	Potassium	Rubidium	Cesium
Flame Colour	Crimson	Yellow	Lilac	Red-violet	Blue

13.3 Group 2 Elements

The elements of group 2 (IIA) are beryllium, magnesium, calcium, strontium, and barium. They are all metals and are known as alkaline earth metals. They are harder, denser and have high melting and boiling points than alkali metals. Alkaline earth metals are always found in combined states with other elements. These are the second most active metals in the periodic table. They must be stored in oil (kerosene) to prevent their reaction with oxygen and water vapours in the air. They are not found as pure elements because of their high chemical reactivity. They are white or silvery except beryllium which is grey in colour.

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Table 13.22: Electronic Configuration of Alkaline Earth Metals

Name	Symbol	Atomic number	Electronic configuration	Valence shell electronic configuration
Beryllium	Be	4	$1s^2 2s^2$	$2s^2$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$	$3s^2$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$4s^2$
Strontium	Sr	38	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$	$5s^2$
Barium	Ba	56	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ $5s^2 4d^{10} 5p^6 6s^2$	$6s^2$
Radium	Ra	88	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ $5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2$	$7s^2$

They have two electrons in the valence shell. They form dipositive ions by losing two valence electrons and attain the stable electronic configuration of noble gases. They show oxidation state of +2. Alkaline earth metals are less reactive than alkali metals.

13.3.1 Atomic and Physical Properties of the Group 2 Elements

The trends in some atomic and physical properties of the group 2 elements are discussed as:

13.3.1.1 Trends in Atomic Radius

The atomic radius of alkaline earth metals increases down the group. This is due to increase in number of shells and shielding effect.

Table 13.23: Atomic Radius of Group 2 Elements

Element	Be	Mg	Ca	Sr	Ba	Ra
Atomic Radius (pm)	112	160	197	215	222	283 (van der Waal's)

Atomic radii of alkaline earth metals are smaller than those of alkali metals in the same period. This is due to high charge density of alkaline earth metals.

13.3.1.2 Trends in Ionization Energies

Alkaline earth metals have two electrons in their valence shell (ns^2). Their valence electrons are more tightly bound to the nucleus than those of alkali metals. They have, therefore, higher first ionization energies than alkali metals.

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Table 13.24: Ionization Energies of Group 2 Elements

Element	Be	Mg	Ca	Sr	Ba	Ra
First Ionization Energy (kJ/mol)	899	737	590	549	503	509
Second Ionization Energy (kJ/mol)	1757	1450	1145	1064	965	979

Their first and second ionization energies decrease down the group due to increase in atomic radii. The ionization energy of radium is, however, higher than barium.

Keep in Mind

The ionization energy of radium is higher than barium. This is because the radium has a filled 4f subshell; the 4f electrons shield very poorly so that nuclear charge for radium is 32 units higher than barium. The higher nuclear charge available for the radium valence electrons causes a contraction of the 7s orbital and an increase of the ionization energy.

13.3.1.3 Trends in Electronegativity Values

The electronegativity values of alkaline earth metals are small, but are higher than values for the alkali metals.

Table 13.25: Electronegativity Values of Group 2 Elements

Element	Be	Mg	Ca	Sr	Ba	Ra
Electronegativity	1.57	1.31	1.00	0.95	0.89	0.89

The values of electronegativity decrease down the group due to increase in atomic size.

13.3.1.4 Trends in Melting and Boiling Points

The melting and boiling points of these elements are higher than alkali metals.

Table 13.26: Melting and Boiling Points of Group 2 Elements

Element	Be	Mg	Ca	Sr	Ba	Ra
Melting Point (°C)	1287	649	839	768	727	700
Boiling Point (°C)	2500	1105	1494	1381	1850	1700

Melting and boiling points of these metals do not show any regular trend because they adopt different crystal structures.

13.3.2 Trends in Reactivity with Water

Although alkaline earth metals are less reactive than alkali metals, but they are still more reactive than the majority of other metals. Alkaline earth metals (except beryllium) react with water to produce hydroxides with the liberation of hydrogen gas.

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

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The reactivity of alkaline earth metals increases down the group due to increase in atomic size. Beryllium does not react with water even at high temperature. Magnesium does not react with water at room temperature (25°C), but it will react with steam to form magnesium hydroxide and hydrogen gas. Whereas calcium, strontium and barium react with water at room temperature to produce hydroxides and hydrogen gas.

13.3.3 Reactions with Oxygen and Nitrogen

13.3.3.1 Formation of Simple Oxides and Peroxides

Alkaline earth metals react with oxygen to form normal oxides except barium and radium. Barium and radium, however, produce peroxides. The tendency of alkaline earth metals to form peroxides increases from top to bottom in a group.

The reactivity of alkaline earth metals with oxygen increases going from the top of the group to the bottom. Beryllium is relatively inert because it has a strong thin layer of oxide on its surface. It reacts with oxygen at 600°C. It is much reactive in the powder form.

Formation of normal oxides:

$2Be + O_2 \longrightarrow 2BeO$

$2Mg + O_2 \longrightarrow 2MgO$

$2Ca + O_2 \longrightarrow 2CaO$

Formation of peroxides:

$Ba + O_2 \longrightarrow BaO_2$

$Sr + O_2 \longrightarrow SrO_2$

13.3.3.2 Formation of Nitrides on Heating in Air

All the alkaline earth metals react with nitrogen to produce nitrides of the general formula, M_3N_2.

$3Be + N_2 \longrightarrow Be_3N_2$

$3Mg + N_2 \longrightarrow Mg_3N_2$

$3Ca + N_2 \longrightarrow Ca_3N_2$

Keep in Mind

Beryllium nitride is a covalent compound due to small size, high charge density and low ionization energy of beryllium. It has weak intermolecular force of attractions, which leads to its volatile nature. On the other hand the nitrides of other alkaline earth metals are ionic or electrovalent and are non-volatile.

13.3.4 Trends in Solubility of the Hydroxides, Sulphates and Carbonates

13.3.4.1 Solubility of Hydroxides

The solubility of hydroxides in water increases gradually on going down the group. $Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble in water whereas the hydroxides of other alkaline earth metals are slightly soluble in water.

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13.3.4.2 Solubility of the Sulphates

The solubility of sulphates in water gradually decrease down the group. Thus $BeSO_4$ and $MgSO_4$ are fairly soluble, however $CaSO_4$ is slightly soluble in water, while the sulphates of strontium, barium and radium are almost water insoluble.

13.3.4.3 Solubility of Carbonates

The carbonates of alkaline earth metals are very slightly soluble in water. The solubility decreases down the group.

13.3.5 Trends in Thermal Stability of Nitrates and Carbonates

13.3.5.1 Trends in Thermal Stability of Carbonates

The carbonates of alkaline earth metals decompose on heating to form metal oxide and give off carbon dioxide gas.

$$CaCO_3 \xrightarrow{\text{Heat}} CaO + CO_2$$

Thermal stabilities of carbonates of alkaline earth metals increase down the group due to increase in ionic radii of cation moving down the group. This increase in atomic radii of metal cations reduces their polarizing power, which results in less polarization of the anion (CO_3^{-2}) by the larger metal cations. Because of this the decomposition of carbonates becomes more difficult.

13.3.5.2 Trends in Thermal Stability of Nitrates

The nitrates of alkaline earth metals decompose on heating to produce metal oxide, nitrogen peroxide and oxygen gas.

$$2Ca(NO_3)_2 \xrightarrow{\text{Heat}} 2CaO + 4NO_2 + O_2$$

The temperature at which thermal decomposition occurs increases moving down the group.

13.3.6 Peculiar behaviour of Beryllium

Beryllium differs in many of its properties from other alkaline earth metals due to its small atomic size and comparatively high electronegativity. The main points of difference of beryllium from other family members are:

i) Beryllium is much harder than other family members.

ii) The melting and boiling points of beryllium are much higher than other alkaline earth metals.

iii) The compounds of beryllium are more covalent than other members of its family. This is due to high charge density of beryllium than the rest. The high charge density of beryllium makes the removal of electron difficult.

iv) Beryllium does not react with either cold water or steam. Other alkaline earth metals react with water to form hydroxides and hydrogen gas.

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

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v) Beryllium reacts with alkalis to produce hydrogen gas while other elements of its group do not react with alkalis.

$$Be + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2$$

vi) The oxides and hydroxides of beryllium are amphoteric. They behave as acids towards strong bases and act as bases towards strong acids.

$$Be(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium tetrahydroxoberyllate (II)}}{Na_2Be(OH)_4}$$

$$Be(OH)_2 + H_2SO_4 \longrightarrow BeSO_4 + 2H_2O$$

The oxides and hydroxides of other elements of group 2 are basic.

vii) Beryllium carbide forms methane gas while other alkaline earth metals form acetylene gas on hydrolysis.

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

viii) The nitride of beryllium, Be_3N_2 is volatile while the nitrides of other alkaline earth metals are non-volatile.

ix) Beryllium forms a large number of stable complex compounds whereas the other alkaline earth metals form very few complex compounds.

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Mining and Extraction of Elements/Metals

Mining of Elements/Metals

The earth crust is made up of various compounds and native elements such as gold, silver, copper and sulphur. The main elements in the earth crust are oxygen (46%) and silicon (28%). The rest of the earth crust is predominantly made up of aluminium (8%), iron (5%), calcium (4%), sodium (3%), magnesium (2%), and potassium (2%). Metals are important to society and support our modern standard of living. The naturally occurring rocks that contain metals or metal compounds in sufficient amounts to make it profitable to extract them are called ores. The extraction of ores from the earth is called mining. Ores are natural resources that human beings have been mining for thousands of years. The ores are mined from the ground, either by surface or underground methods.

Extraction of Elements/Metals from Their Ores

The method of extraction of a metal from its ore depends on the reactivity of metals. The most reactive metals are extracted hardly while the less reactive metals are extracted easily from their ores. The unreactive metals such as gold are not found in ores and are found in un-combined states.

The reactive metals such as potassium, sodium, calcium, magnesium and aluminium are extracted by electrolysis while the less reactive metals such as zinc, iron, tin and lead are extracted by reaction with carbon or carbon monoxide.

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Metal oxide + Carbon ⟶ Metal + Carbon dioxide

The carbon removes the oxygen from the metal oxide and forms carbon dioxide, leaving the pure metal behind. Reactions which involve the removal of oxygen in this way are called reduction reactions.

The native metals such as copper, silver, gold and platinum do not need to be chemically extracted from their ores, but chemical reactions may be required to remove other elements that might contaminate the metals.

13.4 Group 14 Elements

The group 14 (IVA) consists of carbon, silicon, germanium, tin and lead. They have four electrons in the valence shell and can form four covalent bonds. Carbon is an essential constituent of life. It is found in proteins, carbohydrates, fats, etc. Silicon is the second most abundant element in the earth's crust. It is a semiconductor and is commonly used in solar cells, transistors and computer chips. Germanium, a semiconductor, is used in computer industry. Lead, a metal, has been used for plumbing and to block radiation. Nowadays it is mainly used in the manufacture of car batteries, protective shielding around nuclear reactors and containers used for storing and transporting radioactive materials. Tin, a metal, is used to coat other metals to prevent corrosion. It can also be used in alloy formation such as solder, bronze and pewter.

The elements of group IVA show intermediate properties. These elements are present between strongly electropositive elements (Group IA, IIA and IIIA) and strongly electronegative elements (Group VA, VIA and VIIA).

Table 13.27: Electronic Configurations of Group 14 Elements

Name	Symbol	Atomic number	Electronic configuration	Valence shell electronic configuration
Carbon	C	6	$1s^2 2s^2 2p^2$	$2s^2 2P^2$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	$3s^2 3P^2$
Germanium	Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$	$4s^2 4P^2$
Tin	Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$	$5s^2 5P^2$
Lead	Pb	82	$1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^2$	$6s^2 6P^2$

Their valence shell electronic configuration is ns^2np^2.

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13.4.1 Physical Properties of Group 14 (IVA) Elements

The trends in physical properties of group 14 elements are discussed below:

13.4.1.1 Trends in Melting and Boiling Points

The melting and boiling points of group 14 elements decrease down the group. This is due to increase in atomic size and decrease in inter-atomic forces.

Table 13.28: Melting and Boiling Points of Group 14 Elements

Element	C	Si	Ge	Sn	Pb
Melting Point(°C)	3550	1420	945	232	327
Boiling Point(°C)	4830	2480	2850	2623	1751

The melting and boiling points of carbon and silicon are very high because they have tendencies to form macromolecules.

13.4.1.2 Trends from Non-metal to Metal

Metallic character increases down the group. Carbon and silicon are non-metals, germanium is semimetal, and tin and lead are metals. The electrical properties of silicon are similar to that of a semimetal.

13.4.1.3 Oxidation State

The elements of group IVA have four electrons in their valence shells and they have an oxidation state of +4. The first three elements may also have an oxidation state of –4 when they are bonded to more electropositive elements. Tin (Sn) and lead (Pb) also show an oxidation state of +2 that is the only oxidation state in which they produce ionic compounds.

The stability of +4 oxidation state decreases and that of +2 oxidation state increases on moving down the group. For example, the compounds of Ge^{2+} are less stable than Ge^{4+}.The compounds of Ge^{2+} act as strong reducing agents while those of Ge^{4+} act as oxidizing agents.

On the other hand, the compounds of Pb^{2+} ($PbCl_2$) are more stable than Pb^{4+}($PbCl_4$). Therefore, the compounds of Pb^{2+} are ionic and more common than Pb^{4+}. The compounds of Pb^{2+} act as reducing agents while those of Pb^{4+} act as oxidizing agents.

Inert Pair Effect and the Nature of Bond

The tendency of ns^2 electrons of the valence shell of metallic elements to remain unshared or unionized is called inert pair effect. The ability of an electron to get closer to the nucleus is called penetration. The penetration power of *s*-orbital is the maximum and it experiences stronger attraction to the nucleus. As a result of which the *s*-electrons fail to participate in bond formation. So the ns^2 electrons need more energy to remove. Hence, the oxidation states of heavier elements (esp. the last two elements of group IIIA, IVA, VA and VIA) are two less than what would be expected.

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The nature of bond is also affected by oxidation state. The metal compounds in their lower oxidation states are ionic in character while in their higher oxidation states they are covalent. For example, stannous chloride ($SnCl_2$) and plumbous chloride ($PbCl_2$) have +2 oxidation states and they are mainly ionic. Conversely the stannic chloride ($SnCl_4$) and plumbic chloride ($PbCl_4$) have +4 oxidation states and they are fairly covalent. This is because the size of Sn^{4+} and Pb^{4+} ions is smaller than Sn^{2+} and Pb^{2+} ions. The smaller the size of cation, the greater its tendency to form covalent bond. The tendency of cations to form ionic bonds increases down the group.

13.4.2 Chlorides of Carbon, Silicon and Lead

The chlorides of carbon, silicon and lead have general formula MCl_4. They are simple covalent molecules that are held together by weak van der Waal's forces. Since, they have low melting and boiling points and are frequently volatile liquids. Their melting points generally increase with increase in molecular mass. They have tetrahedral geometries.

13.4.2.1 Preparation of Tetrachlorides

The tetrachlorides may be prepared either by heating the element with appropriate halogen or by passing dry halogen over a highly heated mixture of dioxide and carbon.

$$M + 2Cl_2 \longrightarrow MCl_4$$

$$MO_2 + 2C + 2Cl_2 \longrightarrow MCl_4 + 2CO$$

Where, M represents C, Si and Pb.

13.4.2.2 Thermal Stability

The chlorides of carbon and silicon (CCl_4 and $SiCl_4$) are stable at high temperature and does not decompose easily. Conversely, the chloride of lead decomposes on heating. The thermal stability of tetrachlorides decreases from CCl_4 to $PbCl_4$. Thus: $CCl_4 > SiCl_4 > PbCl_4$

13.4.2.3 Reactions with Water (Hydrolysis)

Carbon tetrachloride does not react with water.

$$CCl_4 + H_2O \longrightarrow \text{No reaction}$$

Silicon tetrachloride (or tetrachlorosilane) and plumbic chloride react with water readily.

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

$$PbCl_4 + 2H_2O \longrightarrow PbO_2 + 4HCl$$

Some of the $PbCl_4$ decomposes into $PbCl_2$ due to the instability of $PbCl_4$.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

$PbCl_2$ is ionic in nature and slightly soluble in cold water and more soluble in hot water.

$$PbCl_2 \xrightarrow{\text{Water}} Pb^{2+} + 2Cl^{1-}$$

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13.4.3 Oxides of Group 14 (IVA) Elements

There are two main types of group IVA oxides and they are:

Monoxides: They have general formula MO. Examples are: CO, SnO and PbO.

Dioxides: They have general formula MO_2. Examples are: CO_2, SiO_2, SnO_2 and PbO_2.

13.4.3.1 Structure of Carbon Dioxide and Silicon Dioxide

The physical properties of carbon dioxide are different from silicon dioxide. Carbon dioxide is a colourless and odourless gas. It is commercially used in fire extinguishers and to carbonate beverages. The silicon dioxide is a high melting solid at ordinary temperature. The oxides of the rest of the group are also exist as solid. Because of this the structure of carbon dioxide is different from the rest of the oxides of group IVA.

Structure of Carbon Dioxide

Carbon dioxide consists of simple molecules. The molecule of carbon dioxide is triatomic. The bond strengths and bond lengths show that there are two carbon-oxygen double bonds in the carbon dioxide molecule.



The molecule of carbon dioxide has two dipoles. They are equal and have opposite directions. So they cancel the effect of each other. Therefore, the dipole moment of carbon dioxide is zero. Thus the only intermolecular forces in pure carbon dioxide are London dispersion forces. Hence, CO_2 is a gas. The solid CO_2 is called dry ice and has a face centred cubic structure. It is used in carbonated drinks, freeze meat, frozen foods and ice cream.

Structure of Silicon Dioxide

Silicon dioxide is commonly called silica. Most sands contain particle of silica and some impurities like iron oxide. Silicon dioxide is very stable. The structure of silicon dioxide is very different from carbon dioxide. It has no discrete molecules. It has three dimensional polymeric structure. In the crystal structure of silicon dioxide, each silicon atom is bonded to four oxygen atoms and every oxygen atom is bonded to two silicon atoms.

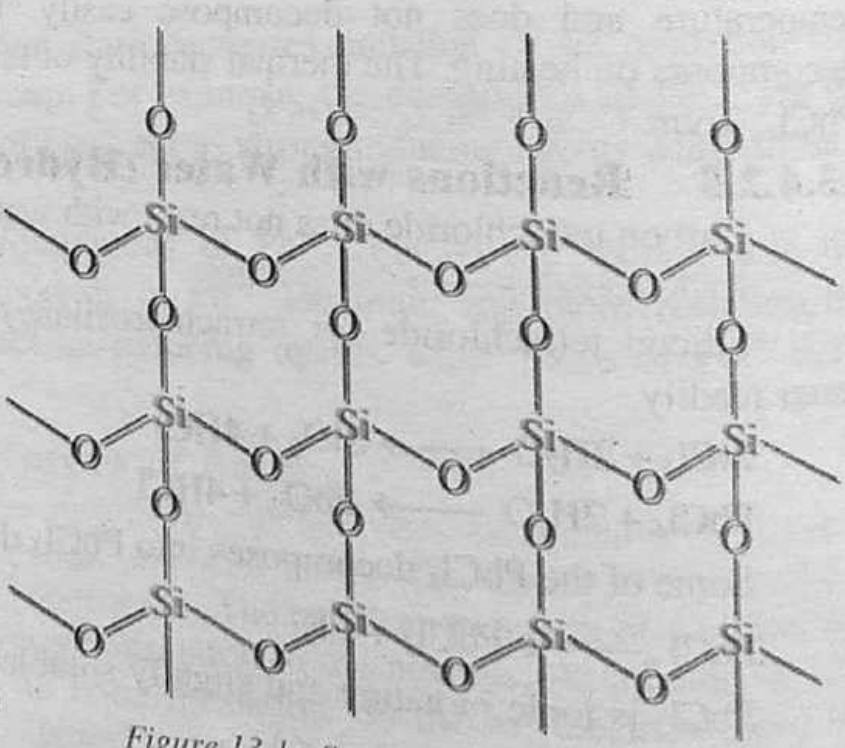


Figure 13.1: Structure of Silicon Dioxide

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There is a regular tetrahedral arrangement of four oxygen atoms around each silicon atom. This arrangement gives a giant structure of silicon and oxygen atoms.

All the bond angles around silicon atom are 109.5°, consequently it has tetrahedral geometry. Silicon atom in silicon dioxide has no free electrons. Thus it does not conduct electricity under normal conditions.

13.4.3.2 Acid-Base Behaviour of Group 14 (IVA) Oxides

The acidity of oxides of group 14 decreases down the group. The dioxides of carbon and silicon are acidic while the dioxides of germanium, tin and lead are amphoteric. The monoxide of carbon (CO) is neutral while those of tin and lead are amphoteric.

Oxides of Carbon and Silicon

Carbon monoxide is often regarded as neutral oxide, but it is very slightly acidic. It does not react with water to produce the expected formic acid, but it can react with hot concentrated sodium hydroxide solution to produce solution of sodium formate.

$$NaOH + CO \longrightarrow HCOONa$$

Carbon dioxide is acidic and reacts slightly (about 0.1%) with water to produce the carbonic acid.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

The carbonic acid then ionizes slightly to form hydrogen ion and bicarbonate ion.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

The bicarbonate ion can further ionize to give carbonate ion.

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$$

Carbon dioxide reacts with cold sodium hydroxide to produce solutions of either sodium carbonate or sodium bicarbonate, depending on the quantity of reactants.

$$NaOH + CO_2 \longrightarrow NaHCO_3$$

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Silicon dioxide does not react with water because it has giant covalent structure. It reacts with hot concentrated sodium hydroxide solution to produce sodium silicate.

$$2NaOH + SiO_2 \longrightarrow Na_2SiO_3 + H_2O$$

The Oxides of Germanium, Tin and Lead

The monoxides of germanium, tin and lead (GeO, SnO and PbO) are amphoteric as they react with both acids as well as bases.

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i) $GeO + 2HCl \longrightarrow GeCl_2 + H_2O$

$GeO + 2NaOH \longrightarrow Na_2GeO_2 + H_2O$

Sodium Germinate (II)

ii) $SnO + 2HCl \longrightarrow SnCl_2 + H_2O$

$SnO + 2NaOH \longrightarrow Na_2SnO_2 + H_2O$

Sodium Stannate (II)

iii) $PbO + 2HCl \longrightarrow PbCl_2 + H_2O$

$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$

Sodium Plumbate (II)

The dioxides of germanium, tin and lead such as GeO_2, SnO_2 and PbO_2 are amphoteric as they react with both acids and bases to form salts.

i) $GeO_2 + 4HCl \longrightarrow GeCl_4 + 2H_2O$

$GeO_2 + 2NaOH \longrightarrow Na_2GeO_3 + H_2O$

Sodium Germanate (IV)

ii) $SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$

$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$

Sodium Stannate (IV)

iii) $PbO_2 + 4HCl \longrightarrow PbCl_4 + 2H_2O$

$PbO_2 + 2NaOH \longrightarrow Na_2PbO_3 + H_2O$

Sodium Plumbate (IV)

Molten NaOH is required for the reaction of PbO_2 to produce sodium plumbate (IV).

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Canning process and the use of Metals

Canning is a method of preserving food from spoilage by storing it in airtight container where the food contents are processed. The concept of canning is to heat a food in a airtight container so that no microbial growth can occur in the food until the package is opened. When the package is opened, the effects of canning will be lost and the food is regarded as perishable. Canning was invented by Nicolas Appert of France in 1809, in response to the need to supply Napoleon's army and navy with good quality food. Appert used glass bottles for preserving foods such as pickles, jams etc. but Durand, an English, used metal and pottery at about the same time. The two ideas together gave us the tin cans. Today, canned foods are stored in steel, tin and aluminum, which keeps the food safe and sealed, and retains the food's nutritional value. Canning is a very effective method of food preservation. Canned food can be stored for a long time.

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13.5 Group 17 Elements

The group 17 (VIIA) elements consist of fluorine, chlorine, bromine, iodine and astatine, and are collectively called halogens. The word 'halogen' comes from the Greek 'halos' and 'genes' meaning 'salt formers'. This is because all of these elements react directly with metals produce salts. They are all poisonous and corrosive. They are the most reactive nonmetals. Fluorine is the most reactive nonmetal known. Because of high chemical reactivity, they cannot exist as free in nature. They are found in combined form as minerals deposits in sea water, salt lakes and in underground salt beds.

Table 13.29: Electronic Configuration of VIIA Group Elements

Name	Symbol	Atomic number	Electronic configuration	Valence shell electronic configuration
Fluorine	F	9	$1s^2 2s^2 2p^5$	$2s^2 2p^5$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$	$3s^2 3p^5$
Bromine	Br	35	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$	$4s^2 4p^5$
Iodine	I	53	$1s^2 2s^2 2p^6$ $3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$	$5s^2 5p^5$
Astatine	At	85	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ $5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^5$	$6s^2 6p^5$

They have seven electrons in their outermost shells. Two electrons in the *ns* orbital and five electrons in the *np* orbital. The fluorine is the only halogen which shows only –1 oxidation sate while other elements show –1 as well as +1, +3, +5, +6 and +7 oxidation states.

The halogens exist as diatomic molecules and they are all coloured. Their molecules are held together by weak van der Waal's forces.

Table 13.30: Physical States and Colours of Halogens

Elements	F_2	Cl_2	Br_2	I_2
Physical States	Gas	Gas	Liquid	Solid
Colours	Pale yellow	Greenish yellow	Reddish brown	Lustrous violet black

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13.5.1 Atomic and Physical Properties of the Group VIIA Elements

The trends in some atomic and physical properties of the group VIIA elements are discussed below:

13.5.1.1 Trends in Atomic Radius

The atomic radii of group VIIA elements go on increasing as we move down the group. This is due to increase in the number of shells.

Table 13.31: Atomic Radius of Halogens

Element	F	Cl	Br	I
Atomic Radii (pm)	72	99	114	133

13.5.1.2 Trends in Electronegativity

Halogens have very high values of electronegativity. These values decrease from fluorine to iodine as the atomic number increases. The fluorine is the most electronegative atom among all of the elements.

Table 13.32: Electronegativity Values of Halogens

Element	F	Cl	Br	I
Electronegativity	3.98	3.00	2.96	2.56

13.5.1.3 Trends in Electron Affinity

Electron affinity values decrease from chlorine to iodine. The electron affinity of fluorine is less than that of chlorine. This is due to smaller size of fluorine. When an extra electron is added to fluorine atom, the high electron density is produced round the fluoride ion. This high electron density increases the repulsion between the electrons already present in the relatively compact 2p orbitals of fluorine and the electron being added. Due to this electron-electron repulsion, the fluorine atom shows lesser tendency to attract an electron towards itself to form fluoride ion and hence the electron affinity of fluorine becomes less than that of chlorine. The order of electron affinity values of halogens is: $Cl < F > Br > I$.

Table 13.33: Electron Affinity of Halogens

Element	F	Cl	Br	I
Electron Affinity (kJ/mol)	–328	–349	–325	–295

13.5.1.4 Trends in Melting and Boiling Points

Halogens have low melting and boiling points. Their melting and boiling points gradually increase down the group. This is because the London dispersion forces become stronger as we move down the group.

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Table 13.34: Melting and Boiling Points of Halogens

Element	F_2	Cl_2	Br_2	I_2
Melting Points (°C)	-220	-101	-7.2	114
Boiling Points (°C)	-188	-35	59	184

13.5.1.5 Bond Enthalpies in Halogens

The amount of energy required to break all bonds in one mole of gaseous substance is called bond enthalpy or bond energy.

Table 13.35: Bond Enthalpies of Halogens

Element	F_2	Cl_2	Br_2	I_2
Bond Enthalpy (kJ/mol)	159	243	193	151

The bond enthalpies of the halogens decrease from chlorine to iodine due to increase in atomic size, but the bond enthalpy of fluorine does not fit the pattern. The expected value of bond enthalpy of F—F bond is about 290 kJ/mol. The actual value of bond enthalpy of fluorine is 159 kJ/mol. The decrease in bond enthalpy of fluorine is due to larger repulsion between the nonbonding electrons of small sized atoms of the molecule.

13.5.1.6 Bond Enthalpies in Hydrogen Halides

The binary compounds of halogens with hydrogen are called hydrogen halides. They are also known as hydrides of halogens or hydrohalic acids.

Table 13.36: Bond Enthalpies of Hydrogen Halides

Hydrogen Halide	HF	HCl	HBr	HI
Bond Enthalpy (kJ/mol)	565	432	366	299

The bond enthalpies of hydrogen halides decrease as we move down the group. This is due to increase in the size of halogen atoms. As the size of halogen atoms increases from fluorine to iodine, the hydrogen and halogen bond length in hydrogen halides (HX) also increase from H—F to H—I. The increase in H—X bond length decreases the bond strength. Because of this the bond enthalpies decrease from H—F to H—I.

13.5.2 Strength of Halogens as Oxidizing Agents

Halogens are strong oxidizing agents because they can easily accept one electron to complete their octet in chemical reactions. The strength of halogens as oxidizing agents decreases as we move down the group. This is due to increase in atomic size and decrease in electronegativity. The oxidizing power of halogens decreases in the following order:

$$F_2 > Cl_2 > Br_2 > I_2$$

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The oxidizing power of fluorine is maximum among the halogens because of its small size and high electronegativity.

The oxidizing properties of halogens can be explained as follows:

The fluorine has ability to oxidize the chloride, bromide and iodide ions to chlorine, bromine and iodine respectively.

$F_2 + 2Cl^- \longrightarrow 2F^- + Cl_2$

$F_2 + 2Br^- \longrightarrow 2F^- + Br_2$

$F_2 + 2I^- \longrightarrow 2F^- + I_2$

The chlorine has ability to oxidize the bromide and iodide ions to bromine and iodine respectively.

$Cl_2 + 2F^- \longrightarrow$ No action

$Cl_2 + 2Br^- \longrightarrow 2Cl^- + Br_2$

$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$

The bromine has ability to oxidize the iodide ions to iodine.

$Br_2 + 2F^- \longrightarrow$ No action

$Br_2 + 2Cl^- \longrightarrow$ No action

$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$

The iodine cannot oxidize any halide ion.

$I_2 + 2F^- \longrightarrow$ No action

$I_2 + 2Cl^- \longrightarrow$ No action

$I_2 + 2Br^- \longrightarrow$ No action

13.5.3 The Acidity of Hydrogen Halides

All the halogens combine with hydrogen to produce hydrogen halides (e.g. HF, HCl ,HBr, HI) and their aqueous solutions are commonly known as hydrohalicacids or simply halogen acids. The general formula of hydrogen halides is HX. All the hydrogen halides are irritant.

$H_2 + X_2 \longrightarrow 2HX$

All the hydrogen halide molecules in the gaseous state are essentially covalent and hence are not able to ionize to give hydrogen ion (proton) but in aqueous solution they ionize to give hydrogen ions. The hydrogen ions combine with water molecules to form hydronium ions, H_3O^+ and hence hydrogen halide molecules act as acids.

$HX + H_2O \longrightarrow H_3O^+ + X^-$

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The acidic strength (proton releasing power) of HX molecules increases from HF to HI. The acidic strength of hydrogen halides is in the following order: HF < HCl < HBr < HI. Thus HF is the weakest and HI is the strongest acid. HF ionizes only slightly and is therefore a weak acid whereas HCl, HBr and HI ionize almost completely and are therefore strong acids.

Table 13.37: Dissociation Energies of Hydrogen Halides

Hydrogen Halide	HF	HCl	HBr	HI
Dissociation Energy (kJ/mol)	565	432	366	299

The weakest acidic nature of HF is due to (i) the high dissociation energy of the H—F bond and (ii) the formation of weakest conjugate base (F^-) during the ionization of HF molecules. Its conjugate base has very little tendency to gain proton from water.

13.5.4 Halide Ions as Reducing Agents and Trends in Reducing Strength of Halide Ions

A substance that loses electrons during a chemical reaction is called reducing agent while a substance that gains electrons during a chemical reaction is called oxidizing agent.

The reducing agent reduces other substances (decrease the oxidation states of other substances) and is oxidized itself (its oxidation state is increased). The halide ions (or hydrogen halides) reduce the oxidizing agents and are oxidized to X_2 molecules. For example,

$$4HX + O_2 \longrightarrow 2H_2O + 2X_2$$

In the above reaction, the halide ion (or hydrogen halide) acts as a reducing agent because it loses electrons.

The trend in the reducing ability of halide ions (or hydrogen halides) is opposite to the trend in the oxidizing power of the halogens. The reducing properties of halide ions (or hydrogen halides) increase from fluoride ion (or HF) to iodide ion (or HI). This is due to increase in the ionic radii of halide ions down the group of periodic table. The reducing properties of halide ions or hydrogen halides are in the following order:

$F^- < Cl^- < Br^- < I^-$ or HF < HCl < HBr < HI

The fluoride ion or HF is the weakest reducing agent while the iodide ion or HI is the strongest reducing agent. In reality, the fluoride ion or HF has no considerable reducing properties at all. The fluoride ion or HF is so weak that it does not reduce

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even very strong oxidizing agents such as SO_2, and HI. It is also not able to reduce any of the halogens (Cl_2, Br_2 and I_2) to its corresponding halide ions (or halogen acids). For example:

$$2F^- + Cl_2 \longrightarrow \text{No action}$$

$$2F^- + Br_2 \longrightarrow \text{No action}$$

$$2F^- + I_2 \longrightarrow \text{No action}$$

The chloride ion (Cl^-) or HCl molecule reduces only strong oxidizing agents like F_2 and is itself oxidized to Cl_2. It can neither reduce Br_2 nor I_2.

$$2Cl^- + F_2 \longrightarrow 2F^- + Cl_2$$

$$2Cl^- + Br_2 \longrightarrow \text{No action}$$

$$2Cl^- + I_2 \longrightarrow \text{No action}$$

The bromide ion (Br^-) or HBr molecule reduces $F_2$and Cl_2 but not I_2.

$$2Br^- + F_2 \longrightarrow 2F^- + Br_2$$

$$2Br^- + Cl_2 \longrightarrow 2Cl^- + Br_2$$

$$2Br^- + I_2 \longrightarrow \text{No action}$$

The iodide ion (I^-) or HI molecule, being the strongest reducing agent, can reduce all of the other three halogens to their corresponding halide ions (or halogen acids).

$$2I^- + F_2 \longrightarrow 2F^- + I_2$$

$$2I^- + Cl_2 \longrightarrow 2Cl^- + I_2$$

$$2I^- + Br_2 \longrightarrow 2Br^- + I_2$$

We may say that a given halide ion (or halogen acid) can reduce only that halogen molecule which lies above it in the group 17 (VIIA) of the periodic table. The halide ion (or halogen acid) cannot reduce that halogen molecule which lies below it in the group.

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Properties and Commercial Uses of the Halogens

Properties and Uses of Fluorine

Fluorine is highly toxic colourless gas. It is the most electronegative and reactive element. It reacts directly with all elements except helium (He), neon (Ne) and argon (Ar). It is used in the manufacture of chlorofluorocarbons, commercially known as Freons.

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Freons are used as refrigerant in refrigerators, cooling agent in air conditioners, aerosol propellants and cleaning agents. Fluorine is also used in the manufacture of Teflon. Teflon is a valuable plastic and is used for coating the electrical wiring. It provides a non-stick surface for frying pans and other cooking related products.

Properties and Uses of Chlorine

Chlorine (Cl_2) is a highly toxic gas with a pale yellow-green colour. Chlorine is chemically less active than fluorine but more active than bromine and iodine. Some of the uses of chlorine depend on its toxic effects. For example, chlorine is used as a disinfectant in swimming pools and water treatment plants. Many organic compounds of chlorine are used in the manufac ure of antiseptics, insecticides, weed killers and herbicides. Chlorine is a very strong oxidizing agent and is used commercially as a bleaching agent. Large amounts of chlorine are used to make solvents such as carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), dichloroethylene ($C_2H_2Cl_2$), and trichloroethylene (C_2HCl_3).

Properties and Uses of Bromine

Bromine (Br_2) is a reddish-orange liquid with an unpleasant, choking odour. The vapours of bromine are irritating to the eyes and throat. The liquid is highly corrosive and can cause serious burns if spilled on the skin. Bromine is chemically less active than fluorine and chlorine but more active than iodine. Bromine is used to prepare flame retardants, fire-extinguishing agents, sedatives, germicides, pesticides, fungicides and insecticides. Bromine can also be used as a disinfectant like chlorine.

Properties and Uses of Iodine

Iodine is an intensely coloured solid with an almost metallic lustre. Iodine vapours are irritating to the eyes and respiratory system. Iodine is chemically less active than other halogens (not counting astatine). Iodine acts as an antioxidant in our blood. It is also used as a cough expectorant, and is also helpful in treating allergies, dermatitis, bladder infections, and moles. The human body uses iodine to make thyroxine, an important hormone (chemical messenger) produced by the thyroid gland. The thyroid is a gland located in the neck that plays an important role in metabolism. The deficiency of iodine in the human body can lead to 'goiter', a swelling around the neck. Iodine can be used as a water purifying agent. It is also used as a sterilizing agent. Iodine can also be used for the preparation of antiseptics such as iodex and tincture.

Properties and Uses of Bleaching Powder

Bleaching powder is also known as calcium hypochlorite or sometimes calcium oxychloride and its chemical formula is $CaOCl_2$. It is a pale yellow powder and has a strong smell of chlorine. It loses chlorine when it reacts with carbon dioxide as:

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$$

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It is mainly used to bleach cotton, wool, linen in textile industries, and wood pulp. It is used as an oxidizing agent in many industries to obtain various chemical products. It is used in the sterilization of water and makes water free from germs. It is used in the manufacture of chloroform, which is used as anaesthetics in hospitals by doctors before surgery. It is used as a disinfectant and germicide in sewers and drains. It is used as bathroom cleanser. It makes wool unshrinkable.

Fluoride Toxicity and Deficiency

Fluoride is a trace mineral, which means it is only needed in a small amount. This trace mineral is currently considered essential by some scientists. The main function of fluoride is to harden the bones and teeth. An adult male needs 1.5 to 4.0 mg daily. An adult woman requires less and children require even less depending on how much they weigh. It is found in grape products, dried fruits, dried beans, cocoa powder and walnuts. The good dietary sources of fluoride are fluorinated water, sea food, seaweed and tea.

Fluoride Deficiency

The term fluoride deficiency means a condition where the concentration of fluoride essential to human health is less than required limit. The reduced intake could lead to a fluoride deficiency and result in the development of dental caries (tooth decay). Deficiency of fluoride can cause dental caries, brittle and weak bones, and fractured hips in the elderly. The dental carries in children is more, where the fluoride in drinking water is less than 0.5 mg/L. Normally water containing 0.5 to 1 mg/L is considered to be sufficient in most parts of the world.

Fluoride Toxicity (Overdose)

The term fluoride toxicity means a condition where the concentration of fluoride essential to human health is high than required limit. Excess fluorine can accumulate in teeth and bones, causing fluorosis. Fluorosis is a cosmetic condition, not a disease. Often, it is so mild that only a dental professional can detect it. Teeth affected by mild fluorosis may show no changes or changes visible only to a dental professional. Mild to moderate fluorosis produces white lines, streaks or spots. In more severe fluorosis, the teeth can become pitted and have brown, grey or black spots. The enamel also may have an unusual shape.

The massive doses of fluoride (20 to 80 ppm daily) can give rise to:

- Skeletal fluorosis, which is a hardening of the bones along with arthritic pain, stiffness, nerve damage and finally paralysis.
- Gastrointestinal irritation and haemorrhage

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Summary of Facts and Concepts

- There are four blocks of elements in the periodic table, namely s-, p-, d- and f-block.
- The s-block elements are those elements in which last electron enters into s-orbitals.
- The elements of group 1A are called alkali metals except hydrogen. They are soft, silvery-white metals and good conductors of heat and electricity.
- The elements of group IIA are called alkaline earth metals. They are harder and denser and have high melting and boiling points than the alkali metals.
- Alkali metals form 1+ ions by losing their one outer s-electron, while the alkaline earth metal form 2+ ions by losing their two outer s-electrons.
- The elements of second period from multiple (double or/and triple) bonds but are generally unable to form more than four bonds.
- The ionization energy and electronegativity generally increase, while atomic radius and metallic character generally decrease from left to right in a period of periodic table.
- The ionization energy and electronegativity generally decrease, while atomic radius and metallic character generally increase from top to bottom in a group of periodic table.
- The electronic configuration of group IVA show that they contain four electrons in their outer most shells, two electrons of which are in s-orbital and the remaining two are in p-orbitals.
- The elements of group IVA (C, Si, Ge, Sn and Pb) show the usual increase in metallic character down the group. They frequently adopt an oxidation state of +4, but the +2 state becomes increasingly more stable from Ge to Sn to Pb.
- Halogens (F, Cl, Br and I) are very reactive non-metals. Oxidizing power of halogens decreases from F_2 to I_2.
- The acidic strength of hydrogen halides increases from HF to HI.
- The reducing properties of hydrogen halides increase from HF to HI.

Multiple Choice Questions

Select one answer from the given choices for each question:

i) Which of the following give strong alkaline solution in water?

(a) Sodium (b) Potassium

(c) Beryllium (d) Magnesium

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ii) The total number of electrons in the valence shell of p-block elements varies from:

(a) 1 to 6 (b) 2 to 7
(c) 3 to 8 (d) 1 to 8

iii) The atomic radii in s-block elements:

(a) Decrease down the group
(b) Increase down the group
(c) Remains same in the group
(d) First decreases and then increases

iv) The general electronic configuration of p-block elements is as:

(a) ns^1, ns^2 (b) ns^1, np^6
(c) ns^2, np^6 (d) ns^2, np^{1-6}

v) Alkali and alkaline earth metals give flame tests when burnt in air. It is due to:

(a) Excitation of electrons
(b) De-excitation of electrons
(c) Smaller ionic radius of these metals
(d) Smaller charge density of these metals

vi) Basic oxides react with acidic oxides to form

(a) Hydrides (b) Halides
(c) Hydrogen halides (d) Salts

vii) The characteristic flame colour of cesium is:

(a) Green (b) Blue
(c) Yellow (d) Violet

viii) Which one of the following oxides is acidic?

(a) CO_2 (b) GeO_2
(c) SnO_2 (d) PbO_2

ix) Which one of the following elements only form dioxide?

(a) Carbon (b) Silicon
(c) Germanium (d) Tin

x) The lowest melting points in carbon family (group IVA) is of:

(a) Silicon (b) Germanium
(c) Tin (d) Lead

xi) Which one of the following reacts with water in elemental form at room temperature?

(a) Argon (b) Sulphur
(c) Chlorine (d) Silicon

xii) Which one of the following is liquid at room temperature?

(a) Fluorine (b) Chlorine
(c) Bromine (d) Iodine

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xiii) Which one of the following is the strongest oxidizing agent?
(a) Fluorine (b) Chlorine
(c) Bromine (d) Iodine

xiv) The bond enthalpy of fluorine is:
(a) Less than chlorine (b) More than chlorine
(c) More than bromine (d) Less than iodine

xv) Which one of the following has giant structure?
(a) SO_2 (b) SiO_2
(c) Cl_2O_7 (d) P_4O_{10}

xvi) Which halogen of the following can oxidize all other halide ions?
(a) Iodine (b) Fluorine
(c) Bromine (d) Chlorine

xvii) The HCl is unable to reduce:
(a) Cl_2 (b) F_2
(c) I_2 (d) HF

xviii) Which halogen acid cannot be stored in glass containers?
(a) HF (b) HCl
(c) HBr (d) HI

Short Answer Questions

Q.1. Why are the alkali metals so reactive?
Q.2. Why are alkali metals stored in oil?
Q.3. Why the reaction of caesium with water is very fast, violent and exothermic?
Q.4. What are the general trends in melting and boiling points going down the alkali metals?
Q.5. What is the effect of atomic radius on the chemical reactivity of the alkali metals?
Q.6. Which are the most and the least reactive alkali metals?
Q.7. What are the products of a reaction between:
(i) An alkali metal and water? (ii) An alkaline earth metal and water?
Q.8. How many electrons do alkaline earth metals have to lose to attain the electronic configuration of noble gases?
Q.9. Why are metals like sodium, potassium and aluminium not available in free state in nature?
Q.10. Why is the ionization energy of radium higher than barium?
Q.11. Why is $BeCl_2$ covalent and not ionic?

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Q.12. $Be(OH)_2$ is amphoteric, how?
Q.13. Can you explain why alkaline earth metals are less reactive than alkali metals?
Q.14. Write an equation to show the thermal decomposition of calcium carbonate.
Q.15. Write an equation to show the reaction of beryllium hydroxide with an acid and base.
Q.16. Why is molten sodium chloride a good conductor of electricity?
Q.17. Why hydrogen and helium belong to s-block elements.
Q.18. Stannous chloride is more stable than stannic chloride, why?
Q.19. SiO_2 is a solid and CO_2 is a gas, why?
Q.20. Why Fluorine is the most reactive element in Group 17?
Q.21. Explain why the electron affinity of fluorine is less than that of chlorine?
Q.22. Why the bond energy of fluorine is less than that of chlorine?
Q.23. Why is HF a weak acid than other hydrohalic acids?
Q.24. Explain why the HCl molecule can reduce only F_2 to HF but neither Br_2 to HBr nor I_2 to HI?
Q.25. Why the reactivity of halogens decreases down the group?
Q.26. Why are iodide ions stronger reducing agents than chloride ions?
Q.27. What makes one atom more electronegative than another?

Long Answer Questions

Q.1. Write a short note on s-block, p-block, d-block and f-block elements?
Q.2. Discuss the atomic and physical properties of period 3 elements.
Q.3. Explain the reactions of period 3 elements with:
(i) water (ii) oxygen (iii) chlorine.
Q.4. Describe physical properties of oxides of period 3 elements.
Q.5. What do you know about acid-base behaviour of the oxides of period 3 elements?
Q.6. Describe reactions of the oxides of period 3 elements with:
(i) water (ii) acids (iii) bases.
Q.7. Write note on structure, electrical conductivity, solubility, melting and boiling points of chlorides of period 3 elements.
Q.8. Write down properties of hydroxides of period 3 elements.
Q.9. What are alkali and alkaline earth metals and draw their electronic configurations?

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Q.10. Describe the atomic and physical properties of alkali metals.
Q.11. Explain the trends in reactivity with water of alkali metals.
Q.12. Explain the reactions of alkali metals with oxygen and halogens.
Q.13. Describe the effect of heat on nitrates, carbonates and hydrogen carbonates of alkali metals.
Q.14. How are the colours produced in the flame tests? Explain.
Q.15. Explain atomic and physical properties of alkaline earth metals.
Q.16. Discuss the trends in reactivity of alkaline earth metals with water.
Q.17. Describe the reactions of alkaline earth metals with oxygen and nitrogen.
Q.18. Discuss the trends in solubility of hydroxides, sulphates, and carbonates of alkaline earth metals.
Q.19. Explain the trends in thermal stability of the nitrates and carbonates of alkaline earth metals.
Q.20. How beryllium differs from other members of its group?
Q.21. Write short note on group 14 (IVA) elements. What are the atomic and physical properties of group IVA elements?
Q.22. Define the term inert pair effect. Explain inert pair effect in the formation of ionic and covalent bonds.
Q.23. Write down preparation and thermal stability of chlorides of carbon, silicon and lead.
Q.24. Describe the reactions of group IVA elements with water.
Q.25. Discuss the important oxides of group IVA elements.
Q.26. Describe the acid-base behaviour of group IVA oxides.
Q.27. What are halogens and draw their electronic configuration?
Q.28. Explain the atomic and physical properties of halogens.
Q.29. Briefly discuss strength of halogens as oxidizing agents.
Q.30. Write note on acidity of hydrogen halides.
Q.31. Halide ions act as reducing agents. Explain.
Q.32. Give the trends in reducing strength of halide ions.
Q.33. Write a balance chemical equation for the reaction of:

i) Calcium with water
ii) Sodium monoxide with water
iii) Aluminium with water
iv) Sulphur trioxide with water
v) Chlorine(VII) oxide (Dichlorine heptaoxide) with water.

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Chapter 14

d- and f-Block Elements: Transition Elements

Major Concepts

14.1 Transition Elements
14.2 Coordination Compounds
14.3 The Chemistry of Some Specific Transition Metals

Learning Outcomes:

Students will be able to:

- Describe electronic structures of elements and ions of d-block elements. **(Applying)**
- Explain why the electronic configuration for chromium and copper differ from those assigned using the Aufbau principle. **(Analyzing)**
- Describe important reactions and uses of Vanadium, Chromium, Manganese, Iron and Copper. **(Understanding)**
- Explain shapes, origin of colors and nomenclature of coordination compounds. **(Applying)**
- Relate the coordination number of ions to the crystal structure of the compound of which they are a part. **(Applying)**
- Define an alloy and describe some properties of an alloy that are different from the metals that compose it. **(Analyzing)**
- Describe the reactions of potassium dichromate with oxalic acid and Mohr's salt. **(Understanding)**
- Describe the reactions of potassium manganate VII with ferrous sulphate, oxalic acid and Mohr's salt. **(Understanding)**

Introduction

The elements that have partially filled *d*- or *f*-orbitals either in atomic states or in other common oxidation states are called transition elements.

The elements from group 3 to 12 are frequently called transition elements because they are located in between *s*-block and *p*-block elements in the periodic table. Their properties are intermediate between those of *s*-block and *p*-block elements.

Series of Transition Elements

Series of *d*-Block Elements

The *d*-block elements make up four complete series (rows) of ten elements in

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the periodic table.

i) **3d Series:** The first series (3d series) comprises the elements from scandium (atomic number 21) to zinc (atomic number 30). These elements are present in 4th period.

ii) **4d Series:** The second series (4d series) comprises the elements from yttrium (atomic number 39) to cadmium (atomic number 48). These elements are present in 5th period.

iii) **5d Series:** The third series (5d series) comprises the element lanthanum (atomic number 57) and the elements from hafnium (atomic number 72) to mercury (atomic number 80). These elements are present in 6th period.

iv) **6d Series:** The fourth series (6d series) comprises the element actinium (atomic number 89) and the elements from rutherfordium (atomic number 104) to copernicium (atomic number 112). These elements are present in 7th period.

The outermost two shells (the valence shell and the penultimate shell) of *d*-block elements are incomplete.

The elements of group 12 (Zn, Cd, Hg) have no partially filled *d*-orbitals and cannot show the typical properties of transition elements. So these elements are not considered as transition elements. Nowadays, transition elements are only those with incompletely filled *d*-orbitals.

Series of *f*-Block Elements

The *f*-block elements make up two complete series (rows) of fourteen elements in the periodic table.

i) **4f Series:** The first series (4f series) comprises the elements from cerium (atomic number 58) to lutetium (atomic number 71). These elements are present in 6th period.

ii) **5f Series:** The second series (5f series) comprises the elements from thorium (atomic number 90) to lawrencium (atomic number 103). These elements are present in 7th period.

14.1 General Features

14.1.1 General Features of Transition Elements

i) They are all metals.

ii) They are hard, strong, ductile and malleable.

iii) They have high melting and boiling points.

iv) They are good conductors of heat and electricity.

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v) They form alloys with one another and also with other metals.

vi) They show variable oxidation states with few exceptions.

vii) Most of their compound are coloured in the solid state or in solution form. For example: $CuSO_4$ (blue) , $NiSO_4$ (green) , $CoCl_3$ (pink), etc.

viii) They usually form paramagnetic compounds due to the presence of unpaired electrons.

ix) Most of transition elements and their compounds act as catalysts.

x) Most of them have ability to form stable complexes with many different ligands. This is due to involvement of partially filled *d*- and *f*-orbitals.

Keep in Mind

Malleable means that the metals can be bent, rolled and pressed into different shapes without breaking. On the other hand, ductile means that they can be drawn out into thin wires. For example, copper is malleable and ductile, and is used in wiring.

14.1.2 Electronic Structure

The general electronic configuration of *d*-block elements is $(n-1)d^{1-10}\ ns^{1-2}$. The specific d-subshell is one less **(n–1)** than the period number.

But it is noted in the elements such as Cr and Mo one electron from ns orbitals get shifted to **(n–1)*d*** orbital and such elements, therefore, have one electron in ns orbital instead of two. This type of shifting makes the **(n–1)*d*** orbitals half-filled. Similarly in the elements such as Cu, Ag and Au one electron from ns orbitals get shifted to **(n–1)*d*** orbital and hence such elements have one electron in ns orbital instead of two. In case of Pd both of the electrons from ns orbital get shifted to **(n–1)*d*** orbital and hence it has no electron in ns orbital instead of two. This type of shifting makes the **(n–1)*d*** orbitals completely filled. The reason for shifting of electrons from ns orbital to **(n–1)*d*** orbitals is that the half-filled and completely filled orbitals are more stable than partially filled orbitals.

It is also noted that the elements of group 3 i.e. scandium, yttrium, lanthanum and actinium have one electron in their *d*-orbitals. When they form ions, they lose the three outer electrons (the two 4s electrons and one 3d electron) to give tripositive ions. These ions have no *d* electrons and so the elements of group 3 are not considered as transition metals.

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Table 14.1: Electronic Configurations of the Atoms of 3d and 4d Series of d-block Elements

3d Series Elements			4d Series Elements		
Element	**Atomic Number**	**Electronic Configuration**	**Element**	**Atomic Number**	**Electronic Configuration**
Sc	21	$[Ar]3d^1 4s^2$	Y	39	$[Kr]4d^1 5s^2$
Ti	22	$[Ar]3d^2 4s^2$	Zr	40	$[Kr]4d^2 5s^2$
V	23	$[Ar]3d^3 4s^2$	Nb	41	$[Kr]4d^4 5s^1$
Cr	24	$[Ar]3d^5 4s^1$	Mo	42	$[Kr]4d^5 5s^1$
Mn	25	$[Ar]3d^5 4s^2$	Te	43	$[Kr]4d^6 5s^2$
Fe	26	$[Ar]3d^6 4s^2$	Ru	44	$[Kr]4d^7 5s^2$
Co	27	$[Ar]3d^7 4s^2$	Rh	45	$[Kr]4d^8 5s^2$
Ni	28	$[Ar]3d^8 4s^2$	Pd	46	$[Kr]4d^{10} 5s^0$
Cu	29	$[Ar]3d^{10} 4s^1$	Ag	47	$[Kr]4d^{10} 5s^1$
Zn	30	$[Ar]3d^{10} 4s^2$	Cd	48	$[Kr]4d^{10} 5s^2$

14.1.3 Binding Energy

Binding energy is the amount of energy that would be required to disassemble the atom into free electrons and a nucleus. It is also known as electron binding energy. This is more commonly known as ionization energy.

The binding energy of most of the *d*-block elements lie in between those of *s*-block and *p*-block elements. It shows that they are more electropositive than *p*-block elements and less electropositive than *s*-block elements.

Trends in Binding Energy

The trend in binding energy can be best explained on the basis of number of unpaired electrons that are involved in bonding. The greater the number of unpaired electrons involved in metallic bonding, the higher will be the binding energy. When we move from left to right in a given series of *d*-block elements, the binding energy increases up to group 5 (VB) or 6 (VIB) due to increase in the number of unpaired electrons and then decreases across the period due to decrease or unavailability of the number of unpaired electrons.

14.1.4 Variable Oxidation States

Most of the transition elements show more than one oxidation state (i.e. variable oxidation state). This is due to the involvement of *d* electrons in addition to *s*

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electrons in bond formation. In transition elements, the energy difference between (n−1)*d* and ns orbitals is very small and they have almost the same energies. Hence the electrons may easily shift from (n−1)*d* to *ns* and vice versa. The oxidation sates of many transition elements range from +2 to +7. But their most frequent oxidation state is +2 and +3.

The stability of +2 oxidation state increases and that of +3 oxidation state decreases as we move from Scandium ($_{21}$Sc) to zinc ($_{30}$Zn) in the series. Hence the +3 oxidation state is more common at the start of the series and +2 oxidation state is more common at the end of the series.

Table 14.2: The Variable Oxidation States of the Atoms of 3d Series of d-block Elements

Element	Atomic Number	Electronic Configuration	Stable Oxidation State	Common Oxidation State
Sc	21	$[Ar]3d^1 4s^2$	+2, +3	+2
Ti	22	$[Ar]3d^2 4s^2$	+2, +3, +4	+2
V	23	$[Ar]3d^3 4s^2$	+2, +3, +4, +5	+2
Cr	24	$[Ar]3d^5 4s^1$	+2, +3, +5	+2
Mn	25	$[Ar]3d^5 4s^2$	+2, +3, +4, +6, +7	+2
Fe	26	$[Ar]3d^6 4s^2$	+2, +3	+3
Co	27	$[Ar]3d^7 4s^2$	+2, +3	+3
Ni	28	$[Ar]3d^8 4s^2$	+2, +3, +4	+3
Cu	29	$[Ar]3d^{10} 4s^1$	+1, +2	+3
Zn	30	$[Ar]3d^{10} 4s^2$	+2	+3

The relative stability of different oxidation states of a particular element can be explained on the basis of the stability of d^0, d^5, and d^{10} orbitals. For example: (i) Sc^{3+} ($3d^0\ 4s^0$) is more stable than Sc^{2+} ($3d^1\ 4s^0$) because of the presence of $3d^0$ orbital in Sc^{3+} ion. (ii) Fe^{3+} ($3d^5\ 4s^0$) is more stable than Fe^{2+} ($3d^6\ 4s^0$) due to the presence of $3d^5$ orbital in Fe^{3+} ion. (iii) Ag^+ ion ($3d^{10}\ 5s^0$) is more stable than Ag^{2+} ($3d^9\ 5s^0$) ion. Because Ag^+ ion has $3d^{10}$ orbital.

14.1.5 Catalytic Activity

Most of the transition elements (e.g. Fe, Ni, Pt etc.) and their compounds (e.g. V_2O_5, MnO_2, $CuCl_2$ etc.) are used as a catalysts in many chemical reactions. Some well-known examples of catalysts are listed in the table:

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Table 14.3: Catalysts and their Uses

Catalyst	Uses
Fe	Finely divided iron is used in the Haber-Bosch process for making ammonia.
Ni	Raney nickel is used in the hydrogenation of vegetable oil to form ghee.
Cu	Copper is used in the oxidation of alcohols to produce aldehydes.
Pt	Platinum is formerly used in the Contact process for making H_2SO_4 for converting SO_2 to SO_3.
V_2O_5	V_2O_5 is used in the oxidation of SO_2 to SO_3 needed for the production of H_2SO_4 in the Contact process.
$TiCl_4$	$TiCl_4$ is used for the manufacture of polythene.
MnO_2	MnO_2 is used for decomposition of $KClO_3$ to produce O_2 gas.
$CuCl_2$	$CuCl_2$ is used for the manufacture of Cl_2 from HCl.

The catalytic behavior of transition elements is due to variable oxidation states. They may form unstable intermediates that help in the formation of desired products. The catalytic behavior is also due to absorbance of gases on metal surfaces.

14.1.6 Magnetic Behaviour

The substances show two different types of behaviours when they are placed in a magnetic field. These substances, on the basis of this behavior, have been classified into two main types: (i) paramagnetic substances (ii) diamagnetic substances. The substances that are attracted by the magnetic field are called paramagnetic substances, while the substances that are repelled by magnetic field are called diamagnetic.

Most of the transition elements and their compounds are paramagnetic. The paramagnetic behaviour of substances is due to the presence of unpaired electrons and the diamagnetic behaviour of substances is due to the absence of unpaired electrons in *d*-orbitals. The paramagnetic behaviour of substances increases with the increase in number of unpaired electrons. The paramagnetism is expressed in terms of magnetic moment (μ). Greater the number of unpaired electrons, greater is the magnetic moment and greater will be the paramagnetic behaviour. The magnetic moment can be measured by magnetic balance (Guoy's balance). The magnetic moment is related to number of unpaired electrons (n) by the equation:

$$\mu = \sqrt{n(n+2)}$$

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The unit of magnetic moment is Bohr's magneton (BM). The value of magnetic moment (μ) for different number of unpaired electrons can be calculated as:

When, n = 0, then $\mu = \sqrt{0(0+2)} = 0.0$ BM

When, n = 1, then $\mu = \sqrt{1(1+2)} = 1.73$ BM

When, n = 2, then $\mu = \sqrt{2(2+2)} = 2.83$ BM

When, n = 3, then $\mu = \sqrt{3(3+2)} = 3.87$ BM

When, n = 4, then $\mu = \sqrt{4(4+2)} = 4.90$ BM

When, n = 5, then $\mu = \sqrt{5(5+2)} = 5.92$ BM

Table 14.4: Number of Unpaired Electrons of the Ions of 3d Series of d-Block Elements

Metal Ion	Atomic Number	No. of Electrons in *d*-orbitals					The No. of Unpaired Electrons	Magnetic Moment (in BM)
		d_{xy}	d_{xz}	d_{yz}	$d_{x^2y^2}$	d_{z^2}		
Sc^{3+}	21						0	0
Ti^{3+}	22	↑					1	1.73
V^{3+}	23	↑	↑				2	2.83
Cr^{3+}	24	↑	↑	↑			3	3.87
Mn^{3+}	25	↑	↑	↑	↑		4	4.90
Mn^{2+}, Fe^{3+}		↑	↑	↑	↑	↑	5	5.92
Fe^{2+}	26	↑↓	↑	↑	↑	↑	4	4.90
Co^{2+}	27	↑↓	↑↓	↑	↑	↑	3	3.87
Ni^{2+}	28	↑↓	↑↓	↑↓	↑	↑	2	2.83
Cu^{2+}	29	↑↓	↑↓	↑↓	↑↓	↑	1	1.73
Zn^{2+}	30	↑↓	↑↓	↑↓	↑↓	↑↓	0	0

In 3d series (first series) of *d*-block elements, the Mn^{2+} and Fe^{3+} both have maximum number of unpaired electrons, hence they are highly paramagnetic.

14.1.7 Alloy Formation

The mixture of two or more metals is called alloy. Due to similar sizes of transition metals, the atoms of one metal can be replaced by the atoms of other metal. This replacement gives rise to the formation of alloys. Some well-known examples of alloys are brass, bronze and stainless steel.

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Table 14.5: Composition of Different Alloys and Their Uses

Alloy	Percent Composition by Mass	Uses
Stainless steel	Iron (Fe) = 74% Chromium (Cr) = 18% Nickel (Ni) = 8%	Surgical instruments, Utensil, knives
Sterling silver	Silver (Ag) = 92.5% Copper (Cu) = 7.5%	Jewellery (ornaments, such as necklaces, rings, or bracelets), table ware
Pewter	Tin (Sn) = 85% Copper (Cu) = 7% Bismuth (Bi) = 6% Antimony (Sb) = 2%	Ornaments
Dental amalgam	Mercury (Hg) = 50% Silver (Ag) = 35% Tin (Sn) = 15%	Dental fillings
Bronze	Copper (Cu) = 80% Zinc (Zn) = 10% Tin (Sn) = 10%	Statues, castings
Brass	Copper (Cu) = 60-85% Zinc (Zn) = 15-40%	Ornaments, plating

Alloys are usually hard, strong, have high melting points and are more resistant to corrosion than their parent metals.

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Comparison of the properties of brass, bronze and their constituent elements

Brass is a metal alloy consisting primarily of copper, usually with zinc as the main additive, but sometimes with other elements such as tin, iron, aluminium, manganese, or silicon. Brass has higher malleability than zinc or copper. It has a low melting point (900°C) and flows when melted making it easy to cast in moulds. Brass resists corrosion.

Bronze is a metal alloy consisting primarily of copper, usually with tin as the main additive, but sometimes with other elements such as phosphorus, manganese, aluminium, or silicon. It is corrosion resistant, hard, and brittle. It is much harder than copper and has dull-gold colour. It is a better conductor of heat and electricity than most steels.

Brass is less strong as compared to bronze and is usually corrodes faster than bronze.

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14.2 Coordination Compounds

Coordination compounds are generally formed by *d*-block elements and are also called complex compounds. These compounds are formed by the linking of number of ions or neutral molecules to the central metal atom or ion by coordinate covalent bonds. Examples are:$[Ni(CO)_4]$,$[CoCl_3(NH_3)_3]$ etc. The complex compounds retain their properties in the solid state as well as when dissolved in any polar solvent.

There are three main types of coordination compounds:

i) Cationic complexes
ii) Anionic complexes
iii) Neutral complexes

Cationic complexes carry positive charge, anionic complexes carry negative charge and neutral complexes carry no charge. Example are:

$[Cu(NH_3)_4]^{2+}$ is a cationic complex, $[Fe(CN)_6]^{4-}$ is an anionic complex and $[Ni(CO)_4]$ is a neutral complex.

Cationic and anionic complexes are complex ions. The complex ion can be defined as: an electrically charged specie in which central metal atom or ion is surrounded by a suitable number of atoms, molecules or ions.

14.2.1 Components of Coordination Compounds

Components of coordination compounds are as follows:

Central Metal Atom or Ion

A metal atom or ion that is surrounded by a suitable number of atoms, molecules or ions is called central metal atom or ion. Examples are:

(i) In $[Ni(CO)_4]$, Ni is the central metal atom.
(ii) In $[Ag(NH_3)_2]^+$, Ag^+ is the central metal ion.

Ligand

The ions or molecules that are attached with the central metal atom or ion by donating the electron pairs are called ligands (from Latin, "to tie or bind). They are present inside the coordination sphere. Examples are:

i) In $[Ni(CO)_4]$, the CO molecules are ligands.
ii) In $[NiCl_4]^{2-}$, the Cl^- ions are ligands.

The ligands are electron pair donors and act as Lewis bases and central metal atom or ion is electron pair acceptor and acts as a Lewis acid. Ligands are mainly divided into two types on the basis of donor sites (electron pair donor atoms): (i)mono-dentate ligands (ii) poly-dentate ligands.

Mono-dentate Ligands

The ligands which donate one electron pair to central atom or ion are called mono-dentate or uni-dentate ligand. Examples are:

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i) Neutral ligands: NH_3, H_2O, CO

ii) Anionic ligands: Cl^-, Br^-, I^-, CN^-, OH^-, CH_3COO^-

Poly-dentate Ligands

The ligands which donate more than one electron pairs to central atom or ion are called poly-dentate ligands or multi-dentate ligands. Examples are:

i) Neutral ligands: $H_2N—NH_2$, $H_2N—CH_2—CH_2—NH_2$

ii) Anionic ligands: CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{3-}

Poly-dentate ligands are further divided into bi-dentate ligands, tri-dentate ligands, tetra-dentate ligands, penta-dentate ligands and hexa-dentate ligands.

Bi-dentate ligands donate two electron pairs to central atom or ion. Examples are:

i) CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$

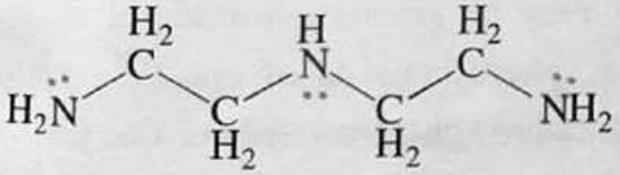
ii) $H_2\ddot{N}—\ddot{N}H_2$, $H_2\ddot{N}—CH_2—CH_2—\ddot{N}H_2$

Hydrazine Ethylene diamine (en)

Tri-dentate ligands donate three electron pairs to central atom or ion. Examples are:

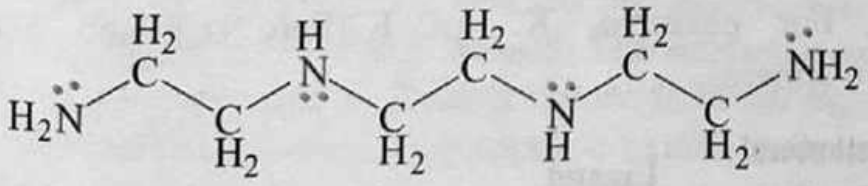
i) PO_4^{3-}

ii)



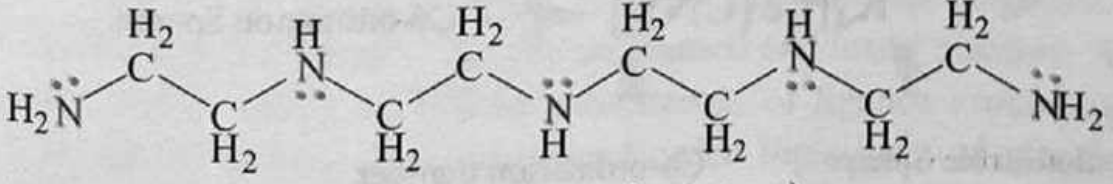
Diethylene triamine (dien)

Tetra-dentate ligands donate four electron pairs to central atom or ion. Example is:



Triethylene tetraamine (trien)

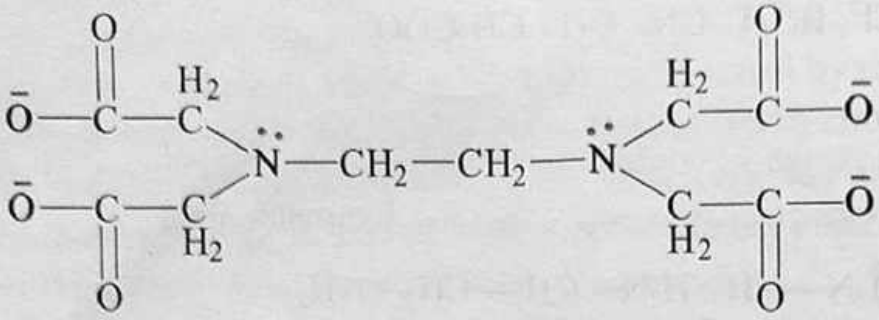
Penta-dentate ligands donate five electron pairs to central atom or ion. Example is:



Tetraethylene Pentamine (tetraen)

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Hexa-dentate ligands donate six electron pairs to central atom or ion. Example is:



Ethylene diaminetetraacetate ion ($EDTA^{4-}$)

Coordination Number

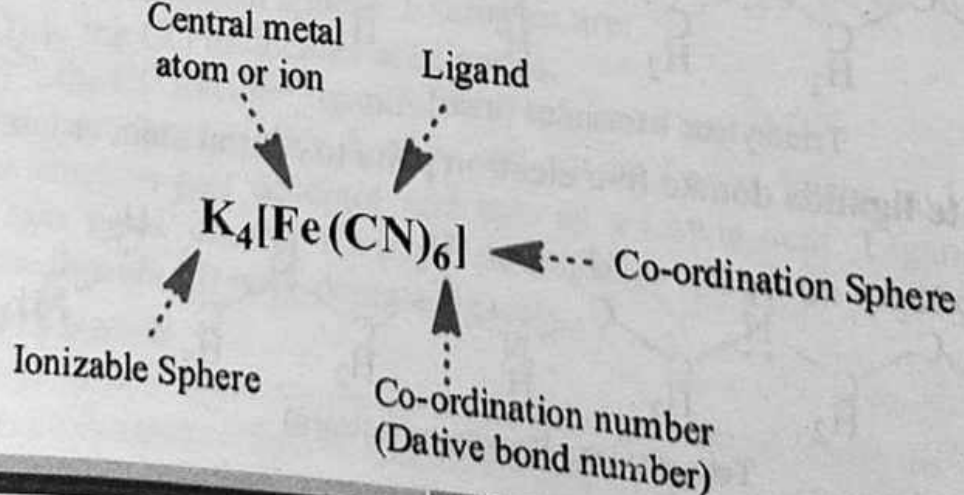
The number of lone pair of electrons provided by the ligands to the central metal atom or ion is called coordination number (CN). For example, the coordination number of Ag^+ ion in $[Ag(NH_3)_2]Cl$ is two and that of Cu^{2+} ion in $[Cu(NH_3)_4]SO_4$ is 4. A metal atom may show more than one coordination number in different complex compounds. For example, the coordination number of Fe^{3+} ion in $[FeCl_4]^-$ is 4 and in $[Fe(CN)_6]^{3-}$ is 6.

Coordination Sphere

The central metal atom or ion along with ligands is called coordination sphere. It is usually placed in square brackets. It may be anionic, cationic or neutral. For example, in $K_4[Fe(CN)_6]$, the coordination sphere consists of one Fe^{2+} ion and six CN^- ions and in $[Cu(NH_3)_4]SO_4$, the coordination sphere consists of one Cu^{2+} ion and four NH_3 molecules.

Ionization Sphere

Ionization sphere is the part of coordination compound that is present outside the co-ordination sphere. For example, K^+ in $K_4[Fe(CN)_6]$ and SO_4^{2-} in $[Cu(NH_3)_4]SO_4$ are ionization spheres.



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Charge on the Coordination Sphere

The sum of charges present on the central metal atom or ion and the total charge on the ligands is termed as charge on the coordination sphere.

Example 1:

The charge on $[Fe(CN)_6]^{4-}$ can be calculated as:

Charge on coordination sphere = [charge on Fe(II)] + 6(charge on CN^{1-})
= (2+) + 6(1−)
= 4−

Example 2:

The charge on $[Co(NH_3)_6]^{3+}$ can be calculated as:

Charge on coordination sphere = [charge on Co(III)] + 6(charge on NH_3)
= (3+) + 6(0)
= 3+

When complex is neutral, the charge on the complex simply equals to oxidation number of metal ion.

14.2.2 Nomenclature of Coordination Compounds

Coordination compounds are named according to the rules recommended by the IUPAC (International Union of Pure and Applied Chemistry). The rules for naming the coordination compounds are discussed as follows:

i) In naming the coordination complex, cations are always named before anions. No matter whether the cation is simple or complex. This is just like naming an ionic compound. There should be a space between the name of cation and the name of anion. For example, in naming $K_4[Fe(CN)_6]$, the simple cation (K^+) is named first and then the complex anion is named. On the other hand, in naming $[Cu(NH_3)_4]SO_4$, the complex cation is named first and then the simple anion, SO_4^{2-} is named.

ii) In naming the coordination sphere, the ligands are named first and then the central metal atom or ion is named. The oxidation number of the central metal atom or ion is written in Roman numerals in parenthesis just after the name of central metal atom or ion. For negative oxidation state a minus sign is used.

[Name of Ligands] + [Name of central metal atom or ion] + [Oxidation number of metal in Roman numerals]

iii) If there are two or more different types of ligands, the negative ligands are named first, and then neutral ligands are named and lastly positive. According to the latest report issued by IUPAC, the names of ligands around central metal atom or ion is written in alphabetical order regardless of whether they are negative or neutral or positive. In this book the recent IUPAC nomenclature system has been followed.

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iv) Ligands are named in alphabetical order. The numerical prefixes such as di, tri, tetra, penta etc. are not considered in determining that order.

v) When there are two or more ligands of same type, the prefixed di, tri, tetra, penta and hexa are used for 2, 3, 4, 5 and 6 respectively.

vi) When the name of the ligand already contains the numerical prefixes such as di, tri, tetra, penta, etc. then the prefixes like bis, tris, tetrakis, pentakis, are used to indicate their number. The ligand name is kept within parenthesis to avoid ambiguity.

vii) The names of negative ligands end in suffix *o*.

Table 14.6: The Names of Some Common Anionic Ligands

Formula	Name	Formula	Name
F^-	Fluoro	NH_2^-	Amido
Cl^-	Chloro	CH_3COO^-	Acetato
Br^-	Bromo	CO_3^{2-}	Carbonato
I^-	Iodo	SO_4^{2-}	Sulphato
CN^-	Cyano or cyno	SO_3^{2-}	Sulphito
OH^-	Hydroxo	HCO_3^{1-}	Bicarbonato
NO_3^{1-}	Nitro or nitrito	$C_2O_4^{2-}$	Oxalato

viii) The names of positive ligands end in 'ium'.

Table 14.7: The Names of Some Common Positive Ligands

Formula	Name	Formula	Name
$NH_2—NH_3^+$	Hydrazinium	NO^+	Nitrosylium
NO_2^+	Nitronium	NH_4^+	Ammonium

ix) The names of neutral ligands have no special ending. Their names are not systematic.

Table 14.8: The Names of Some Common Neutral Ligands

Formula	Name	Formula	Name
NH_3	Ammine	CO	Carbonyl
H_2O	Aqua or aquo	NO	Nitrosyl
N_2	Dinitrogen	O_2	Dioxygen
C_5H_5N	Pyridine	H_2NNH_2	hydrazine
$H_2NCH_2CH_2NH_2$	Ethylenediamine		

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x) When the complex is anionic, then suffix 'ate' is added to the name of metal. The –ate tends to replace –um, –ium, or –enum in the metal names if present.

Table 14.9: The Names of Metals in Anionic Complexes

Name of Metal	Greek or Latin Name of Metal	Name of Metal in an Anion Complex
Iron	Ferrum	Ferrate
Copper	Cuprum	Cuprate
Lead	Plumbum	Plumbate
Silver	Argentum	Argentate
Gold	Aurum	Aurate
Tin	Stannum	Stannate

The rest of the metals simply have '-ate' added to the end as shown in the table below.

Table 14.10: The Names of Metals in Anionic Complexes

Name of Metal	Name of Metal in an Anion Complex	Name of Metal	Name of Metal in an Anion Complex
Aluminum	Aluminate	Manganese	Manganate
Antimony	Antimonate	Mercury	Mercurate
Chromium	Chromate	Nickel	Nickelate
Cadmium	Cadmate	Platinum	Platinate
Cobalt	Cobaltate	Zinc	Zincate

xi) When the complex is cationic or neutral, no suffix will come at the end of the name of metal.

Examples for the systematic names of complexes:

i) $K_4[Fe(CN)_6]$ Potassium hexacynoferrate(II)
ii) $K_3[Fe(CN)_6]$ Potassium hexacynoferrate(III)
iii) $Na[Mn(CO)_5]$ Sodium pentacarbonylmanganate(−I)
iv) $Na_2[Ni(CN)_4]$ Sodium tetracynonickelate(II)
v) $K[Ag(CN)_2]$ Potassium dicynoargentate(I)
vi) $Na_2[Sn(OH)_6]$ Sodium hexahydroxostannate(II)
vii) $Na_2[Fe(NO)(CN)_5]$ Sodium pentacynonitrosylferrate(III)
viii) $[Ni(CO)_4]$ Tetracarbonyl nickel(0)
ix) $[Pt(NH_3)_2Cl_4]$ Diamminetetrachloro platinum(IV)
x) $[CoCl_6]^{3-}$ Hexachlorocobaltate(III) ion

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xi)	$[ZnCl_4]^{2-}$	Tetrachlorozincate(II) ion
xii)	$[Cr(en)_3]^{3+}$	Tris(ethylenediamine)chromium(III) ion
xiii)	$[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
xiv)	$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
xv)	$[Cu(NH_3)_4]SO_4$	Tetraamminecopper(II) sulphate
xvi)	$[Cr(H_2O)_4Cl_2]NO_3$	Tetraaquadichlorochromium(III) nitrate
xvii)	$[Co(en)_3](NO_3)_3$	Tris(ethylenediamine)cobalt(III) nitrate

Keep in Mind

According to the latest report issued by IUPAC, the names of ligands around central metal atom or ion is written in alphabetical order regardless of whether they are negative or neutral or positive. For example, in the complex $[PtCl(NO_2)(NH_3)_4]SO_4$, the ligands are named in the order ammine, chloro and nitro.

Keep in Mind

Give systematic names for the following compounds.

i) $K_4[Ni(CN)_4]$ ii) $Ca_2[Fe(CN)_6]$ iii) $K[Au(CN)_4]$
iv) $H[Co(NH_3)_2(C_2O_4)_2]$ v) $NH_4[Cr(NH_3)_2Br_4]$ vi) $[Fe(CO)_5]$
vii) $[Ni(NH_3)_4(NO_2)_2]$ viii) $[Cr(NH_3)_4(H_2O)_2]^{3+}$ ix) $[Fe(H_2O)_6]SO_4$
ix) $[Co(en)_2Cl_2]Cl$

14.2.3 Shapes of Complex ions with Coordination Number 2, 4, and 6

There are four typical shapes of complex ions. They are usually linear, tetrahedral, square planar and octahedral. The shape of complex ions depends upon the number of ligands. Two ligands give linear shape, four ligands give either tetrahedral shape or square planar and six ligands give octahedral shape.

Linear Complexes

The coordination number of linear complexes is two. In these complexes two ligands are attached to central metal atom or ion. Their bond angles are of 180°. Both the ligands lie in the same plane. Examples are: $[Ag(NH_3)_2]^{1+}$, $[Ag(CN)_2]^{1-}$, $[Hg(NH_3)_2]^{2+}$, $[Hg(CN)_2]^0$, $[CuCl_2]^{1-}$, $[Au(CN)_2]^{1-}$, etc.

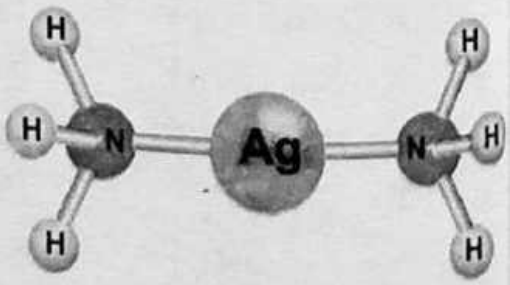


Figure 14.1: Structure of $[Ag(NH_3)_2]^{1+}$

Tetrahedral Complexes

The coordination number of tetrahedral complexes is four. In these complexes the four monodentate ligands are attached to central metal atom or ion. Their bon

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angles are of 109.5°. The ligands lie at corners of a tetrahedron. Examples are: $[Ni(CO)_4]^0$, $[MnCl_4]^{2-}$, $[Zn(NH_3)_4]^{3+}$, $[Cu(CN)_4]^{2-}$, etc.

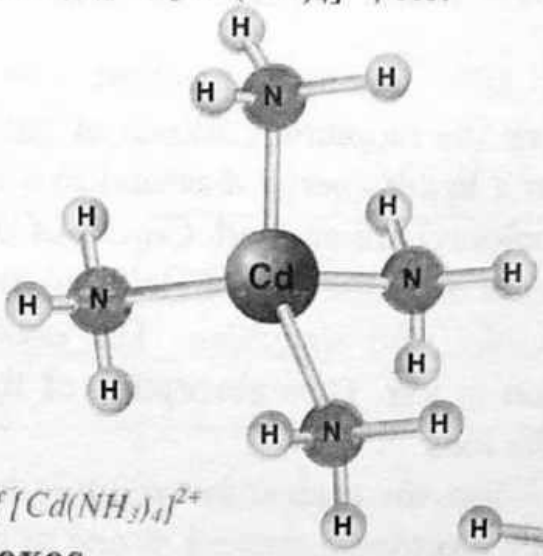


Figure 14.2: Structure of $[Cd(NH_3)_4]^{2+}$

Square Planar Complexes

The coordination number of square planar complexes is also four. In these complexes four ligands are attached to central metal atom or ion. All of the ligands lie in the same plane at the corners of a square. Examples are: $[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$, $[Cu(en)_2]^{2-}$, $[AuCl_4]^{1-}$, etc.

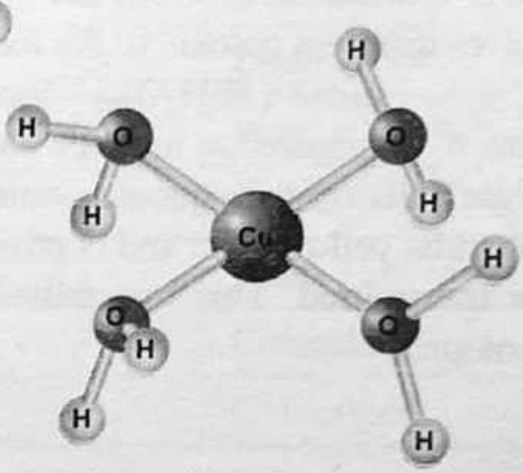


Figure 14.3: Structure of $[Cu(H_2O)_4]^{2+}$

Octahedral Complexes

The coordination number of octahedral complexes is six. In these complexes six ligands are attached to central metal atom or ion. Four ligands lie in the same plane and the other two ligands lie above and below the plane. Examples are: $[Co(NH_3)_6]^{3+}$, $[AlF_6]^{3-}$, $[Fe(H_2O)_6]^{3+}$, $[PtCl_6]^{2-}$, etc.

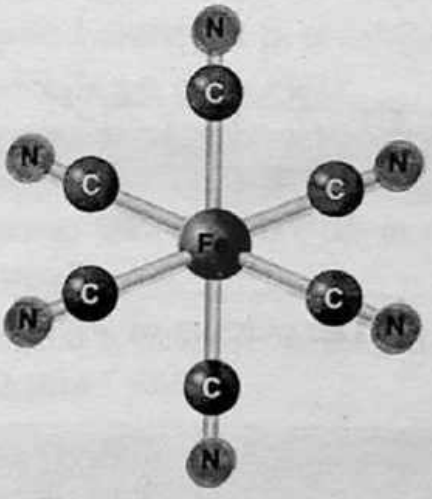


Figure 14.4: Structure of $[Fe(CN)_6]^{4-}$

14.2.4 Colour of Complexes

Most of the compounds of *s*- and *p*-block elements are colourless while those of transition elements are coloured. The colour of complexes (coordination compounds) is due to the absorption of some radiation of a particular colour from visible light to promote an electron from one of the *d*-orbitals to another.

The *d*-orbitals of isolated transition elements are degenerate (all the *d*-orbitals have same energy). However, when the transition atom or ion is surrounded by ligands in a complex ion, the five *d*-orbitals split up into two sets of *d*-orbitals (called

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t_{2g} and e_g orbitals) having slightly different energies. The t_{2g} orbitals (triply degenerate orbitals) are d_{xy}, d_{xz} and d_{yz} and the e_g orbitals (equidegenerate orbitals) are $d_{x^2} - d_{y^2}$ and d_{z^2}.

When white light falls on the transition elements that have partially filled *d*-orbitals, they absorb the radiation (colour) of particular wavelengths for the promotion of electron from a lower energy *d*-orbital to a higher energy *d*-orbital and the remaining radiations (colours) are emitted. Colour of the complex is the colour of emitted radiation. The process of promotion of electrons from lower energy *d* level to higher *d* energy level is called d-d transition. The energy difference of two sets of *d*-orbitals varies from ion to ion. Thus absorption of light of various wavelengths gives different colours to the ions.

In the $[Ti(H_2O)_6]^{3+}$ ion, the central metal ion is titanium (Ti^{3+}). The Ti^{3+} ion has d^1 configuration and this electron is present in one of the t_{2g} orbitals. When white light falls on the aqueous solution of $[Ti(H_2O)_6]^{3+}$ ions, then d^1 electron of Ti^{3+} ion absorbs yellow light and is promoted to e_g orbital. Here most of the blue and red light is transmitted. This transmitted light looks violet. Therefore, its solution has violet colour.

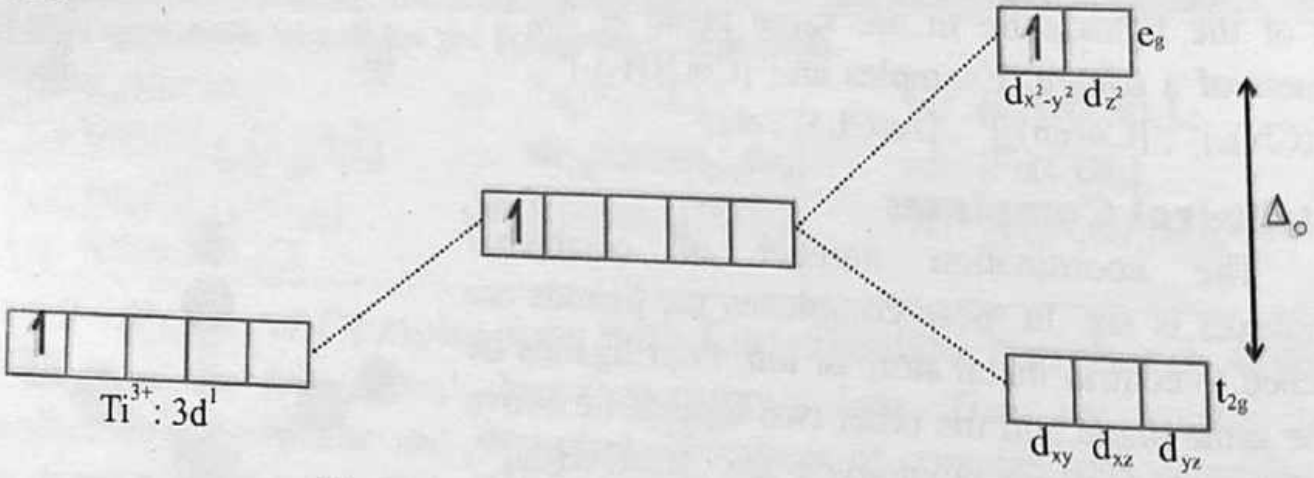


Figure 14.5: d-d transition of $[Ti(H_2O)_6]^{3+}$ ion

The colours of some hydrated transition metal ions are given in the table.

Table 14.11: Colours of Some Hydrated Transition Metal Ions

Transition Metal Ion	No. of Electrons in *d*-orbitals	No. of Unpaired Electrons In *d*-orbitals	Colour of Hydrated Ions
Sc^{3+}	$3d^0$	0	Colourless
Ti^{4+}	$3d^0$	0	Colourless
Ti^{3+}	$3d^1$	1	Purple
V^{4+}	$3d^1$	1	Blue
V^{3+}	$3d^2$	2	Green

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Transition Metal Ion	No. of Electrons in *d*-orbitals	No. of Unpaired Electrons In *d*-orbitals	Colour of Hydrated Ions
V^{2+}	$3d^3$	3	Violet
Cr^{3+}	$3d^3$	3	Green
Cr^{2+}	$3d^4$	4	Blue
Mn^{3+}	$3d^4$	4	Violet
Mn^{2+}	$3d^5$	5	Light pink
Fe^{3+}	$3d^5$	5	Yellow
Fe^{2+}	$3d^6$	4	Light green
Co^{2+}	$3d^7$	3	Pink
Ni^{2+}	$3d^8$	2	Green
Cu^{2+}	$3d^9$	1	Blue
Cu^{1+}	$3d^{10}$	0	Colourless
Zn^{2+}	$3d^{10}$	0	Colourless

From the above table, it is cleared that the metal ions having vacant or completely filled *d*-orbitals are colourless while those having partially filled *d*-orbitals are coloured. In other words the metal ions having unpaired electrons in *d*-orbitals are coloured and those having no unpaired electrons in *d*-orbitals are colourless.

Keep in Mind

All of the five *d*-orbitals in a complex ion are higher in energy than the *d*-orbitals in an isolated transition metal ion.

The s- and *p*-block elements have no partially filled *d*-orbitals so there is no any d-d transition and thus their compounds are colourless.

Keep in Mind

The colour of transition metal complex ions depends on:

i) The number of d electrons present in the central metal atom or ion.
ii) The arrangement of ligands around the central metal ion.
iii) The nature of the ligands.
iv) The number of ligands around the central metal ion.
v) The nature of the transition metal ion
vi) The oxidation number of the metal

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14.3 Chemistry of Some Important Transition Elements

14.3.1 Vanadium

Vanadium is silver grey metallic element and is an abundant element which is found in about 65 minerals. It generally occurs in low concentrations.

14.3.1.1 Oxidation States

Vanadium has the electronic configuration [Ar] $3d^3\ 4s^2$. The most common oxidation states of vanadium are +2, +3, +4 and +5 corresponding to d^3, d^2, d^1 and d^0 electronic configurations. The vanadium shows highest oxidation states when it combines with the highly electronegative element oxygen. The oxidation states from +3 to +5 can be maintained in aqueous solutions. The most stable state of vanadium in acidic solution is +3. When a solution of vanadium(V) such as $[VO_2]^+$ is mixed with the solution of vanadium(II), the +5 state oxidizes the +2 state to the most stable state (i.e. +3 state) in acidic solution.

$$VO^{+}_{2(aq)} + 2V^{2+}_{(aq)} + 4H^{+}_{(aq)} \longrightarrow 3V^{3+}_{(aq)} + 2H_2O_{(l)}$$

Table 14.12: Vanadium Oxides and Their Oxidation States

Oxides of Vanadium	Formulae	Oxidation States
Vanadium(II) oxide (Vanadium monoxide)	VO	+2
Vanadium(III) oxide (Vanadium trioxide)	V_2O_3	+3
Vanadium(IV) oxide (Vanadium dioxide)	VO_2	+4
Vanadium(V) oxide (Vanadium pentoxide)	V_2O_5	+5

The compounds of vanadium in their lower oxidation states (i.e. +2 oxidation state) are reducing agents whereas in their higher oxidation states (i.e. +5 oxidation state) are oxidizing agents. The complexes of vanadium(II) and (III) are reducing and those of vanadium(IV) and (V) are oxidizing. The compounds of vanadium in their +5 oxidation states are colourless due to vacant *d*-orbitals.

Keep in Mind

The compounds of vanadium in their lower oxidation states are ionic and in their higher oxidation states are covalent.

14.3.1.2 As a Catalyst in Contact Process

The vanadium(V) oxide (i.e. vanadium pentoxide, V_2O_5) is a powerful catalyst that is used widely in industrial processes. Vanadium pentoxide can be used for the

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production of sulphuric acid in the Contact Process. It oxidizes sulphur dioxide (SO_2) to sulphur trioxide (SO_3).

$$SO_2 + V_2O_5 \longrightarrow SO_3 + 2VO_2$$

In this reaction, the vanadium(V) oxide is reduced to vanadium(IV) oxide. The vanadium pentoxide is produced again by the oxidation of air.

$$2VO_2 + 1/2\ O_2 \longrightarrow V_2O_5$$

14.3.2 Chromium

The name of chromium is taken from the Greek word 'khroma' that means "colour" because it gives a large number of colourful compounds. Their compounds have violet, blue, green, yellow and orange colours.

Chromium does not occur in free state. It occurs naturally as chromite ($FeO.Cr_2O_3$) ore. The 96% of the world's reserves are found in southern Africa. In Pakistan, it is found in Muslim Bagh (District Killa Saifullah) and Khanozai (District Pishin) of Balochistan Province. It is used to make stainless steel and some other alloys.

14.3.2.1 Oxidation States

The electronic configuration of chromium is $[Ar]3d^5 4s^1$. The common oxidation states of chromium in compounds are +2, +3 and +6 corresponding to d^4, d^3 and d^0 configuration. The most common oxidation state of chromium is +3.

Table 14.13: Compounds of Chromium and their Oxidation States

Oxides of Chromium	Formula	Oxidation State	Nature
Chromium(II) oxide	CrO	+2	Basic
Chromium(III) oxide	Cr_2O_3	+3	Amphoteric
Chromium(VI) oxide (Chromium trioxide)	CrO_3	+6	Acidic

The compounds of chromium in their lower oxidation states (i.e. +2 oxidation state) are reducing agents whereas in their higher oxidation states (i.e. +6 oxidation state) are oxidizing agents. The acidic character of oxides of chromium increases while basic character decreases by increasing oxidation states.

Keep in Mind

The compounds of chromium in their lower oxidation states are ionic and in their higher oxidation states are covalent.

14.3.2.2 The Chromate—Dichromate Equilibrium

Chromates (e.g. Na_2CrO_4 and K_2CrO_4) are the salt of chromic acid (H_2CrO_4) and dichromates (e.g. $Na_2Cr_2O_7$ and $K_2Cr_2O_7$) are the salts of dichromic acid ($H_2Cr_2O_7$). Sodium chromate(VI), Na_2CrO_4 is a yellow crystalline solid and sodium

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dichromate is an orange-red crystalline solid. They both are water soluble. When sodium dichromate is dissolved in water the resulting solution is orange containing sodium ($Na^{+}_{(aq)}$) ions and dichromate ($Cr_2O^{2-}_{7(aq)}$) ions. The yellow colour of solution is due to dichromate ions. The orange-red dichromate ions in aqueous solution are in equilibrium with the yellow chromate ions as shown by the equation:

$$\underset{\text{Orange-red}}{Cr_2O^{2-}_{7(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\text{Yellow}}{2CrO^{2-}_{4(aq)}} + 2H^{+}_{(aq)}$$

The dichromate and chromate ions are in dynamic equilibrium. The equilibrium is sensitive to pH changes. It means the equilibrium can be moved from one side to the other by addition of acid or base. The decrease in pH favours the orange dichromate ions and increase in pH favours the yellow chromate ions. The shifting of equilibrium is observed by colour change.

Adding hydrochloric acid (an acid) to the solution will increase the concentration of hydrogen ions and pushes the equilibrium to the left to increase the concentration of $Cr_2O^{2-}_{7(aq)}$ ions. Now the predominant colour will be orange. On the other hand when an alkali (i.e. NaOH, KOH) is added to the solution, the concentration of hydrogen ions decreases by neutralization and hence the reaction proceeds in the forward direction to increase the concentration of $CrO^{2-}_{4(aq)}$ ions. Now the yellow colour becomes more intense.

It is concluded that from the above discussion, the chromate(VI) is stable in basic solution whereas the dichromate(VI) is stable in acidic solution.

Keep in Mind

In both the chromate and the dichromate ions, chromium has d^0 configuration. We might expect all d^0 configurations to be colourless but the colour of these compounds comes from an electron transition from the ligand to the metal. The electron is excited from a filled ligand *p*-orbital through a π interaction into the empty metal ion *d*-orbitals. The colour of the complexes of a given transition metal ion depend both on the metal ion and the ligand.

14.3.2.3 Reduction of Dichromate(VI) Ions with Zinc and an Acid

Potassium dichromate(VI) reacts with zinc in the acidic solution to form chromium(III) ions. The colour of solution shift from orange to green.

$$Cr_2O^{2-}_7 + 14H^{+} + 3Zn \longrightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$$

The chromium(III) ions further react with zinc to form chromium(II) ions. The colour of solution shifts from green to blue.

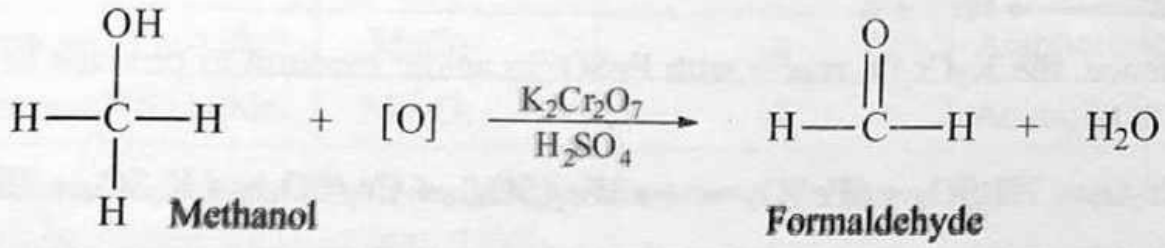
$$2Cr^{3+} + Zn \longrightarrow 2Cr^{2+} + Zn^{2+}$$

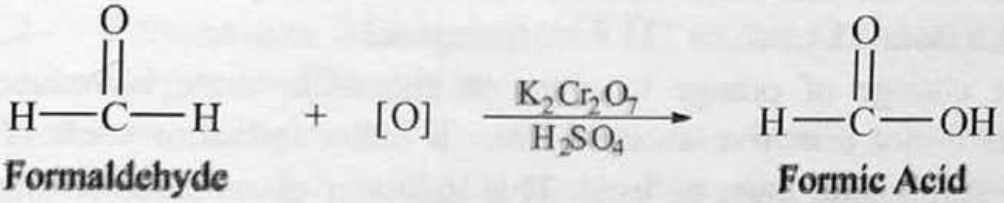
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14.3.2.4 Potassium Dichromate(VI) as an Oxidizing Agent in Organic Chemistry

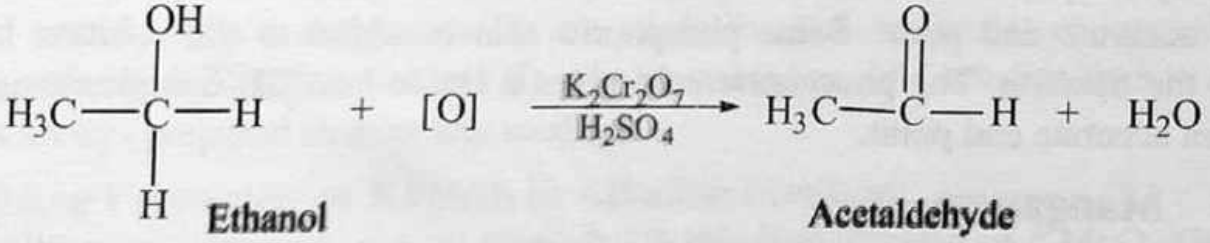
Dichromate(VI) ion is a very powerful oxidizing agent in acidic solution. It is commonly used as an oxidizing agent in organic chemistry. It is commonly used to oxidize alcohols.

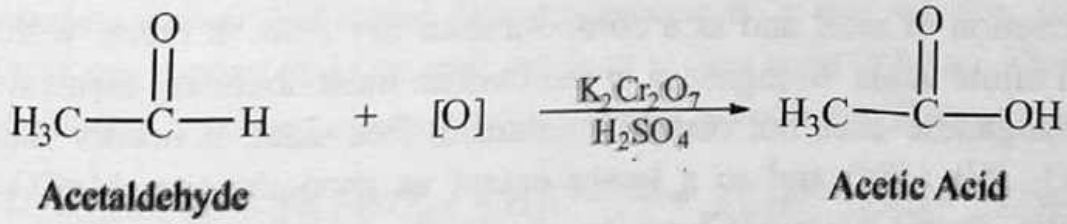
i) It is used to oxidize methanol t(formaldehyde and then to formic acid.



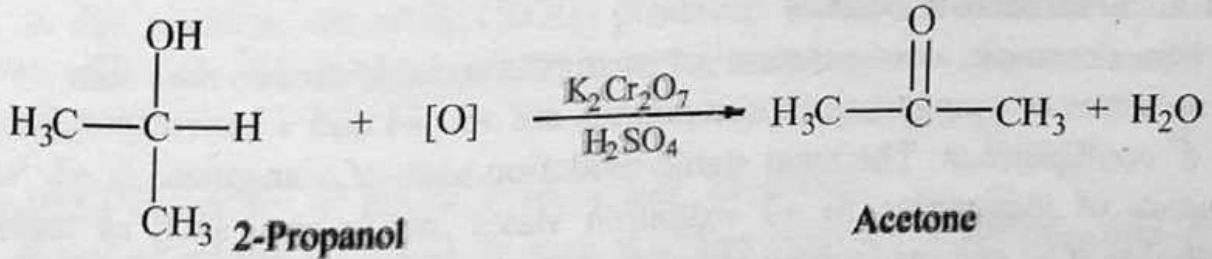


ii) It oxidizes primary alcohols first to aldehydes and then to carboxylic acids.





iii) Secondary alcohols are oxidized to ketones. Ketones are not oxidized easily.



iv) Tertiary alcohols are not oxidized by potassium dichromate under acidic conditions.

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14.3.2.5 Potassium dichromate as an Oxidizing Agent in Titrations

Potassium dichromate is used in redox titrations to estimate the concentration of iron(II) ions in solution. The dichromate(VI) ion is a good oxidizing agent and is reduced to chromium(III) ion.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

The iron(II) ion is oxidized to iron(III) ion.

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Hence, the $K_2Cr_2O_7$ reacts with $FeSO_4$ in acidic medium to produce $Fe_2(SO_4)_3$ and $Cr_2(SO_4)_3$.

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

In this reaction, the oxidation state of chromium changes from +6 to +3 and that of iron changes from +2 to +3.

The colour change of orange to green as the dichromate is reduce to the chromium(III) ion is not sensitive enough. Thus a redox indicator such as barium diphenylammine sulphonate must be used. This indicator gives a violet-blue colour when all the iron(II) ions have been converted to iron(III) ions. The indicator is affected by the presence of free iron(III) ions in the solution and thus it is difficult to get the accurate end point. Some phosphoric acid is added to the solution before starting the titration. The phosphoric acid gives a stable iron(III) complex thus give rise to an accurate end point.

14.3.3 Manganese

Manganese is a grey white, active metallic element. It is hard and brittle. It is used in the production of steel and as a component of dry cells. It reacts with water and dissolves in dilute acids. Manganese is the twelfth most abundant element in the earth's crust. Manganese does not occur in nature in free state. It occurs mainly as pyrolusite, MnO_2 (60–63%) and to a lesser extent as rhodothrosite, $MnCO_3$. It is found in Australia, Brazil, Gabon, China, India, Russia, Ukraine, Georgia and South Africa.

14.3.3.1 Oxidation States

The electronic configuration of manganese is [Ar] $3d^5\ 4s^2$. The common oxidation states of manganese in compounds are +2, +4 and +7 corresponding to d^5, d^3 and d^0 configuration. The most stable oxidation state of manganese is +2. Various compounds of manganese in +2 oxidation states are known, such as manganese sulphate ($MnSO_4$) and manganese chloride ($MnCl_2$). Manganese dioxide (MnO_2) with +4 oxidation state is the most common compound of manganese. The compounds of

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manganese such as potassium manganate (K_2MnO_4) and potassium permanganate ($KMnO_4$) in their higher oxidation states (i.e. +6 and +7 oxidation states) are oxidizing agents.

Table 14.14: Compounds of Manganese and Their Oxidation States

Oxides of Vanadium	Formula	Oxidation State	Nature
Manganese(II) oxide	MnO	+2	Basic
Manganese(IV) oxide	MnO_2	+4	Amphoteric
Manganese(VII) oxide	Mn_2O_7	+7	Acidic

The acidic character of oxides of manganese increases while basic character decreases by increasing oxidation states.

14.3.3.2 Potassium Manganate(VII) as an Oxidizing Agent in Organic Chemistry

Potassium manganate(VII), $KMnO_4$ is usually known as potassium permanganate is powerful oxidizing agent. It is probably the most useful of the oxidizing agents in organic chemistry. It oxidizes a wide range of organic molecules. $KMnO_4$ can be used in acidic, basic or neutral medium. The oxidation of $KMnO_4$ in acidic medium gives manganese(II) ion while in alkaline (basic) or neutral media MnO_2 is formed. The manganate(VII) is more stable in acidic solution than in alkaline and is always prepared in an acidic medium.

Oxidizing Properties of $KMnO_4$ in Alkaline Medium

When an alkene is passed through 1% alkaline solution of $KMnO_4$ (Baeyer's reagent) then vicinal diol called glycol is produced. In this reaction, the pink colour of $KMnO_4$ is discharged and you will get dark brown solid (MnO_2). This test is used for the detection of unsaturation in a molecule and is known as Baeyer's test.

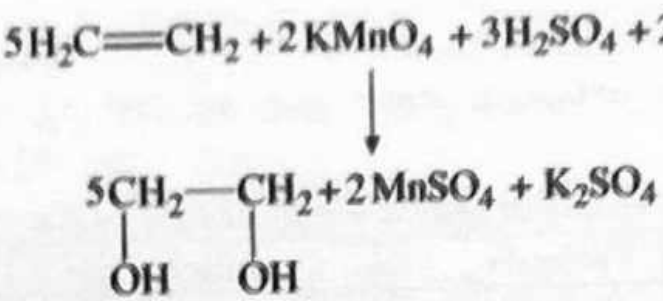
$$3\,CH_2{=}CH_2 + 2\,KMnO_4 + 4\,H_2O \xrightarrow[OH^-]{Cold} 3\,\underset{OH}{CH_2}{-}\underset{OH}{CH_2} + 2\,KOH + 2\,MnO_2$$

In this reaction, the alkali (KOH) produced makes the medium alkaline even when we start with neutral solutions. Thus this reaction can also be done under neutral conditions.

Oxidizing Properties of $KMnO_4$ in Acidic Medium

When an alkene is passed through acidified solution of $KMnO_4$ then glycol is produced. In this reaction, the pink colour of $KMnO_4$ solution disappears because the colourless manganese(II) ions are formed.

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14.3.3.3 Potassium Manganate(VII) as an Oxidizing Agent in Titrations

Potassium permanganate, $KMnO_4$ in the presence of H_2SO_4 is a powerful oxidizing agent and is used for various volumetric estimations. Titration is the most commonly used method to determine the concentration of a substance that is unknown. The titrations based upon the reactions between oxidizing agents such as $KMnO_4$ and reducing agents such as $FeSO_4$ are called redox titrations. The redox titration involving $KMnO_4$ are called $KMnO_4$ titrations. The common example is the titration of standard solution of $KMnO_4$ against an analyte containing an unknown concentration of iron(II) ions. The balanced chemical equation for the reaction is as:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The use of $KMnO_4$ as a titrant is useful here because it can act as self-indicator. This is due the fact that the $KMnO_4$ solution has a deep violet colour that is highly visible to the naked eye. When this solution is titrated against the iron (III) solution, the colour of $KMnO_4$ solution becomes pinkish.

Another example is the reduction of oxalates. It oxidizes oxalic acid to CO_2. The equation for this reaction is as under:

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

14.3.4 Iron

Iron is the fourth most abundant element in the earth crust. It is highly reactive and corrodes much more easily than many other metals. It does not occur in the free state. It occurs in combined state. The most important ores of iron are magnetite (Fe_3O_4), haematite (Fe_2O_3) and limonite ($2Fe_2O_3 . 3H_2O$). The largest producers of iron in the world are china, Australia, Brazil, India, and Russia. The important deposits of iron ore are found in various places of Pakistan that are Kalabagh, Nokundi, and Chinot. Kalabagh iron deposits are the largest.

14.3.4.1 Oxidation States

The electronic configuration of iron is [Ar] $3d^6\ 4s^2$. Iron exists in a wide range of oxidation states, −2 to +6. The most common oxidation states of iron in compounds are +2 and +3. The compounds of iron such as $[Fe(H_2O)_6]^{2+}$ and $FeSO_4 . 7H_2O$ in their +2 oxidation states are reducing agents.

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The Fe^{2+} has a $3d^6$ electronic structure and the electronic structure of Fe^{3+} is $3d^5$. The extra stability associated with a half-filled *d*-subshell makes the change from Fe^{2+} to Fe^{3+} very favourable. For example, the oxide of iron(III) known as ferric oxide (Fe_2O_3) is more stable than the oxide of iron(II) that is known as ferrous oxide (FeO). The piece of apple turns brown in open air due to conversion of iron(II) into iron(III). It means that the +2 state of iron is easily oxidized to the +3 state in an open air.

14.3.4.2 Iron as Catalyst in Haber's Process

Haber was a German research chemist. All of the ammonia that is produced worldwide is synthesized by Haber's process. In the Haber's process, nitrogen reacts with hydrogen to form ammonia. The major source of nitrogen is air and that of hydrogen gas is methane from natural gas.

$$N_2 + 3H_2 \overset{Fe}{\rightleftharpoons} 2NH_3$$

This reaction is reversible and the equilibrium is reached very slowly. Hence it is better to carry out the reaction in the presence of a suitable catalyst to achieve the equilibrium rapidly. The suitable catalyst for this reaction is magnetite (Fe_3O_4) mixed with KOH, SiO_2 and Al_2O_3. The incoming gases are purified before entering the catalyst chamber so that avoid the poisoning of catalyst. Iron is a cheap catalyst and it reduces the cost of the process.

14.3.4.3 Iron as Catalyst in Reaction between Persulphate and Iodide Ions

Persulphate ions ($S_2O_8^{2-}$) are strong oxidizing agents. They oxidize iodide ions easily.

$$S_2O_{8(aq)}^{2-} + 2I_{(aq)}^{-} \longrightarrow 2SO_{4(aq)}^{2-} + I_{2(aq)}$$

However this reaction proceeds very slowly at room temperature in an aqueous solution. A catalyst such as iron(II) or iron(III) is used to speed up the reaction by lowering the activation energy.

In the first step, the Persulphate ions oxidize iron(II) to iron(III):

$$S_2O_{8(aq)}^{2-} + 2Fe_{(aq)}^{2+} \longrightarrow 2SO_{4(aq)}^{2-} + 2Fe_{(aq)}^{3+}$$

In the second step, the Fe^{2+} ions oxidizes I^- ions to I_2:

$$2Fe_{(aq)}^{3+} + 2I_{(aq)}^{-} \longrightarrow 2Fe_{(aq)}^{2+} + I_{2(aq)}$$

The catalyst has been regenerated.

14.3.4.4 Reaction of Hexaaquairon(II) and Hexaaquairon(III) with Water and Ammonia

Reaction of Hexaaquairon(II) and Hexaaquairon(III) with Water

The pale green hexaaquairon(II) and the yellow hexaaquairon(III) ions are both acidic. They both act as acids by donating hydrogen ions to water molecules in the solution.

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In case of iron(II) complex:

$$[Fe(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{+} + H_3O^{+}$$

In case of iron(III) complex:

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^{+}$$

The greater the charge density on central metal cation, greater the ability of a substance to give proton (hydrogen ion) and the greater the acidity of a substance. For example, hexaaquairon(III) is more acidic than hexaaquairon(II).

Reaction of Hexaaquairon(II) and Hexaaquairon(III) with Ammonia

Ammonia is a stronger base than water. It acts as a base by accepting proton (hydrogen ion) from hexaaquairon(II) and hexaaquairon(III) ions in the solution.

In case of iron(II) complex:

$$[Fe(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Fe(H_2O)_4(OH)_2]^{+} + 2NH_{4(aq)}^{+}$$

In case of iron(III) complex:

$$[Fe(H_2O)_6]^{3+} + 3NH_3 \rightleftharpoons [Fe(H_2O)_3(OH)_3]^{+} + 3NH_{4(aq)}^{+}$$

14.3.4.5 Reaction of iron(II) and iron(III) Ions with Carbonate and Cyanate Ions

Reaction of iron(II) and iron(III) Ions with Carbonate

The less acidic iron(II) complex (green solution) reacts with weakly basic carbonate ion to form the iron(II) carbonate (Green precipitate).

$$[Fe(H_2O)_6]^{2+} + CO_3^{2-} \longrightarrow FeCO_3 + 6H_2O$$

The more acidic iron(III) complex reacts with weakly basic carbonate ion to form the hydrated metal hydroxide ion complex and CO_2 effervescence.

$$\underset{\text{(Brown solution)}}{2[Fe(H_2O)_6]^{3+}} + 3CO_3^{2-} \longrightarrow \underset{\text{(Brown ppt. and effervescence)}}{2[Fe(H_2O)_3(OH)_3]} + 3H_2O + 3CO_2$$

In the above equations the $CO_{3(aq)}^{2-}$ ion is unable to deprotonate the $[Fe(H_2O)_6]^{2+}$, because of the lesser acidity of iron(II). In contrast, the $CO_{3(aq)}^{2-}$ ion can deprotonate the $[Fe(H_2O)_6]^{3+}$ to form the hydrated metal hydroxide ion complex, because of the greater acidity of iron(III).

Reaction of iron(II) and iron(III) Ions with Thiocyanate Ions

This is an example of ligand exchange reaction. When we add thiocyanate ions (e.g. from sodium or potassium or ammonium thiocyanate solution) to a solution containing hexaaquairon(III) ions, we get an intense blood red solution containing the $[Fe(H_2O)_5(SCN)]^{2+}$ ion. In this reaction the aqua ligand is replaced by thiocyanato ligand.

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$$[Fe(H_2O)_6]^{3+} + SCN^- \longrightarrow [Fe\ (H_2O)_5(SCN)]^{2+} + H_2O$$

This reaction is NOT given by hexaaquairon(II) ions.

14.3.5 Copper

It is a reddish orange soft, malleable and ductile metal and has high thermal and electrical conductivity. It tarnishes to a dull brownish colour when exposed to air. It is often used in alloys, including brass and bronze. It is also used in electrical cables and in electrical appliances.

Copper can be found as a pure native form but it mostly occurs in combination with other elements. Copper is found in Chile, China, Peru, and USA. In Pakistan, it is found in Reko Diq Balochistan. The major ores of copper are: (i) Cuprite, Cu_2O containing about 88% copper (ii) Chalcocite, Cu_2S containing about 80% copper (iii) Azurite (blue), $2CuCO_3.Cu(OH)_2$ containing about 65% copper (iv) Malachite (green), $CuCO_3.Cu(OH)_2$ containing about 57% of copper. (v) Chalcopyrite, $CuFeS_2$ ($Cu_2S + Fe_2S_3$) is the most common source of copper ore. It contains about 34% copper. It accounts for about 50% of the world's copper production.

14.3.5.1 Oxidation States

The electronic configuration of copper is [Ar] $3d^{10}\ 4s^1$. The common oxidation states of copper in compounds are +1 and +2 corresponding to d^{10} and d^9 configuration. Copper(I) is often called cuprous and copper(II) is often called cupric. Copper is the only transition metal for which the oxidation state +1 is important. An example of +1 oxidation state is copper(I) oxide, Cu_2O and an example of +2 oxidation state is copper(II) oxide, CuO.

Copper(II) is the most stable oxidation state in solution as well as the solid state and it is the most abundant one. Copper(I) is often the more stable state in the solids at moderate temperatures. In aqueous solutions, the copper(I) is readily oxidized to copper(II).

$$Cu^{1+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + e^-$$

The copper(I) ion is thus a reducing agent. The concentration of copper(II) ions in solution can be determined by titration with oxidants.

14.3.5.2 The Reaction of Hexaaquacopper(II) Ions with Hydroxide Ions, Ammonia and Carbonate ions

Reaction of Hexaaquacopper(II) Ions with Hydroxide Ions

The hydroxide ion reacts with hexaaquacopper(II) ion to produce the insoluble pale blue copper(II) hydroxide.

$$[Cu(H_2O)_6]^{2+} + 2OH^-_{(aq)} \longrightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$$

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Reaction of Hexaaquacopper(II) Ions with Ammonia

The reaction of aqueous copper(II) ions with ammonia solution occurs in two steps:

Step 1: When a small amount of ammonia is added to the solution of hexaaquacopper(II) ions, the ammonia molecules pulls out the hydrogen ions from the water ligands.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \longrightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

Step 2: When ammonia is added to the above solution in excess, the light blue ppt. of $[Cu(H_2O)_4(OH)_2]$ dissolves to form a deep blue solution of tetramminedihydroxocopper(II) ions.

$$[Cu(H_2O)_4(OH)_2] + 4NH_3 \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^- + 2H_2O$$

In this reaction the two aqua ligands and two hydroxo ligands are replaced by four ammine ligands.

Reaction of Hexaaquacopper(II) Ions with Carbonate Ions

The hydroxide ion reacts with the hexaaquacopper(II) ion to form the insoluble compound, copper(II) carbonate.

$$[Cu(H_2O)_6]^{2+} + CO_3^{2-} \longrightarrow CuCO_3 + 6H_2O$$

Uses of Transition Metal Compounds in Paints

Pure transition metals are valued for many reasons, one being their ability to form highly coloured compounds. The transition elements such as chromium, iron, copper, cobalt, and titanium can form numerous coloured compounds with oxygen. For example, red paint comes from the compounds of iron and oxygen while green and blue paints come from different compounds of copper, chromium and cobalt. Titanium makes white paint with oxygen.

Summary of Facts and Concepts

- The elements in Group 1B and Groups 3B–8B are collectively called the transition elements or the transition metals. They have partially filled *d* or *f*-subshells either in atomic states or in any other common oxidation states. The general electronic configuration of *d*-block elements is $(n-1)\,d^{1-10}\,ns^{1-2}$.
- Most of the transition elements and their compounds are used as catalysts. Catalytic behaviour is due to variable oxidation states.
- Binding energy, paramagnetic behaviour and melting points of transition elements increase with increasing number of unpaired electrons.

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- The substances that are attracted by the magnetic field are called paramagnetic substances, while the substances that are repelled by magnetic field are called diamagnetic.
- The compounds having complex molecules or ions and can exist independently are called complex compounds or coordination compounds. In coordination compounds, a central metal atom (or ion) is attached to a group of ligands by coordinate covalent bonds.
- The ions or molecules that are attached with the central metal atom or ion by donating the electron pairs are called ligands. Ligands can be mono-dentate or poly-dentate, depending on the number of ligand donor atoms attached to the metal.
- The number of lone pair of electrons provided by the ligands to the central metal atom or ion is called coordination number. Common coordination numbers of coordination complexes are 2, 4 and 6. The coordination number of linear complexes is two, tetrahedral or square planar complexes is four and that of octahedral complexes is six.
- Most of the coordination compounds are coloured in the solid state or in solution form. The coordination compounds with metal ions whose *d* atomic orbitals are filled, like Zn^{2+}, or have no *d* electrons, like Sc^{3+}, are colourless.

Multiple Choice Questions

Select one answer from the given choices for each question:

i) Which of the following have completely filled *d*-subshell?

(a) Fe, Co, Ni (b) Cu, Ag, Au

(c) Ni, Pd, Pt (d) Zn, Cd, Hg

ii) Which one of the following does not belong to transition elements?

(a) Lead (b) Gold

(c) Tin (d) Arsenic

iii) Which one of the following belongs to first transition series?

(a) Silver (b) Gold

(c) Iron (d) Mercury

iv) Substance that are repelled by a magnetic field are known as:

(a) Paramagnetic substances

(b) Diamagnetic substances

(c) Ferromagnetic substances

(d) Paramagnetic and Diamagnetic substances

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v) Elements found in *d*-block of periodic table are termed as:
(a) Main group elements (b) Normal elements
(c) Transition elements (d) Representative elements

vi) The most common oxidation states of iron are:
(a) +1 and +2 (b) +1 and +3
(c) +2 and +3 (d) +3 and +4

vii) What is the correct electronic configuration for Ti^{2+} ion?
(a) $[Ar]4s^2 3d^0$ (b) $[Ar]4s^0 3d^2$
(c) $[Ar]4s^0 3d^0$ (d) $[Ar]4s^1 3d^1$

viii) The number of unpaired electrons in zinc atom is:
(a) O (b) 1 (c) 2 (d) 3

ix) Which of the following has the highest magnetic moment?
(a) Cu^{2+} (b) Ni^{2+} (c) Co^{2+} (d) Mn^{2+}

x) In $K_4[Fe(CN)_6]$, coordination number of iron is:
(a) 2 (b) 4 (c) 6 (d) 8

xi) Brass is a metal alloy that contains:
(a) Cu and Zn (b) Cu and Sn
(c) Zn and Sn (d) Sn and Mn

xii) Give the IUPAC name for $K_3[Fe(CN)_6]$:
(a) Potassium hexacyanoferrate (II)
(b) Potassium hexacyanoferrate (III)
(c) Potassium hexacyanoiron (II)
(d) Potassium hexacyanoiron (III)

xiii) The oxidation state of vanadium in V_2O_5 is:
(a) +2 (b) +3 (c) +4 (d) +5

xiv) The coordination number of metal atom or ion in a tetrahedral complex is:
(a) 2 (b) 4 (c) 6 (d) 8

xv) Which one of the following oxides is more acidic?
(a) MnO (b) Mn_2O_3 (c) MnO_2 (d) Mn_2O_7

xvi) Which period starts from scandium to zinc?
(a) 2nd period (b) 3rd period
(c) 4th period (d) 5th period

xvii) Vanadium pentaoxide is used as a catalyst in the manufacture of:
(a) HNO_3 (b) H_2SO_4
(c) NH_3 (d) $CO(NH_2)_2$

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xviii) Which one of the following act as a reducing agent?

(a) HNO_3 (b) $KMnO_4$

(c) $LiAlH_4$ (d) $K_2Cr_2O_7$

xix) In the reaction given below, the oxidation state of vanadiumchanges from:2 $VO_2 + 1/2\ O_2 \longrightarrow V_2O_5$

(a) +2 to +3 (b) +3 to +4

(c) +4 to +5 (d) +5 to +6

xx) Which is true for transition elements?

(a) They have low melting and boiling points

(b) They are insulators

(c) They are diamagnetic

(d) They show variable oxidation states

Short Answer Questions

Q.1. Define the following terms:

(a) Central metal atom

(b) Coordination number

(c) Coordination sphere

Q.2. Why most of the transition ions are coloured?

Q.3. Why majority of the transition metals are paramagnetic in nature?

Q.4. Why are the elements of group 12 (IIB) are excluded from the transition series elements?

Q.5. The elements of group 3 (IIIB) are excluded from the transition series elements, why?

Q.6. Write down the electronic configuration of Fe^{3+} (Z = 26) and Zn^{2+} (Z = 30).

Q.7. Why do transition elements show variable oxidation states?

Q.8. Discuss catalytic behaviour of transition elements.

Q.9. Why Ag^+ ion is more stable than Ag^{2+} ion?

Q.10. What is binding energy? Explain the trends in binding energy.

Q.11. Melting points of *d*-block elements increase up to the middle of series and thereafter decrease, why?

Q.12. What is the oxidation state of zinc in $[Zn(NH_3)_4]^{2+}$ ion?

Q.13. Why Cu^{2+} ions are paramagnetic while Zn^{2+} ions are diamagnetic?

Q.14. Which ion shows a lower magnetic moment: Fe^{3+} or Cr^{3+}?

Q.15. Determine the oxidation state of cobalt in $[Co(NH_3)_4(OH_2)Cl]Cl_2$.

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Long Answer Questions

Q.1. What are transition elements? Describe the general features of transition elements?

Q.2. What do you know about the transition series of *d*-block and *f*-block elements? Explain concisely.

Q.3. What is binding energy? Discuss the trend in binding energy of transition elements?

Q.4. Discuss the electronic configuration of *d*-block elements.

Q.5. What is magnetic behaviour? Describe the magnetic behaviour of substances.

Q.6. What are alloys? Give composition and uses of some well-known alloys.

Q.7. Describe some properties of an alloy that are different from the metals that compose it.

Q.8. What are coordination compounds? How transition elements from these compounds?

Q.9. What are the components of complex compounds?

Q.10. Explain different types of ligands with suitable examples.

Q.11. Describe the rules for naming coordination compounds'.

Q.12. Give systematic names for the following compounds.

i) $K_3[Fe(C_2O_4)_3]$

ii) $K_2[PtCl_4]$

iii) $H[AuCl_4]$

iv) $Na_2[Fe(CN)_5NO]$

v) $(NH_4)_2[PbCl_6]$

vi) $[Cr(NO)_4]$

vii) $[Ag(CN)_2]^{1-}$

viii) $[Zn(NH_3)_4]^{2+}$

ix) $[Os(en)_4]Cl_4$

x) $[Co(SO_4)(NH_3)_4]NO_3$

xi) $[Co(NH_3)_4(OH_2)Cl]Cl_2$

Q.13. Write chemical formulae of the following complexes:

i) Hexaamminechromium(III) nitrate

ii) Hexaamminenickel(II) bromide

iii) Hexaaquaferrate(II) ion

iv) Tetrahydroxoaluminate(III) ion

v) Tetraamminedihydroxoplatinate(IV) sulphate

vi) Tetraamminechloronitrocobalt(III) nitrate

vii) Tetramminechloronitroplatinum(IV) sulphate

viii) Ammonium hexachlorotitanate(IV)

ix) Sodium hexafluorocobaltate(III)

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x) Sodium hexahydroxostannate(IV)

xi) Tris(ethylenediamine)cobalt(II) sulphate

Q.14. Describe the chemistry of vanadium, manganese, iron and copper.

Q.15. Explain the chemistry of chromium, cobalt and nickel.

Q.16. Find the charge on the central metal ion in:

i) $[Cu(CN)_2]^{1-}$ ii) $[Co(NH_3)_6]^{3+}$

iii) $Na_2[CoCl_4]$ iv) $[Cr(H_2O)_6]Cl_3$

Q.17. Describe shapes of coordination compounds.

Q.18. Describe origin of colours of complex compounds.

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Chapter 15

Organic Compounds

Major Concepts

15.1 Sources
- 15.1.1 Fossil remains: Coal, Petroleum, and Natural Gas
- 15.1.2 Plants and Natural Products
- 15.1.3 Partial and Total Synthesis
- 15.1.4 Biotechnology

15.2 Coal as a source of Organic Compounds
- 15.2.1 Destructive Distillation of Coal
- 15.2.2 Conversion of Coal to Petroleum

15.3 Characteristics of Organic Compounds

15.4 Uses of Organic Compounds

15.5 New Allotrope of Carbon: Bucky Ball

15.6 Functional Groups and Homologous Series

15. 7 Detection of Elements in Organic Compounds

Learning Outcomes:

Students will be able to:

- Define organic chemistry and organic compounds. **(Remembering)**
- Explain why there is such a diversity and magnitude of organic compounds. **(Analyzing)**
- Classify organic compounds on structural basis. **(Analyzing)**
- Explain the use of coal as a source of both aliphatic and aromatic hydrocarbons. **(Understanding)**
- Explain the use of plants as a source of organic compounds. **(Understanding)**
- Explain that organic compounds are also synthesized in the lab. **(Understanding)**
- Define functional groups and homologous series. **(Remembering)**

Introduction

In the late eighteen and the early nineteenth centuries, the chemists classified compounds into two main classes, organic and inorganic. Compounds obtained from plants or animals were called organic, whereas compounds obtained from non-living sources were called inorganic. For example, the acetic acid (from vinegars) and tartaric acid (from grapes) were called organic, whereas the marbles (from rocks) and sodium chloride (from rocks) were called inorganic.

Today organic compounds are the chemical compounds containing carbon and many other elements such as hydrogen, oxygen, nitrogen, sulphur, phosphorus and the

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halogens. A small number of carbon containing compounds not categorized as organic include carbonates, bicarbonates, carbides, cyanides, cyanates, CO, CO_2 and CS_2. Carbon is the major element in organic compounds. Carbon is highly essential to life. All living things such as plants, animals, fungi and micro-organism on earth are made of carbon compounds. Because of the great variety of ways that carbon can link with itself and other elements, there are more than 16 million carbon containing compounds. Chemists make thousands of new compounds every year, about more than 90% of them contain carbon. Much more than half of the world's chemists are organic chemists.

A somewhat more useful definition of organic compounds is: the hydrocarbons and their derivatives are called organic compounds. The compounds that contain carbon and hydrogen atoms are called hydrocarbons and the compounds that contain oxygen, nitrogen, sulphur, phosphorus and the halogens along with carbon and hydrogen are called derivatives of hydrocarbons.

Definition of organic chemistry

The branch of chemistry in which we study about hydrocarbons and their derivatives is called organic chemistry.

15.1 Sources of Organic Compounds

There are two main sources of organic compounds: (i) natural sources and (ii) synthetic sources. Natural organic compounds are present in our earth throughout our environment and they do not need to be made whereas the synthetic organic compounds are man-made and they do not occur naturally in the environment. The natural sources of organic compounds are: (i) fossil remains i.e. coal, petroleum and natural gas (ii) Plants (iii) animals.

15.1.1 Fossil Remains: Coal, Petroleum, Natural Gas

There are three major types of fossil remains: coal, petroleum and natural gas. They are formed by long time (over millions of years) decay of plants and animals.

Coal

Coal is a major source of organic compounds. It is a black solid fuel found under the earth. It is formed by decay of plants which were buried under the surface of earth for hundred millions (about 300 million) of years at high temperature and pressure. It yields coke (mostly carbon) and coal tar (complex mixture of organic compounds) on destructive distillation.

There are three main types of coal on the basis of carbon content that are lignite (about 70% C), bituminous (about 80% C) and anthracite (92–98% C). The

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quality of coal mainly depends on carbon content. Higher the carbon content better is the quality of coal. Older coal generally has higher carbon content than young ones.

Petroleum

Petroleum is the major sources of organic compounds. Petroleum (Latin: petra= rock, oleum = oil) is formed by bacterial decomposition of plants and animals buried deep under porous rocks due to pressure and heat. The deposits of petroleum are comparatively younger than coal. It is a mixture of gaseous and liquid hydrocarbons. Petroleum on fractional distillation yields gasoline, kerosene, diesel, lubricating oil, paraffin waxes etc.

Natural Gas

Natural gas is also the major sources of organic compounds. It is a mixture of low molecular mass hydrocarbons such as methane, ethane, propane and butane. Methane is nearly 85% while other compounds are present in very small amounts. It is formed by decay of organic matter. It is found in porous rocks near petroleum deposits.

15.1.2 Plants and Natural Products Chemistry

Plants and animals are the major sources of organic compounds. Many organic compounds are obtained directly from plants and animals by using suitable methods of isolation. The compounds that are obtained from living organisms (plants and animals) are called natural products and the study of such compounds is called natural product chemistry. The important natural products that are obtained from animals are proteins, hormones, animal fats, urea, insulin and the important natural products that are obtained from plants are carbohydrates (cellulose, sugars, starches), vitamins, alcohols, acetone, acids, esters, vegetable oil, dyes, drugs, perfumes and fibres (cotton, jute).

Society, Technology and Science

Important Medicines Obtained from Plants

Many plants are used to extract medicines. These medicines are useful in treating many diseases. Medicines obtained from plants are used in Ayurveda, Unani and Siddha systems of medicines. The ancient Chinese, Egyptians and Native Americans all used medicinal plants for the treatment of diseases. Some important medicinal plants, names of medicines and their uses are:

Medicine	Use	Medicinal Plants
Caffeine	CNS stimulant	Tea leaves, coffee beans, kola nuts, etc.
Aspirin	Analgesic, antipyretic	Willow tree and bark
Quinine	Antimalarial, antipyretic	Cinchona bark

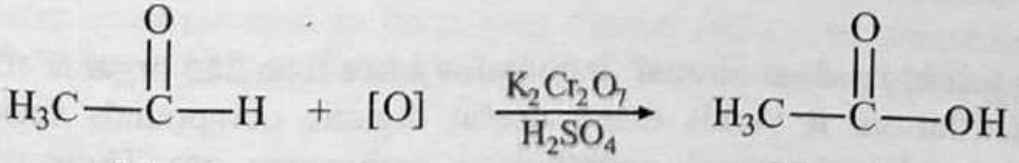
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Cocaine	Local anaesthetic	Coca plant
Ephedrine	hypotension, antihistamine	Ephedra
Morphine	Analgesic	Opium Poppy
Rutin	Treatment for capillary fragility	Citrus fruits such as orange, grapefruit, etc.
Papain	Proteolytic, mucolytic	Papaya
Nicotine	Neuroprotective, anti-inflammatory, insecticide	Tobacco
Menthol	Rubefacient	Mint
Gossypol	Male contraceptive	Cotton
Camphor	Rubefacient	Camphor tree
Bromelain	Anti-inflammatory, proteolytic	Pineapple
Senna glycoside	Laxative	Cinnamon

15.1.3 Partial and Total Synthesis

Many useful organic compounds including ether, glycol, drugs, rubber, fibres, dyes, plastics etc. are synthesized in the laboratory. Now-a-days synthesis is the most important source of organic compounds. The organic compounds that are synthesized in the laboratory are called synthetic compounds and the study of chemistry of such compounds is called synthetic chemistry.

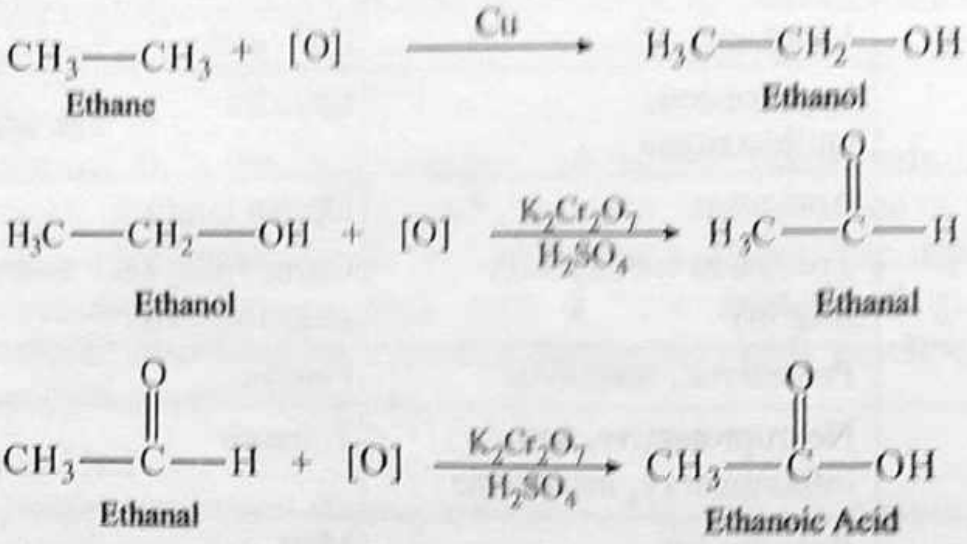
Organic compounds can be synthesized either through partial synthesis or through total synthesis. The difference between partial and total synthesis is the starting material. In partial synthesis (semi-synthesis), the desired product is obtained from an intermediate product of reaction. For example, carboxylic acid is obtained by the oxidation of aldehyde by passing the oxidation of alkane and alcohol.



Ethanal Ethanoic Acid

However, in total synthesis the starting material converts through various steps into desired product. For example, carboxylic acid can be obtained by the oxidation of alkane through various steps.

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15.1.4 Products of Biotechnology

Biotechnology involves the use of living organisms' especially microorganisms or other biological systems in the manufacture of products or in industrial, agricultural, medical and technological applications. The compounds that are obtained by means of biotechnology are called products of biotechnology. Some of the important products of biotechnology are ethylene glycol, ethyl alcohol, hormones, acids, vitamins, vaccines, antibiotics, etc.

15.2 Coal as a Source of Organic Compounds

Coal is a most important source of organic compounds.

15.2.1 Destructive Distillation of Coal

When coal is heated strongly at 500–1000°C, in the absence of air, it is converted into various useful organic and inorganic products. This process is called destructive distillation of coal. The major products of coal are: coal gas, coal tar, ammoniacal liquor, and coke.

Coal Gas

It is mixture of hydrogen (H_2), methane (CH_4), carbon monoxide (CO) and other gases. It is an excellent fuel. In the past, it was used for domestic cooking and lighting. Nowadays it is used as fuel in industries.

Coal Tar

It is a liquid product of coal. It contains more than 215 organic compounds. On fractional distillation, it yields many useful organic compounds such as benzene, toluene, xylene, phenol, cresol, naphthalene, anthracene, etc. These compounds are used in the manufacture of explosives, pesticides, perfumes, synthetic fibres, naphthalene balls, dyes and paints. Now a days these compounds are generally obtained from petroleum. The residue left is called pitch and is used for metalling of roads and as a binder for roof making.

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Ammoniacal liquor

Ammonium compounds are obtained during the destructive distillation of coal. When dissolved in water, they produce ammoniacal liquor. It is used for making nitrogenous fertilizers such as ammonium sulphate, ammonium superphosphate etc.

Coke

It is a solid product. It is an almost pure form of carbon. It is an excellent fuel and burns without smoke. It is used in the manufacture of steel, calcium carbide, graphite, silicon carbide, and carbon disulphide as a reducing agent. It can also be used for making fuel gases such as water gas ($CO + H_2$) and producer gas ($CO + 2N_2$).

15.2.2 Conversion of Coal to Petroleum

The coal can be converted into a liquid fuel such as gasoline, kerosene or diesel through Fischer-Tropsch process. In this process, the coal gas that is obtained during the destructive distillation of coal, is converted into high quality, ultraclean liquid fuel products. The Fischer–Tropsch process is a collection of chemical reactions that converts a water gas into liquid hydrocarbons. The water gas is mixed with half of its volume of hydrogen. These reactions occur at temperatures of 150–300°C and pressures of 1 to 10 atmosphere in the presence of certain metal catalysts (cobalt, iron, nickel and ruthenium).

$$\underset{\text{(Water Gas)}}{CO + H_2} \xrightarrow{\text{Cobalt}} \text{Mixture of hydrocarbons} + H_2O$$

Liquid coal can become a petroleum substitute (gasoline, kerosene or diesel) and can be used in the transportation industry. It is used in synthetic lubricants and synthetic waxes.

15.3 Characteristic of Organic Compounds

Organic compounds, in the same way as inorganic compounds, obey all the fundamental laws of chemistry. There is no clear cut division in the properties among organic and inorganic compounds. It is, therefore, difficult to isolate the properties of organic compounds from inorganic compounds. However, organic compounds are studied as a separate branch of chemistry due to the following reasons:

Catenation

The self-linking property of an element by which an atom combines with the other atoms of the same element to form long chains and cyclic structures is called catenation. Carbon has ability to form long chains, loops, sheets, and rings of carbon atoms.

Isomerism

Carbon atoms combine with other atoms in different ways to form different compounds. Such compounds have same molecular formula but different structural formulas. This process is called isomerism. Organic compounds show the phenomenon of isomerism.

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Non-polar Character

Most of the organic compounds are non-polar and poor conductors of heat and electricity.

Solubility

Most of the organic compounds do not dissolve in water (polar solvents) but dissolve in non-polar solvents like ether, benzene, alcohol, acetone, etc.

Rate of Reactions

Organic compounds are generally covalent and hence their reactions are usually slow. They usually need heating, thoroughly mixing and catalyst to speed up the reaction.

Melting and Boiling Points

They generally have low melting and boiling points. This is due to the presence of weak intermolecular forces.

Flammability

They are generally volatile and flammable. Thus, many of fuel like natural gas, coal, wood, oil are all flammable and provides energy to us in the form of heat and light.

Stability

Most of the organic compounds are thermally unstable and decompose on heating (above 500°C).

15.4 Uses of Organic Compounds

Organic compounds play an important role in our daily life. The food we eat, the clothes we wear, the medicines we take for cure of disease, the paper we write on, the cosmetic we use for makeup, the soaps we use for washing the clothes are all organic compounds. The importance of organic compounds in our daily use is illustrated by the following list:

i) **Food:** Proteins, Carbohydrates, Fats, etc.
ii) **Clothes:** Cotton, Silk, Wool, Nylon, Rayon, etc.
iii) **Fuels:** Wood, Coal, Natural gas, etc.
iv) **Medicines and Drugs:** Penicillin, Aspirin, Cocaine, Morphine, etc.
v) **Insecticides and Herbicides:** DDT, Malathion, Treflan, etc.
vi) **Dyes:** Indigo, Alizarin, Malachite green, etc.
vii) **Explosives:** Trinitrotoluene (TNT), Nitroglycerine, etc.
viii) **Daily life Materials:** Soaps, Detergents, Perfumes, Flavours, Cosmetics, Plastics, Rubber, Resins, Paints, Varnishes, Inks, Leather, Preservatives, Fertilizers, etc.

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15.5 New Allotrope of Carbon: Bucky balls (Fullerenes)

Until the mid-1980s, the scientists thought that the pure carbon exist in only two allotropic forms i.e. diamond and graphite. In 1985, the new allotropic form of carbon i.e. the buckminsterfullerene, commonly known as a "buckyball." was discovered by Richard Smalley, Robert Curl and Harry Kroto. Chemists worked with various models of carbon structures until they determined that 60 carbons were most stable when joined together in a shape that resembles a soccer ball. They proposed that the structure of the buckyball (C_{60}) was identical to that of a soccer ball, with 32 faces, 12 of them pentagons and 20 hexagons. Fullerenes (Bucky balls) consist of molecules composed entirely of carbon atoms arranged in the form of hollow spheres, ellipsoids or tubes. Each molecule generally has both pentagonal and hexagonal faces. The 1996 Nobel Prize in Chemistry was awarded to Robert Curl, Richard Smalley and Harold Kroto for their discovery of a third allotropic form of carbon, buckminsterfullerene. The smallest member of bucky ball has 20 carbon atoms (C_{20}). The fullerenes up to 100 carbon atoms are commonly obtained. The largest member of fullerenes has more than 600 carbon atoms. The most common bucky ball is C_{60}. Fullerenes are rare in nature. Small amounts of the fullerenes (bucky balls), in the form of C_{60}, C_{70}, C_{76}, C_{82} and C_{84} molecules, are produced in nature, have been found in soot and in the residue of carbon arc lamp. They are also formed by lightning discharges in the atmosphere. Bucky balls are a new family of aromatic organic molecules. They are soft like graphite.

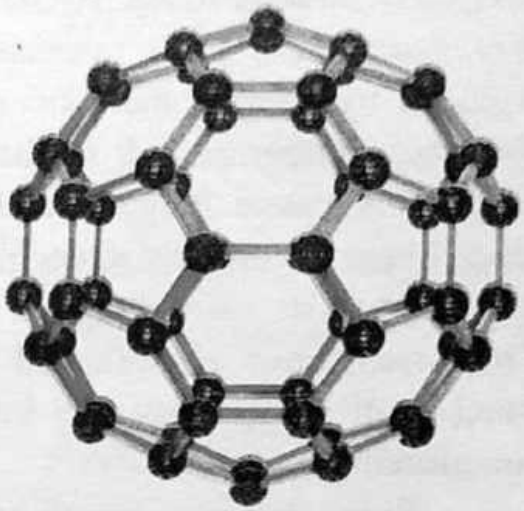


Figure 15.1: Buckyball C_{60}

15.6 Functional Groups and Homologous Series

Functional Groups

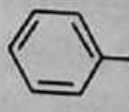
Carbon forms millions of different organic compounds. It is difficult to study the properties of such a large number of organic compounds. Hence, a system is necessary for grouping of these compounds in an organized way. The organic compounds, are therefore, divided into different families on the basis of functional groups in order to make their study easy. A functional group is an atom or group of atoms in a molecule that is mainly responsible for the chemical behaviour of the molecule. Double and triple bonds are functional groups. Different compounds that contain the same functional groups have similar chemical properties, regardless of the

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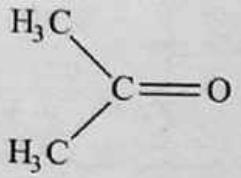
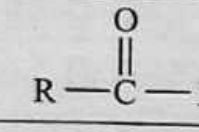
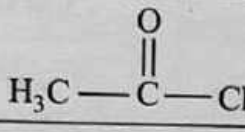
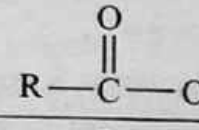
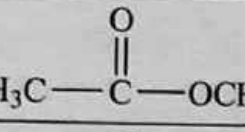
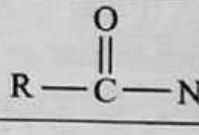
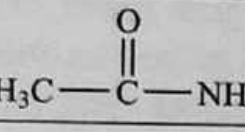
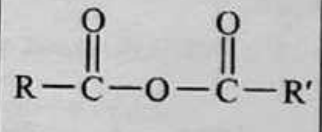
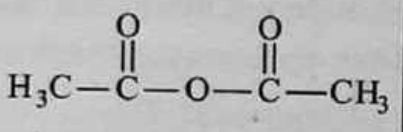
compound of which it is a part. For example, the chemical properties of methanol (CH_3OH), ethanol (CH_3CH_2OH), and propanol ($CH_3CH_2CH_2OH$) are similar because they contain the same functional group (—OH group). If one functional group is replaced by another the properties of molecule will also change. For example, the chemical properties of methanol (CH_3OH) and methanoic acid (HCOOH) are different because they have different functional groups. Functional group is the reactive part of organic molecule; while the hydrocarbon portion is inert. A compound that has two or more than two functional groups is called polyfunctional compound. They may have complicated properties because the chemical behaviour of one functional group may be influenced significantly by the presence of another functional group.

Some common functional groups and classes of organic compounds are given in the table.

Table 15.1: Common Functional Groups in Organic Compounds for Nomenclature

Class	General Formula	Examples	IUPAC Name	Suffix / Prefix
Hydrocarbons				
Alkanes	R—H	$CH_3—CH_3$	Ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	Ethene	-ene
Alkynes	$RC{\equiv}CR'$	$CH{\equiv}CH$	Ethyne	(-yne)
Arenes	Ar—H		Benzene	-ene
Halogen-containing Compounds				
Alkyl halides	R—X	$CH_3—CH_2Cl$	Chloroethane	halo-
Oxygen Containing Compounds				
Alcohols	R—OH	$CH_3CH_2—OH$	Ethanol	-ol
Phenols	Ar—OH		Phenol	-ol
Ethers	R—O—R	$CH_3—O—CH_3$	Methoxymethane	
Aldehydes	R—CHO	$CH_3—CHO$	Ethanal	-al

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Ketones	$RR'C{=}O$		2-Propanone	-one
Carboxylic acids	$R{-}COOH$	$CH_3{-}COOH$	Ethanoic acid	-oic acid
Carboxylic Acid Derivatives				
Acyl halides			Ethanoyl chloride	-oyl halide
Esters			Methyl ethanoate	-oate
Amides			Ethanamide	-amide
Acid anhydrides			Ethanoic anhydride	-oic anhydride
Nitrogen Containing Compounds				
Amines	$R{-}NH_2$	$H_3C{-}NH_2$	Methanamine	-amine

Homologous Series

A group of organic compounds in which each member differs from the next member by a methylene group ($-CH_2-$) is called homologous series. The members of homologous series are called homologs. For example, butane ($CH_3CH_2CH_2CH_3$) and pentane ($CH_3CH_2CH_2CH_2CH_3$) are homologs.

Table 15.2: The Homologous Series of Alkanes

Name of Alkanes	Number of C Atoms	Molecular Formula	Condensed Structural Formula
Methane	1	CH_4	CH_4
Ethane	2	C_2H_6	CH_3CH_3
Propane	3	C_3H_8	$CH_3CH_2CH_3$
Butane	4	C_4H_{10}	$CH_3(CH_2)_2CH_3$
Pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$

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Name of Alkanes	Number of C Atoms	Molecular Formula	Condensed Structural Formula
Hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$
Heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$
Octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$
Nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$
Decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$

General Characteristics of Homologous Series

i) All the members of homologous series have same structural formula.
ii) All the members of homologous series have same functional groups.
iii) They have similar chemical properties due to same functional groups.
iv) They have different physical properties because different members of homologous series have different molecular masses.
v) The molecular mass of the successive members of a homologous series differ by 14 unit ($CH_2 = 12 + 2 = 14$).
vi) The molecular formula of each successive homolog differs by a CH_2 group.
vii) All compounds in the series have same type of elements.
viii) All the members of homologous series are prepared by the same methods.
ix) All the members of homologous series are represented by the same general formula. For example:

Alkane: C_nH_{2n+2}

Alkene: C_nH_{2n}

Alkyne: C_nH_{2n-2}

Alcohol: $C_nH_{2n+1}OH$

Alkyl Halide: $C_nH_{2n+1}X$

Where 'n' is number of carbon atoms.

15.7 Detection of Elements in Organic Compounds

All the organic compounds contain carbon and most of the organic compounds (except CCl_4, CS_2, etc.) contain hydrogen. Oxygen is generally present in organic compounds. In addition to carbon, hydrogen, and oxygen other elements which are less commonly present in organic compounds are nitrogen, sulphur, halogens and phosphorus. Some metals like sodium, calcium, iron, magnesium, and copper are also present in some organic compounds but they are rare. Since, nearly all the organic compounds contain carbon as well as hydrogen and it is usually not necessary to test

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the presence of these two elements. There is no direct method for the detection of oxygen. The presence of other elements which are less commonly present are usually detected by Lassaigne's Test.

Preparation of Lassaigne's Solution for the detection of Nitrogen, Halogens and Sulphur

Take a small piece of freshly cut sodium metal (pea size) in a fusion tube. Heat the tube with a flame until the sodium melts. Then add a small amount of unknown organic compound. Heat the tube first gently and then strongly till its bottom become red hot. The red hot tube is then plunged into a china dish containing about 10-15 mL of cold distilled water. The contents are crushed, boiled and then filtered. The filtrate obtained is called Lassaigne's solution or sodium extract. The fusion reactions are shown by the following equations:

$Na + C + N \longrightarrow NaCN$ (Sodium cyanide)

$Na + C + N + S \longrightarrow NaCNS$ (Sodium sulphocyanide)

$2Na + S \longrightarrow Na_2S$ (Sodium sulphide)

$Na + X \longrightarrow NaX$ (Sodium halide)

Caution

- Never touch sodium metal with your fingers, use forceps.
- Sodium metal reacts violently with water and it cause serious burns.
- Carry out the fusion reaction in the hood and wear safety googles.

The Lassaigne's solution is divided into four portions and is used for the detection of nitrogen, sulphur and halogens (Cl, Br and I).

Detection of Nitrogen

The sodium extract is boiled with freshly prepared ferrous sulphate solution in the presence of a little sodium hydroxide solution. The mixture is cooled and then a few drops of ferric chloride solution and excess of conc. hydrochloric acid are added to it. The formation of a green or Prussian blue colour confirms the presence of nitrogen in an organic compound. The reactions are shown by the following equations:

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$\underset{\text{(Green ppt.)}}{Fe(OH)_2} + \underset{\text{(From sod.extract)}}{6NaCN} \longrightarrow \underset{\text{(Sod.ferrocyanide)}}{Na_4[Fe(CN)_6]} + 2NaOH$$

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\substack{\text{(Ferric ferrocyanide)}\\ \text{(Prussian Blue)}}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

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Keep in Mind

It is noted that when sulphur is present along with nitrogen in the given organic compound, a blood red colouration of ferric sulphocyanide is obtained.

$$3NaCNS + FeCl_3 \longrightarrow \underset{\text{(Ferric sulphocyanide)}}{Fe(CNS)_3} + 3NaCl$$

(Blood Red Colouration)

Detection of Sulphur

Sodium Nitroprusside Test

Sodium nitroprusside solution is added to the sodium extract. The formation of deep violet colour confirms the presence of sulphur in the given organic compound.

$$2Na + S \longrightarrow Na_2S$$

$$Na_2S + \underset{\text{(Sodium nitroprusside)}}{Na_2[Fe(CN)_5 NO]} \longrightarrow \underset{\text{(Deep violet colouration)}}{Na_4[Fe(CN)_5 NOS]}$$

Lead Acetate Test

Freshly prepared lead acetate solution is added to the sodium extract in the presence of dilute acetic acid. The formation of black ppt. of lead sulphide confirms the presence of sulphur in the given organic compound.

$$Na_2S + (CH_3COO)_2 Pb \longrightarrow \underset{\text{(Black ppt.)}}{PbS} + 2CH_3COONa$$

Detection of Halogens

The sodium extract is boiled with concentrated nitric acid for some time (to expel the HCN or H_2S if produced that would otherwise give a white ppt. of silver cyanide or a black ppt. of silver sulphide with silver nitrate that is needed for identification of halogen). Cool the mixture and add silver nitrate solution to it. The formation of: (i) white precipitate, soluble in cold ammonium hydroxide, indicates the presence of chlorine (ii) light yellow precipitate, sparingly soluble in cold ammonium hydroxide and soluble in hot conc. ammonium hydroxide, indicates the presence of bromine while (iii) yellow precipitate, insoluble in ammonium hydroxide, indicates the presence of iodine in the given organic compound.

The reactions are shown by the following equations:

$$2Na + X_2 \longrightarrow 2NaX$$

$$NaX + AgNO_3 \longrightarrow AgX\downarrow + NaNO_3$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{(Soluble)}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

$$AgBr + 2NH_4OH \longrightarrow \underset{\text{(Sparingly Soluble)}}{[Ag(NH_3)_2]Br} + 2H_2O$$

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Summary of Facts and Concepts

- Organic chemistry is the sturdy of hydrocarbons and their derivatives.
- Chemical compounds were generally classified as organic and inorganic on the basis of their origin. The compounds obtained from living things were called organic and those obtained from mineral sources were called inorganic.
- The natural sources of organic compounds are: (i) fossil remains i.e. coal, petroleum and natural gas (ii) Plants (iii) animals.
- The abundance of organic compounds is mainly due to unique behaviour of carbon.
- Most of commercially important products such as carbohydrates, proteins, nylon, natural gas, aspirin, penicillin, treflan, TNT, soaps, detergents, perfumes, flavours, plastics, rubber, paper, paints, etc. are organic in nature.
- Bucky ball is the allotropic form of carbon consisting of molecules composed entirely of carbon atoms arranged in the form of hollow spheres, ellipsoids or tubes. Each molecule generally has both pentagonal and hexagonal faces.
- A functional group is an atom or group of atoms in a molecule that is mainly responsible for the chemical behaviour of the molecule. Functional group is the active part of organic compounds. Different compounds that contain the same functional groups have similar chemical properties, regardless of the compound of which it is a part.
- A group of organic compounds in which each member differs from the next member by a methylene group (—CH_2—) is called homologous series. The members of homologous series are called homologs. For example, ethane (C_2H_6) and propane (C_3H_8) are homologs.

Multiple Choice Questions

Select one answer from the given choices for each question:

) The conversion of coal into petroleum products is carried out by
   a) Fischer-wood process
   b) Fischer-Tropsch process
   c) Brikeland-Eyde's process
   d) Landler process

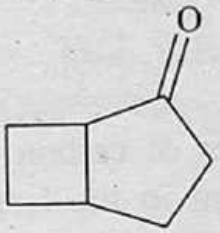
i) Organic compounds that show weak attractive forces have:
   a) High boiling points
   b) High melting points
   c) Low melting points
   d) Low vapour pressure

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ii) Bucky ball consist of commonly
   a) C_{60}, having 30 faces (20 hexagonal and 10 pentagonal)
   b) C_{60}, having 32 faces (20 hexagonal and 12 pentagonal)
   c) C_{60}, having 60 faces (40 hexagonal and 20 pentagonal)
   d) C_{60}, having 62 faces (40 hexagonal and 22 pentagonal)

iv) All the members of homologous series have:
   a) Different types of elements
   b) Different physical properties
   c) Different chemical properties
   d) Different functional groups

v) Which type of functional group is present in the given compound

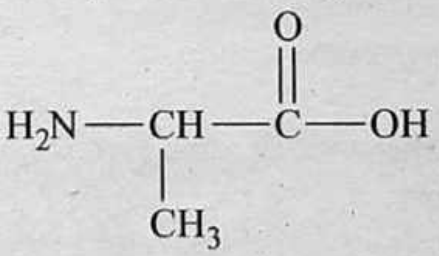


   a) Carboxylic acid
   b) Aldehyde
   c) Ketone
   d) Acid amide

vi) Homologous compounds differ from each other by
   a) Alkyl group
   b) Methylene group
   c) Methine group
   d) Methyl group

vii) When hydrogen is removed from alkanes, the product obtained has general formula
   a) C_nH_{2n+2}
   b) C_nH_{2n-2}
   c) C_nH_{2n+1}
   d) C_nH_{2n-1}

viii) Which functional groups are present in the given amino acids:



   a) Amino and hydroxyl group
   b) Amino and alcoholic group

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c) Amino and carboxylic acid group
d) Amino, carboxylic acid and alkyl group

ix) When nitrogen containing compounds are treated with Lassaigne' solution, the solution obtained is of :
a) Red colour
b) Prussian blue colour
c) Mixture of blue and green colour
d) Black colour

x) Black colour solution is obtained when sulphur containing compounds are treated with:
a) Sodium nitroprusside solution
b) Lead acetate solution
c) Tollens reagent
d) Both a and b

Short Answer Questions

Q.1. Where natural gas is usually found? Give its two important uses.
Q.2. What are the uses of coal tar?
Q.3. What is coke? What are its uses?
Q.4. Who discovered the bucky ball? How many sides are there on a bucky ball?
Q.5. What is the geometrical shape of a bucky ball?
Q.6. Can a bucky ball conduct electricity?
Q.7. Define synthetic compounds and synthetic chemistry.
Q.8. What are the two main functional groups found in amino acids?
Q.9. Why sodium metal is stored in kerosene oil?
Q.10. Why are organic compounds fused with sodium metal for preparing Lassaigne's solution?
Q.11. Why solution of ferrous sulphate is freshly prepared during detection of nitrogen?

Long Answer Questions

Q.1. Define organic chemistry. What is the importance of organic chemistry in our daily life?
Q.2. Define organic compounds. What are the uses of organic compounds?
Q.3. What are the natural sources of organic compounds? Explain.
Q.4. What are the common varieties of coal? Which variety of coal has the highest carbon content?

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Q.5. Define natural product chemistry and describe the use of plants and animals as a source of organic compounds.

Q.6. Describe the synthesis of organic compounds in the lab. What is partial and total synthesis?

Q.7. What do you know about products of biotechnology?

Q.8. What do you know about destructive distillation of coal? What are the various products obtained from it? Discuss.

Q.9. How can coal be converted into petroleum? Discuss briefly.

Q.10. What are the important characteristics of organic compounds?

Q.11. Define and explain bucky ball.

Q.12. Define functional group. How does a functional group affect the properties of an organic compound? Give common examples of functional groups.

Q.13. What is meant by homologous series of carbon compounds? Give homologous series of alkanes.

Q.14. What are the general features of homologous series?

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Chapter 16

Hydrocarbons

Major Concepts

16.1 Hydrocarbons
16.2 Alkanes and Cycloalkanes
16.3 Radical Substitution Reactions
16.4 Oxidation of Organic Compounds
16.5 Alkenes
16.6 Isomerism
16.7 Alkynes
16.8 Addition Reactions of Alkynes
16.9 Benzenes and Substituted Benzenes

Learning Outcomes:

Students will be able to:

- Classify hydrocarbons as aliphatic and aromatic. **(Understanding)**
- Describe nomenclature of alkanes and cycloalkanes. **(Understanding)**
- Explain the shapes of alkanes and cycloalkanes exemplified by ethane and cyclopropane. **(Applying)**
- Explain unreative nature of alkanes towards polar reagents. **(Applying)**
- Define homolytic and heterolytic fission, free radical initiation, propagation and termination. **(Remembering)**
- Describe the mechanism of free radical substitution in alkanes exemplified by methane and ethane. **(Understanding)**
- Identify organic redox reactions. **(Understanding)**
- Explain what is meant by a chiral centre and show that such a centre gives rise to optical isomerism. **(Understanding)**
- Identify chiral centers in given structural formula of a molecule. **(Analyzing)**
- Explain the nomenclature of alkenes. **(Understanding)**
- Explain shape of ethene molecule in terms of sigma and pi C—C bonds. **(Understanding)**
- Describe the structure and reactivity of alkenes as exemplified by ethene. **(Applying)**
- Define and explain with suitable examples the terms isomerism, stereoisomerism and structural isomerism. **(Remembering)**
- Explain dehydration of alcohols and dehydrohalogenation of RX for the preparation of ethene. **(Understanding)**
- Describe the chemistry of alkenes by the following reactions of ethene:
  Hydrogenation, hydrohalogenation, hydration, halogenation, halohydration,

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epoxidation, ozonolysis, polymerization. **(Understanding)**

- Explain the concept of conjugation in alkenes having alternate double bonds. **(Understanding)**
- Use the IUPAC naming system for alkenes. **(Applying)**
- Explain the shape of benzene molecule (molecular orbital aspect). **(Understanding)**
- Define resonance, resonance energy and relative stability. **(Understanding)**
- Compare the reactivity of benzene with alkanes and alkenes. **(Applying)**
- Describe what is meant by the term delocalized electrons in the context of the benzene ring. **(Understanding)**
- Describe addition reactions of benzene and methyl benzene. **(Applying)**
- Describe the mechanism of electrophilic substitution in benzene. **(Understanding)**
- Discuss chemistry of benzene and methyl benzene by nitration, sulphonation, halogenation, Friedal Craft's alkylation and acylation. **(Applying)**
- Apply the knowledge of positions of substituents in the electrophilic substitution of benzene. **(Applying)**
- Use the IUPAC naming system for alkynes. **(Applying)**
- Compare the reactivity of alkynes with alkanes, alkenes and arenes. **(Analyzing)**
- Discuss the shape of alkynes in terms of sigma and pi C-C bonds. **(Applying)**
- Describe the preparation of alkynes using elimination reactions. **(Applying)**
- Describe acidity of alkynes. **(Understanding)**
- Discuss chemistry of alkynes by hydrogenation, hydrohalogenation, hydration, bromination, ozonolysis, and reaction with metals. **(Understanding)**
- Describe and differentiate between substitution and addition reactions. **(Understanding)**
- Explain isomerism in alkanes, alkenes, alkynes and substituted benzene. **(Understanding)**

Introduction

Hydrocarbons are the simplest organic compounds composed of only carbon and hydrogen atoms. The carbon and hydrogen atoms are bonded to each other by covalent bonds. Examples are: methane (CH_4), ethylene (C_2H_4), acetylene (C_2H_2), benzene (C_6H_6) etc. Hydrocarbons are further classified as aliphatic or aromatic hydrocarbons depending on the presence of benzene ring.

16.1 Types of Hydrocarbons

There are two types of hydrocarbons:

i) Aliphatic hydrocarbons and
ii) Aromatic hydrocarbons.

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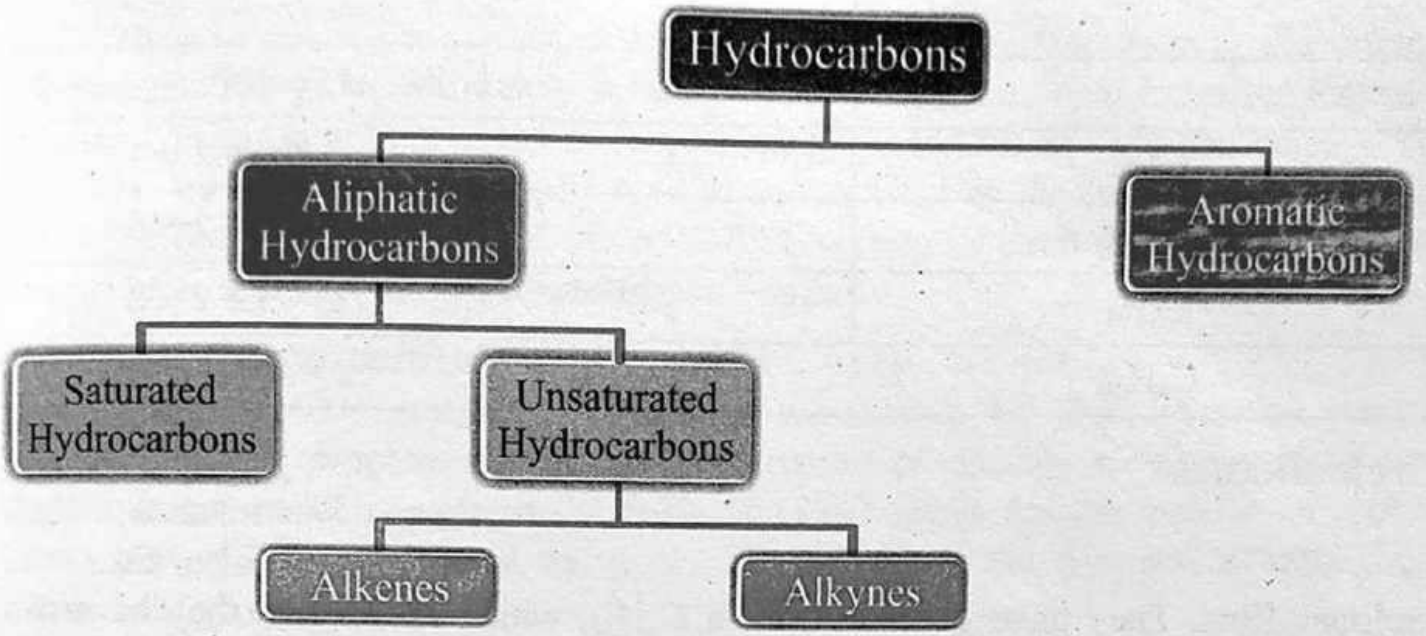


Figure 16.1: Classification of Hydrocarbons

Aliphatic Hydrocarbons

Hydrocarbons that are straight chained, branched or non-aromatic are called aliphatic hydrocarbons. They may also be linear or cyclic. Most of the aliphatic hydrocarbons are volatile and flammable. They may be classified as saturated or unsaturated.

Keep in Mind

In a straight chain compound, the carbon atom is never bonded to more than two carbon atoms. In branched compound, the carbon atom may be bonded to three or four carbon atoms at a time.

Saturated hydrocarbons contain only single bonds between carbon atoms. These hydrocarbons include alkanes and cycloalkanes. **Unsaturated hydrocarbons** have at least one double or triple bond between two carbon atoms. These hydrocarbons include alkenes and alkynes.

Aromatic Hydrocarbons

Hydrocarbons which have at least one benzene ring in their structures are called aromatic hydrocarbons.

16.2 Alkanes and Cycloalkanes

Alkanes

Hydrocarbons that contain only single bonds between carbon atoms are called alkanes. They are also known as paraffins. The word paraffin is derived from the Latin words "parum" meaning "little", and "affin", meaning "affinity". Thus the combination of words means "little affinity" or "the least reactive". Petroleum and natural gas are usually composed of alkanes. They have general formula C_2H_{2n+2}, where n is the number of carbon atoms for each molecule.

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Table 16.1: The Calculation of Number of Carbon and Hydrogen Atoms

Molecular Formula of Alkanes	No. of C-atoms = n	No. of H-atoms = 2n + 2
CH_4	1	$2 \times 1 + 2 = 4$
C_2H_6	2	$2 \times 2 + 2 = 6$
C_3H_8	3	$2 \times 3 + 2 = 8$
C_4H_{10}	4	$2 \times 4 + 2 = 10$

Cycloalkanes

The saturated hydrocarbons in which the carbon atoms are linked by single covalent bonds to form a ring are called cycloalkanes. They are also known as cycloparaffins. They have general formula C_nH_{2n}, which shows that they have two hydrogen atoms less than the corresponding alkanes due to ring structure.

16.2.1 Nomenclature

System of naming compounds is called nomenclature. There are two main systems for naming of organic compounds:

(i) Common System
(ii) IUPAC System

(i) Common System

In the early days, organic compounds were named according to their plant or animal sources or name of discoverer. These names are called common names. For example, methane is called marsh gas because it is found in marshy places. Acetic acid got its name from the Latin word *acetum*, which means vinegar because acetic acid is found in vinegar. The methyl alcohol is known as wood spirit because it is obtained by destructive distillation of wood. Other compounds were named by their discoverer for more personal reasons. For example, Adolf von Baeyer supposedly named barbituric acid after a woman named Barbara. Common name system does not follow rules of any formal system. Hence, it is impossible to give common names to millions of organic compounds and we cannot remember all of them by their common names. However, common names for compounds are still in wide use today.

Keep in Mind

Common names are normally beneficial when the alternate IUPAC names are lengthy and complicated. For example, it is easy to say "tartaric acid" than its IUPAC name "2,3-Dihydroxybutanedioic acid".

(ii) IUPAC System

To avoid memorizing the names of millions of organic compounds, the commission of 34 chemists from nine countries met at Geneva (Switzerland) in

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1892. They developed a system called the Geneva system for naming the organic compounds. The group ultimately became known as International Union of Pure and Applied Chemistry (abbreviated as IUPAC and pronounced as "eye-you-pack"). The IUPAC rules have been continually revised and updated by the commission since that time. The fundamental principle of the IUPAC system is: **each different compound should have a different and unambiguous name.**

16.2.1.1 Nomenclature of Straight Chain Alkanes

The first four members of alkanes are known by their common names: methane, ethane, propane and butane. The names of alkanes with more than four carbon atoms are derived from the Latin or Greek prefix for the number of carbon atoms per molecule followed by *–ane*. The names of the first ten straight-chain alkanes are given in the table below:

Table 16.2: The first 10 Straight-Chain Alkanes

IUPAC Name	Number of C-atoms	Molecular Formula	Condensed Structural Formula	Line-Angle Formula
Methane	1	CH_4	CH_4	
Ethane	2	C_2H_6	CH_3CH_3	
Propane	3	C_3H_8	$CH_3CH_2CH_3$	
Butane	4	C_4H_{10}	$CH_3(CH_2)_2CH_3$	
Pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	
Hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	
Heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	
Octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	
Nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	
Decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	

In the common system, all the isomeric alkanes have the same parent name. For example, the parent names of three isomeric C_5H_{10} alkanes are pentanes. The prefixes n, iso or neo are used to differentiate between the names of isomers.

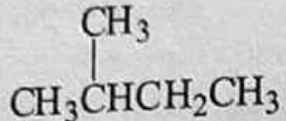
The prefix "**n-**"(or **normal**) is used for those alkane in which all carbon atoms form a continuous, unbranched chain.

$CH_3CH_2CH_2CH_2CH_3$ $\qquad$ $CH_3CH_2CH_2CH_2CH_2CH_3$

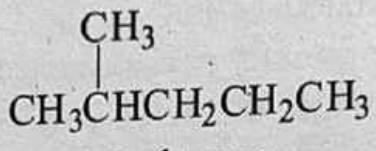
n-Pentane $\qquad$ **n**-Hexane

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The prefix "**iso-**" is used for those alkanes which have a methyl group bonded to the second carbon atom of the continuous chain.

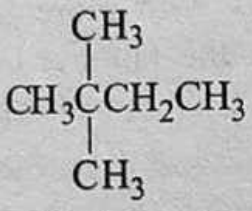


Isopentane

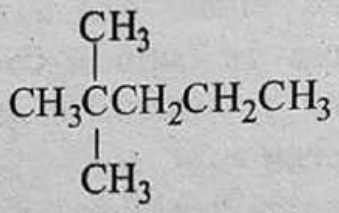


Isohexane

The prefix "**neo-**" is used for those alkanes which have two methyl groups bonded to the second carbon atom of the continuous chain.



Neohexane



Neoheptane

In the IUPAC system, the name of every organic compound has three parts: (i)root (ii) suffix and (iii) prefix. The **root** shows the number of carbon atoms in the longest continuous chain in the compound. The **suffix** shows the family of the organic compounds. The **prefix** shows the identity, position, and number of substituents attached to the carbonchain.

Table 16.3: Parts of the Name of Organic Compounds

1	2	3
Prefix	**Base or Root**	**Suffix**
What substituents?	How many carbon atoms?	Which family?

The names given in table 16.4 for the simple alkanes consist of the parent name, which shows the number of carbon atoms in the longest continuous chain, and the suffix '*-ane*' shows that the compounds are alkanes. The root name for one carbon is meth-, for two carbons is eth-, for three carbons is prop-, and so on.

Table 16.4: Parent Names for Alkanes

No. of C-atoms	Base or Root name	Parent Name
1	*Meth*	Methane
2	*Eth*	Ethane
3	*Prop*	Propane
4	*But*	Butane

No. of C-atoms	Base or Root name	Parent Name
5	*Pent*	Pentane
6	*Hex*	Hexane
7	*Hept*	Heptane
8	*Oct*	Octane

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No. of C-atoms	Base or Root name	Parent Name
9	Non	Nonane
10	*Dec*	Decane
11	*Undec*	Undecane
12	*Dodec*	Dodecane
13	*Tridec*	Tridecane
14	*Tetradec*	Tetradecane

No. of C-atoms	Base or Root name	Parent Name
15	*Pentadec*	Pentadecane
16	*Hexadec*	Hexadecane
17	*Heptadec*	Heptadecane
18	*Octadec*	Octadecane
19	*Nonadec*	Nonadecane
20	*Icos*	Icosane

Naming an Alkyl Group

The group that is formed by the removal of one hydrogen atom from an alkane is called an alkyl group. The symbol R is used to indicate an alkyl group.

$$\underset{\text{Alkane}}{R{-}H} \xrightarrow{-H} \underset{\text{Alkyl}}{R{-}}$$

Alkyl groups are named by replacing the "ane" of the alkane with "yl".

$$\underset{\text{Methane}}{CH_3{-}H} \xrightarrow{-H} \underset{\text{Methyl}}{CH_3{-}}$$

$$\underset{\text{Ethane}}{CH_3{-}CH_3} \xrightarrow{-H} \underset{\text{Ethyl}}{CH_3{-}CH_2{-}}$$

The naming of three carbon alkyl group is more difficult because the parent hydrocarbon has more than one kind of carbon atom. For example, propane has both primary and secondary carbon atoms, and removal of H-atoms from each of these carbon atoms gives a different alkyl group with a different name, n-propyl or isopropyl.

$$\underset{\text{Propane}}{CH_3{-}CH_2{-}CH_3}$$

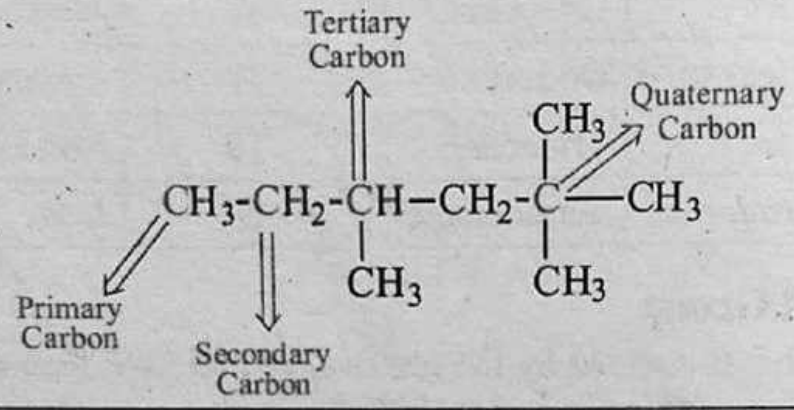
Removal of H from I° carbon | Removal of H from 2° carbon

$$\underset{\text{n-Propyl}}{CH_3{-}CH_2{-}CH_2{-}} \qquad \underset{\text{Isopropyl}}{CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3}$$

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Keep in Mind

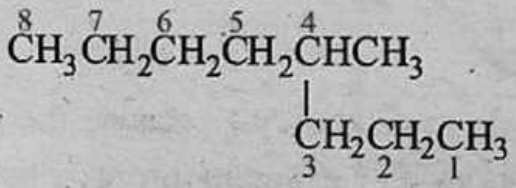
A **primary carbon** atom is directly bonded to only one other carbon atom.
A **secondary carbon** atom is directly bonded to two other carbon atoms.
A **tertiary carbon** atom is directly bonded to three other carbon atoms.
A **quaternary carbon** atom is directly bonded to four other carbon atoms.



16.2.1.2 Nomenclature of Branched Chain Alkanes

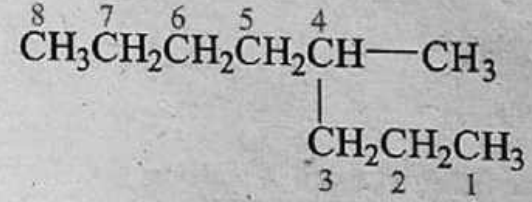
Names of branched chain alkanes are obtained by using the following IUPAC rules:

i) Select the longest continuous chain of carbon atoms and name it. This is the stem name or parent name. The longest continuous chain is not always in a straight line; sometimes you must "turn a corner" to obtain the longest continuous chain.



The parent name of the compound is octane because there are eight carbon atoms in the longest continuous chain.

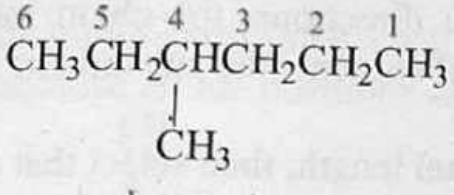
ii) Indicate the position of substituent (branch) by the number of carbon atom to which it is bonded.



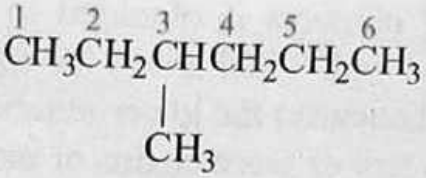
The methyl branch is bonded to carbon 4, hence the name of compound is 4-methyloctane.

iii) Number the longest chain from that end which is nearer to the substituents. Consider the two different structures for the same compound shown below:

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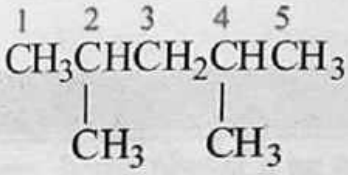
Incorrect



Correct

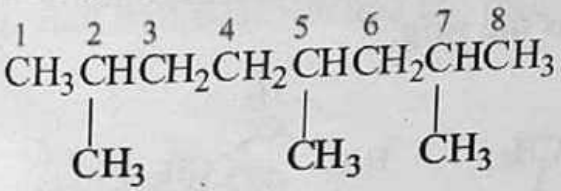
The compound on the right is numbered correctly because the methyl group is located at carbon 3 of the hexane chain; in the compound on the left, the methyl group is located at carbon 4. Thus, the name of the compound is 3-methylhexane, and not 4-methylhexane.

iv) If two or more identical substituents are bonded to the parent hydrocarbon, then the prefixes "di", "tri", "tetra", "penta" etc. are used to indicate how many identical substituent the compound has.

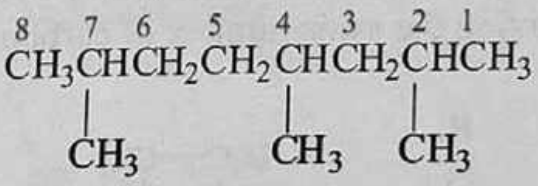


The hydrocarbon has two identical methyl groups. One methyl is bonded to carbon 2 and the other one is bonded to carbon 4. The name of compound is 2,4-**dimethyl**pentane.

v) If the first substituent has the same distance from both ends, number the chain to give the second substituent the lower number. Always look for the first point of difference in numbering from each end of the longest chain.



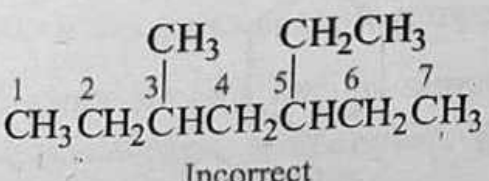
Incorrect



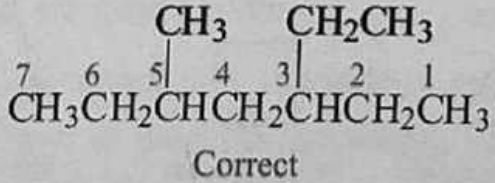
Correct

The correct name of compound is 2,4,7-**trimethyl**octane and not 2,5,7-trimethyloctane.

vi) If two or more different substituents are bonded to a parent chain, then they are named in alphabetical order, as in 3-**ethyl**-5-**methyl**heptane. The prefixes "di,""tri,""tetra," "penta," "sec," and "tert" are ignored in alphabetizing substitucnts, but the prefixes "iso" and "cyclo" are not ignored in alphabetizing.



Incorrect

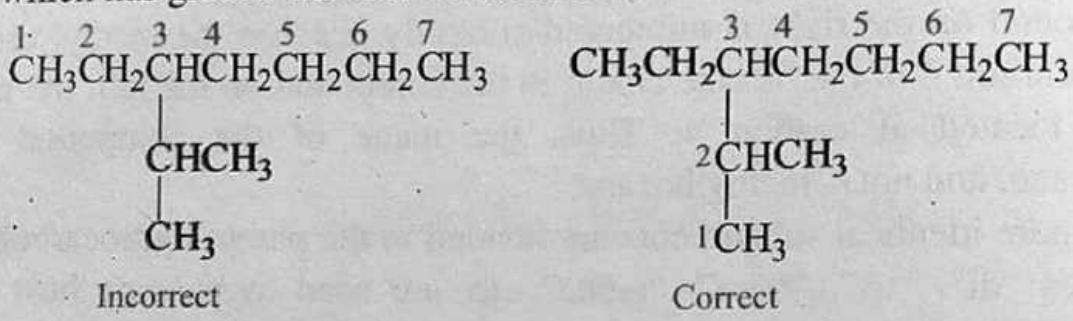


Correct

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If the same set of numbers is obtained in both directions, the chain must be numbered from that end, which gives the first substituent (the substituent which is listed first alphabetically) the lower number.

vii) If a compound has two or more chains of the equal length, then select that chain which has greater number of substituents.



Incorrect Correct

The name of this compound is 3-ethyl-2-methylheptane but not 3-isopropylheptane.

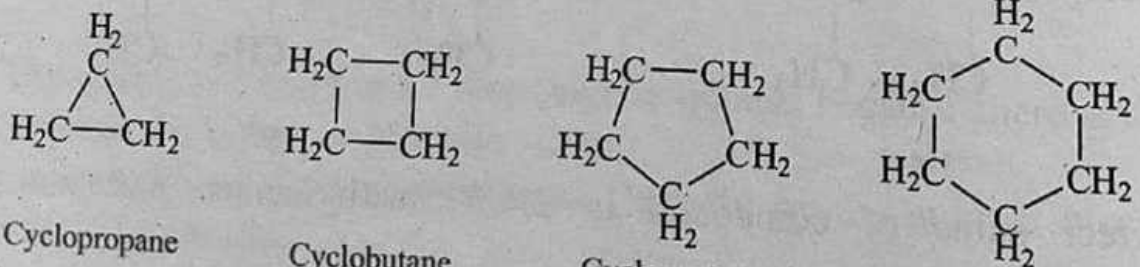
Keep in Mind

- **Note that the branch name and the parent name are written as a single word, and a hyphen follows the number.**
- **The numbers that show the positions of the identical substituents are separated from each other by commas while the number and the word are separated by a hyphen.**

16.2.1.3 Nomenclature of Cycloalkanes

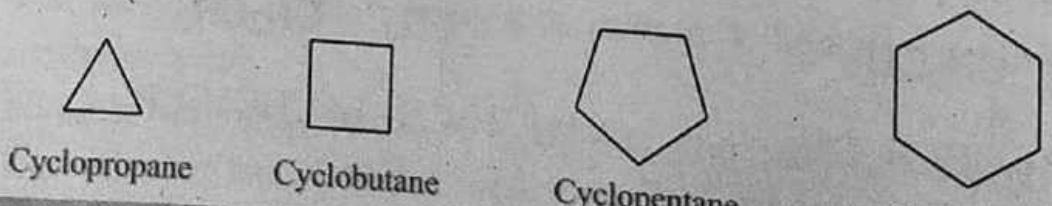
The IUPAC rules for naming cycloalkanes are as follows:

i) They are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring.



Cyclopropane Cyclobutane Cyclopentane Cyclohexane

They are often shown by simple geometric figures. Cyclopropane is shown by a triangle, cyclobutane is shown by a square, cyclopentane is shown by a pentagon and cyclohexane is shown by a hexagon. In their figures each corner shows one carbon and two hydrogen atoms.



Cyclopropane Cyclobutane Cyclopentane Cyclohexane

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iii) Alkanes having 18 or more carbon atoms are colourless waxy solids at room temperature. They are used as lubricants. Vaseline is a semisolid, made up of mixture of alkanes with more than 25 carbon atoms.

iv) They are mostly non-polar in nature and are insoluble in polar solvents like water. They are soluble in non-polar solvents like benzene, ether, carbon tetrachloride, acetone etc.

v) The boiling points and melting points of alkanes increase with the increase in the number of carbon atoms but the increase in melting point is not very regular. The boiling point increases by 20 to 30°C for addition of each methylene group ($—CH_2—$) to the molecule.

vi) The boiling points of straight chain alkanes are higher than branched chain alkanes. For example, the boiling point of n-butane (55°C) is higher than isobutane (−10.2°C).

Keep in Mind

Straight chain alkanes have higher boiling points than their corresponding branched chain alkanes. This is because straight chain alkanes have the larger surface area of contact between the molecules as compared to branched chain alkanes. With increasing surface area, the van der Waals forces between molecules increase; therefore, more energy is required to remove such molecules. As a result straight chain alkanes have higher boiling point than branched chain alkanes.

vii) The densities of alkanes increase gradually with increase in the number of carbon atoms. They have densities from 0.62g/mL to about 0.79g/mL. They are less dense than water (1.0g/mL) and therefore, float on the surface of water.

viii) The viscosity of alkanes increases with increasing molecular mass.

Table 16.5: Physical Properties of Normal Chain Alkanes

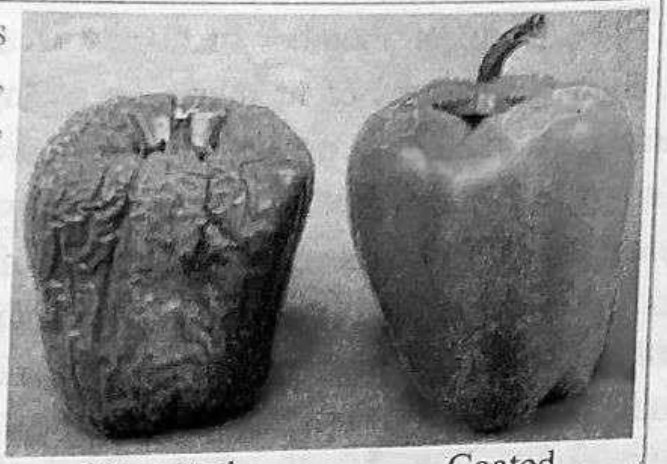
No. of Carbon Atoms	Name	Melting Point (°C)	Boiling Point (°C)	Density (g/mL)
1	Methane	−182.5	−161.7	—
2	Ethane	−183.5	−88.6	—
3	Propane	−187.7	−42.1	—
4	Butane	−138.3	−0.5	0.5787
5	Pentane	−129.8	36.1	0.5572
6	Hexane	−95.3	68.7	0.6603
7	Heptane	−90.6	98.4	0.6837
8	Octane	−56.8	125.7	0.7026
9	Nonane	−53.5	150.8	0.7177
10	Decane	−29.7	174.0	0.7299

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Interesting Information

The solid alkanes are used in waxy coatings added to fruits (apples, plums, oranges, pears, etc.) and vegetables (cucumber, turnips, green tomatoes etc.) to:

- Prevent loss of water that helps to maintain firmness and juiciness
- Improve appearance and increase visual freshness
- Slow down the natural degradation by microbes



Uncoated Coated

16.2.2.2 Physical Properties of Cycloalkanes

i) Cyclopropane and cyclobutane are gases at room temperature.

ii) Cycloalkanes having five or more carbon atoms are liquids at room temperature.

iii) Cycloalkanes are soluble in non-polar solvents like benzene, ether etc. and are insoluble in polar solvents.

iv) The melting and boiling points of cycloalkanes show gradual increase with the increase in molecular mass.

v) They have low densities like alkanes. Alkanes and cycloalkanes are the least dense of all groups of organic compounds.

vi) Liquid cycloalkanes are soluble in one another.

Table 16.6: Physical Properties of Cycloalkanes

No. of Carbon Atoms	Name	Melting Point (°C)	Boiling Point (°C)	Density (g/mL)
3	Cyclopropane	−126.6	−33	—
4	Cyclobutane	−90	13	—
5	Cyclopentane	−94	49	0.751
6	Cyclohexane	6.5	81	0.779
7	Cycloheptane	−12	118.5	0.811
8	Cyclooctane	13.5	149	0.834

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i) The carbon-hydrogen bond is the least polar.
ii) The carbon-carbon bond is completely non-polar.
iii) There is no unshared pair of electrons.
iv) There is no unsaturation point.
v) There is no electrophilic and nucleophilic centre.

16.2.5 Reactivity of Alkanes and Cycloalkanes

Alkanes have only strong sigma bonds. Furthermore, the electrons in the C—H and C—C sigma bonds are shared equally by the bonding atoms, so none of the bonding atoms in an alkane has significant charge. This means that they neither act as electrophile nor nucleophile. Because of this they are the least reactive organic compounds and they do not react with acids, bases, strong oxidizing agents or with some other reagents at room temperature. Most useful reactions of alkanes occur under drastic conditions. However alkanes show two types of reactions: (i) substitution reactions (ii) thermal and catalytic reactions. The properties of cycloalkanes are similar to those of alkanes except cyclopropane and cyclobutane. The reactivity of cyclopropane and cyclobutane is due to the largest ring strain.

16.3 Radical Substitution Reactions

A radical (free radical) is a highly reactive specie containing an atom with an unpaired electron, formed by homolysis of a covalent bond.



The products A and B are called free radicals. They are electrically neutral. They are very reactive and unstable due to incomplete octet. Radical process involves single electron, so half-headed arrows are used to show the movement of electrons. One half-headed arrow is used for each electron.

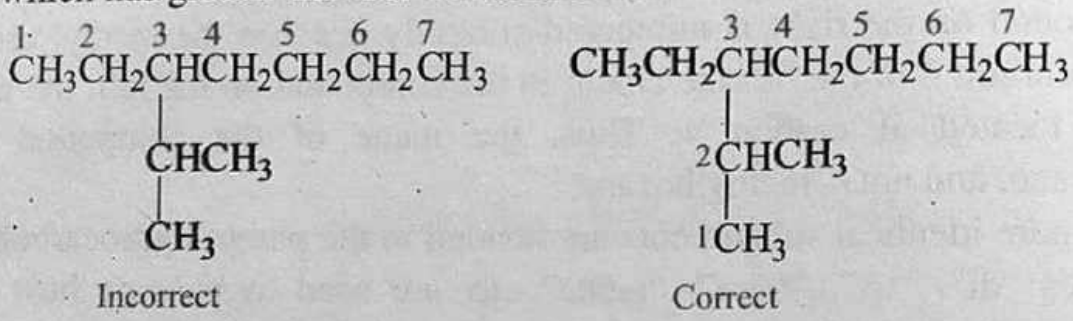
16.3.1 Overview

i) The reactions in which an atom or group of atoms in a molecule is replaced by another atom or group of atoms are called substitution reactions.
ii) Alkanes react with chlorine (Cl_2) or bromine (Br_2) to form alkyl chlorides and alkyl bromides.
iii) The reactivity order for alkanes is: tertiary > secondary > primary > methyl
iv) The reactivity order for halogens is: $F_2 > Cl_2 > Br_2 > I_2$
v) Chlorination gives the less stable and bromination gives the most stable radical.
vi) Reaction proceeds via radical chain mechanism which involves radical intermediates.
vii) The termination steps are of low probability due to the low concentration of the radical species meaning that the chances of collisions are very low.

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If the same set of numbers is obtained in both directions, the chain must be numbered from that end, which gives the first substituent (the substituent which is listed first alphabetically) the lower number.

vii) If a compound has two or more chains of the equal length, then select that chain which has greater number of substituents.



Incorrect Correct

The name of this compound is 3-ethyl-2-methylheptane but not 3-isopropylheptane.

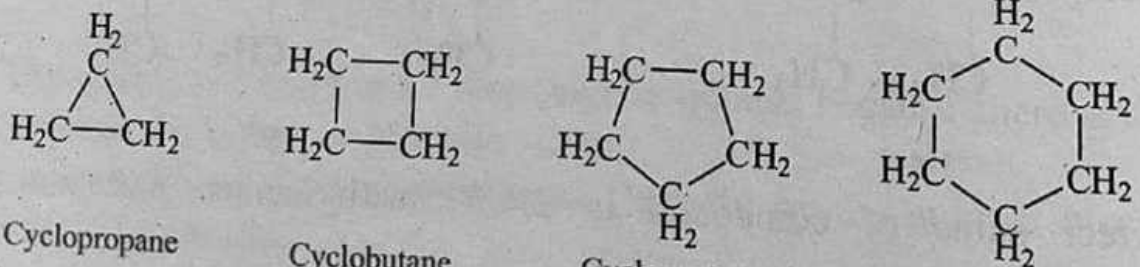
Keep in Mind

- **Note that the branch name and the parent name are written as a single word, and a hyphen follows the number.**
- **The numbers that show the positions of the identical substituents are separated from each other by commas while the number and the word are separated by a hyphen.**

16.2.1.3 Nomenclature of Cycloalkanes

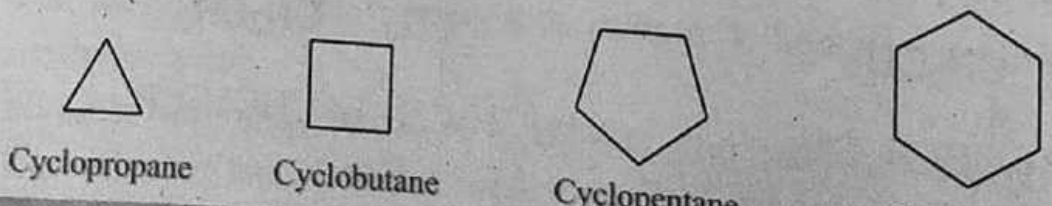
The IUPAC rules for naming cycloalkanes are as follows:

i) They are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring.



Cyclopropane Cyclobutane Cyclopentane Cyclohexane

They are often shown by simple geometric figures. Cyclopropane is shown by a triangle, cyclobutane is shown by a square, cyclopentane is shown by a pentagon and cyclohexane is shown by a hexagon. In their figures each corner shows one carbon and two hydrogen atoms.



Cyclopropane Cyclobutane Cyclopentane Cyclohexane

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16.2.3 Structure of Alkanes and Cycloalkanes

16.2.3.1 Structure of Alkanes

The simplest member of alkane is methane (CH_4). The hydrogen atoms of methane are arranged around the central carbon atom in order that each hydrogen atom is as far apart from other hydrogen atoms as possible. Methane gives tetrahedral geometry with an angle of 109.5°.

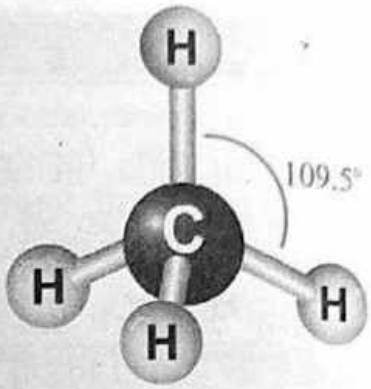
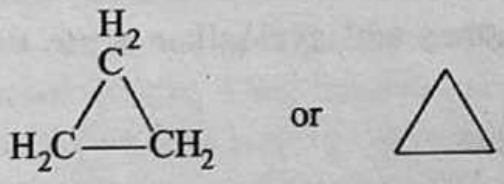


Figure 16.2: Methane Molecule

Although the three dimensional shapes of higher alkanes are more complex than that of methane, the four bonds about each carbon are still arranged in a tetrahedral manner, and all the bond angles are nearly 109.5°.

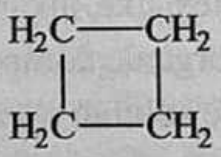
16.2.3.2 Structure of Cycloalkanes

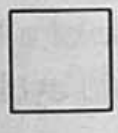
The simplest member of cycloalkane is cyclopropane. When writing structural formulas for cycloalkanes, chemists use line-angle formula to represent cycloalkane ring. Each ring is represented by a regular polygon that has the same number of sides as there are carbon atoms in the ring. For example, chemists represent cyclopropane by a triangle, cyclobutane by a square, cyclopentane by a pentagon, and cyclohexane by a hexagon.



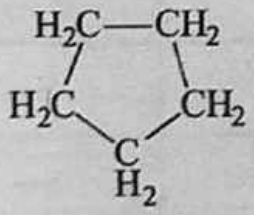
or

Cyclopropane



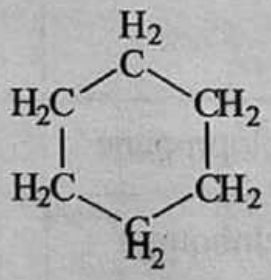
or


Cyclobutane



or


Cyclopentane



or


Cyclohexane

16.2.4 Relative Stability of Alkanes and Cycloalkanes

Alkanes are relatively stable. Branched chain alkanes are more stable than straight chain (linear), unbranched alkanes. For example, 2-methlylpropane is more stable than n-butane. On the other hand, the cycloalkanes are stable except cyclopropane and cyclobutane. The inertness of alkanes is due to the following reasons:

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Keep in Mind

When a bond breaks so that both of its electrons stay with one of the atoms, the process is called **heterolytic bond cleavage** or **heterolysis**.

i) $A—B \longrightarrow A^+ + :B^-$

ii) $A—B \longrightarrow A:^- + B^+$

When a bond breaks so that each of the atoms retains one of the bonding electrons, the process is called **homolytic bond cleavage**, or **homolysis**.

$A—B \longrightarrow \dot{A} + \dot{B}$

16.3.2 Reaction Mechanism

The halogenation of alkanes occurs through the formation of free radical and is called free radical mechanism. It takes place in three steps:

Initiation Step

In this step, the chlorine free radicals are formed by homolytic fission of Cl_2 molecule in the presence of heat or light. Each atom takes one of the bonding electrons and two highly reactive chlorine atoms are produced. This is called initiation step because it produces radicals.

$Cl—Cl \longrightarrow \dot{Cl} + \dot{Cl}$

Propagation Step

i) The chlorine radical produced in the initiation step abstracts a hydrogen atom from the methane, forming a molecule of HCl and a methyl radical.

$Cl—Cl + CH_3—H \longrightarrow \dot{C}H_3 + HCl$

ii) The methyl radical abstracts a chlorine atom from a chlorine molecule (Cl_2), forming a molecule of methyl chloride and another chlorine radical, which can then abstracts a hydrogen atom from another molecule of methane.

$\dot{C}H_3 + Cl—Cl \longrightarrow CH_3Cl + \dot{Cl}$

These two steps (i) and (ii) are repeated again and again and a chain reaction starts. These steps are called propagation steps because they propagate the reaction.

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Termination Step

Free radicals of similar and dissimilar types combine together to give neutral molecules.

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3{-}CH_3$$

$$\dot{C}l + \dot{C}l \longrightarrow Cl_2$$

$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3{-}Cl$$

The combination of these radicals is called a termination step because it helps to carry the reaction to an end by decreasing the number of radicals available to propagate the reaction.

The reaction of methane with chlorine also produces the highly halogenated products such as CH_2Cl_2, $CHCl_3$ and CCl_4 as well as additional HCl.

16.4 Oxidation of Organic Compounds

16.4.1 Complete Oxidation

Oxidation of organic molecule generally corresponds to increasing its oxygen content and to decreasing its hydrogen content. The reverse of oxidation is reduction. Oxidation and reduction take place simultaneously, therefore they are redox reactions.

Alkanes such as natural gas, gasoline, and diesel burn readily in the presence of oxygen to produce carbon dioxide, water vapours, and energy.

$$Alkane_{(g)} + O_{2(g)} \xrightarrow{\text{Flame or Ignition}} CO_{2(g)} + H_2O_{(g)} + Energy$$

The burning of organic compounds in the presence of oxygen is called combustion. Methane gas is found in natural gas and is used for cooking and heating. The equation for the combustion of methane is written as:

$$CH_{4(g)} + 2O_{2(g)} \xrightarrow{\text{Flame or Ignition}} CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H = -891 \text{ kJ/mol}$$

The amount of heat evolved when one mole of hydrocarbon is completely burnt to give CO_2 and H_2O is called heat of combustion.

16.4.2 Incomplete Oxidation

When there is an insufficient supply of oxygen or air, then hydrocarbons on combustion produce carbon monoxide, water vapours and carbon black.

$$3CH_{4(g)} + 4O_{2(g)} \xrightarrow{\text{Flame or Ignition}} 2CO_{(g)} + 6H_2O_{(g)} + C_{(s)} + Energy$$

16.4.3 Catalytic Oxidation

When lower alkanes are burnt in the presence of metallic catalyst at high temperature and pressure, then they form many useful products.

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i) The oxidation of methane at 400°C and 200atm in the presence of copper catalyst forms methyl alcohol.

$$CH_4 + [O] \xrightarrow[\text{Cu catalyst}]{\text{400°C and 200atm}} CH_3OH$$

ii) The methyl alcohol is further oxidized to formaldehyde.

$$CH_3OH + [O] \xrightarrow[\text{Cu catalyst}]{\text{400°C and 200atm}} HCHO + H_2O$$

iii) The formaldehyde is further oxidized to formic acid.

$$HCHO + [O] \xrightarrow[\text{Cu catalyst}]{\text{400°C and 200atm}} HCOOH$$

16.5 Alkenes

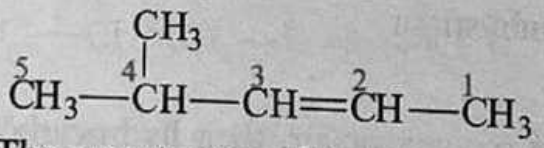
The unsaturated hydrocarbons that contain one or more carbon-carbon double bonds (C=C) are called alkenes. They are also known as olefins. The word olefin is derived from French word "olefiant" which means oil forming because the lower members of alkenes give oily products on treatment with chlorine or bromine. Alkenes are present in natural gas, coal gas and gasoline in small amounts. They are produced in large amounts by cracking of petroleum. Alkenes (monoenes) have general formula C_nH_{2n}, where n is the number of carbon atoms. Ethylene is the first member of the series.

16.5.1 Nomenclature

Alkenes are normally named using the IUPAC system, but many older names are still in common use. Ethene is often called ethylene and propene is called propylene.

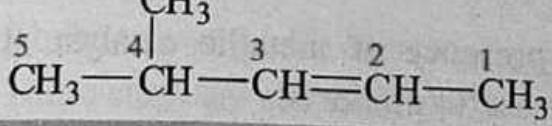
The IUPAC name of an alkene is obtained by replacing the ending "ane" of the corresponding alkane with "ene." For example, $CH_2{=}CH_2$ is called ethene and $CH_3CH{=}CH_2$ is called propene. When there are two or more possible locations for the double bond in a molecule, its position is shown by a number. The IUPAC rules for naming of alkenes are similar to those used for naming alkanes, with a few additions to indicate the position and presence of double bonds.

Step 1. Select the longest chain of carbon atoms that contains the double bond and name it.



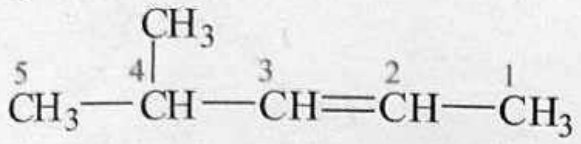
The parent name of the compound is pentene. It means that there are five carbon atoms in the longest chain.

Step 2. Number the longest chain of carbon atoms from that end which is closer to the double bond. Alkenes with two or three carbon atoms do not need numbers.



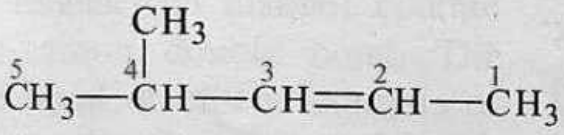
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Step 3. Indicate the position of the double bond by the lower numbered carbon atom bound by the double bond.



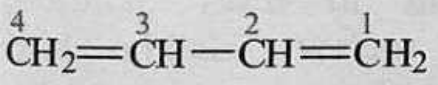
The double bond is present between carbon 2 and 3, so the name of compound is 2-pentene.

Step 4. Indicate the position of the substituent by the number of that carbon to which it is attached and name it in a manner similar to alkanes. The name of substituent is stated before the name of the longest continuous chain of carbon atoms that contains the double bond, together with a number to designate the carbon to which the substituent is bonded. Note that if a compound's name contains both a double bond suffix and a substituent, the double bond suffix gets the lowest possible number.



The methyl group is located at carbon 4 and the name of compound is 4-methyl-2-pentene or 4-methylpent-2-ene.

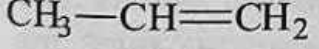
Step 5. If an alkene has two or more double bonds, the "ne" of the corresponding alkane is replaced with "diene," "triene," "tetraene," and so on depending upon the number of double bonds present in the parent alkene.

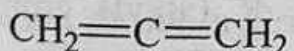


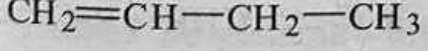
The compound has two double bonds and the name of compound is 1,3-butadiene or buta-1,3-diene.

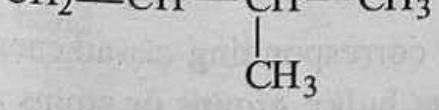
Practice Exercise - 1

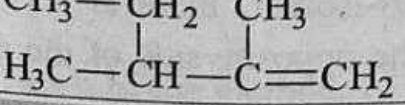
Give the IUPAC name for each of the following:

i) 

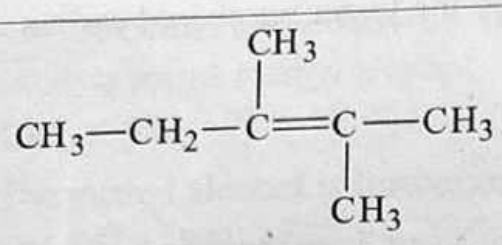
ii) 

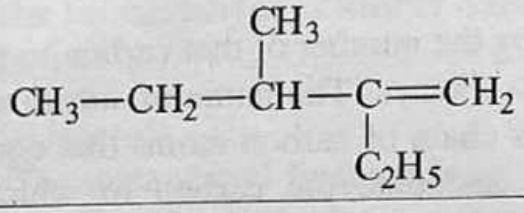
iii) 

iv) 

v) 

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vi) 

vii) 

Practice Exercise - 2

Draw the structure for each of the following:

i) 2-Butene

ii) 2-Methyl-1-butene

iii) 3,4-Dimethyl-2-pentene

iv) 1,3-Butadiene

v) 3-Ethyl-2-pentene

vi) 3-Ethyl-4-methylhex-3-ene

vii) 1,3,5-Hexatriene

viii) 2,3-dimethyl-1,3,5-hexatriene

16.5.2 Relative Stability

There are three factors that influence the relative stability of alkene:

i) Degree of Substitution

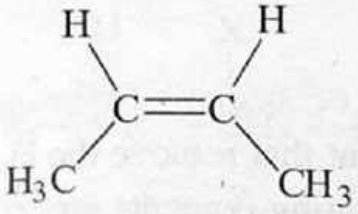
The stability of alkene increases as the number of R (alkyl) groups on the C=C increases. The increasing order of stability of alkenes is as:

$$CH_2=CH_2 < RCH=CH_2 < RCH=CHR < R_2C=CHR < R_2C=CR_2$$

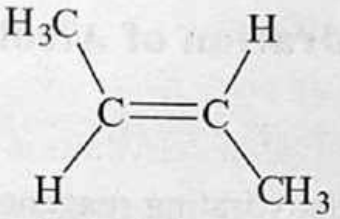
ii) Stereochemistry

Trans-alkenes are usually more stable than the corresponding *cis*-alkenes. In a *cis*-isomer, there is more steric hindrance, because the bulky groups or atoms are on the same side of the double bond whereas in a *trans*-isomer, there is less steric hindrance, because the bulky groups or atoms are on the opposite side of the double bond.

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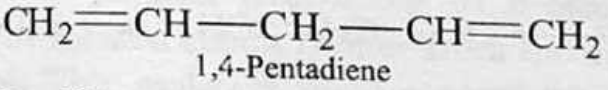
Cis-2-butene (Less Stable)



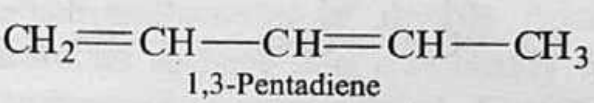
Trans-2-butene (More Stable)

iii) Conjugation

Conjugated alkenes are more stable than isolated alkenes. For example, 1,3-pentadiene is more stable than 1,4-pentadiene.



1,4-Pentadiene



1,3-Pentadiene

16.5.3 Structure

Ethene (an alkene) contain carbon-carbon double bond. The double bond of ethene consists of one sigma bond and one pi bond. The carbon atoms attached through pi bond are sp^2 hybridized. Hence, each doubly bonded carbon has three sp^2 hybrid orbitals and one pure p-orbital. Each of these sp^2 hybrid orbitals overlaps an orbital of another atom to form a sigma bond. The remaining p-orbital of one of the sp^2 carbon atoms overlap with the remaining p-orbital of the other sp^2 carbon atom to form a pi bond. Sigma bonds are formed by head-to-head overlap of hybrid orbitals and pi bond is formed by side-to-side overlap of pure p-orbitals. All six atoms of the double-bond system are in the same plane. Hence, ethene has trigonal planar structure in which HĈH and HĈC bond angles are approximately equal to 120°. The carbon-carbon double bond length is 134pm and carbon-hydrogen bond lengths are 109pm.

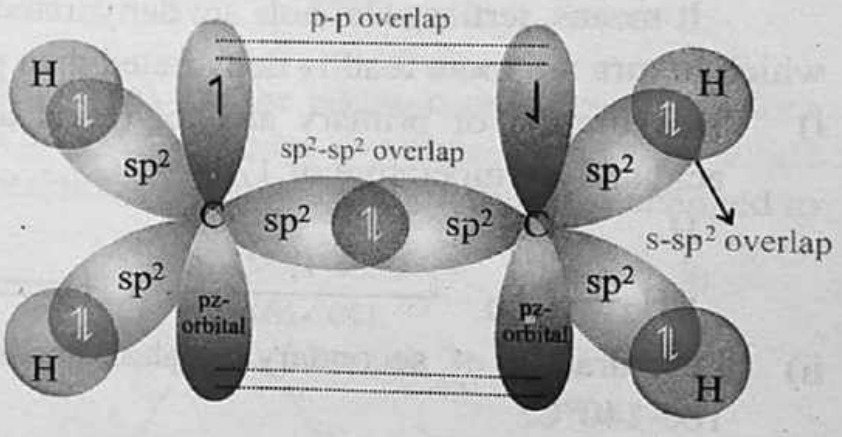
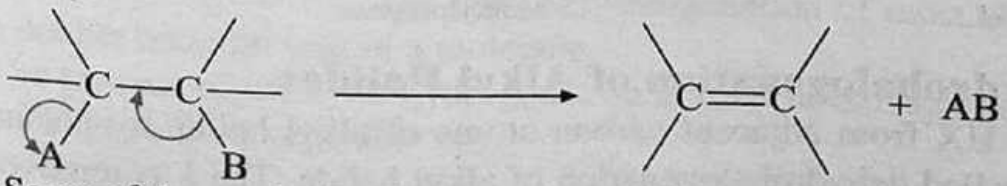


Figure 16.2: C_2H_4 Molecules

16.5.4 Preparation of Alkenes

Alkenes are generally prepared through β-elimination reactions, in which two atoms or groups on adjacent carbon atoms are removed, resulting in the formation of a double bond.

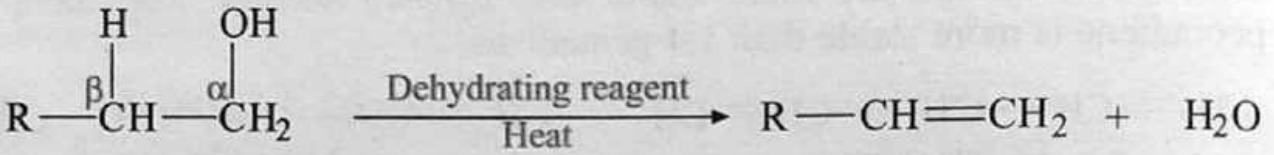


Some of the methods of preparation of alkenes are given:

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16.5.4.1 Dehydration of Alcohols

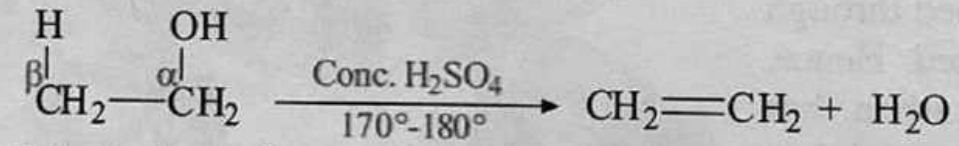
The removal of H_2O from adjacent carbon atoms of alcohols by heating with dehydrating agent is called dehydration of alcohol. Reagent that remove the H_2O from alcohols are called dehydrating reagents. The best dehydrating reagents are: (i) Conc. H_2SO_4 (ii) Al_2O_3 (iii) P_2O_3. All the dehydrating reagents work at high temperature. The *OH* is removed from α-carbon and *H* is removed from β-carbon.



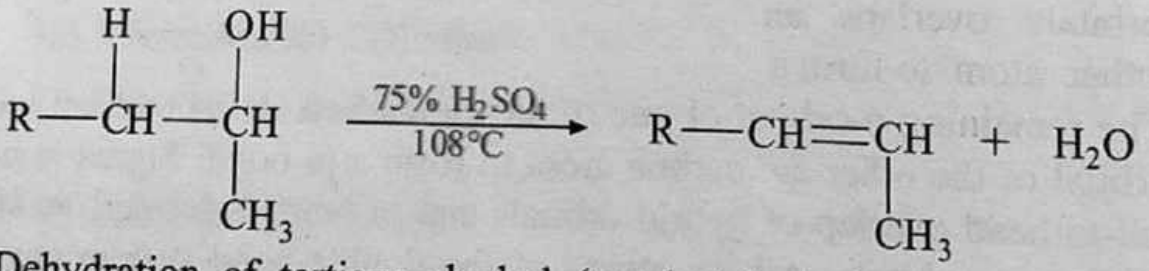
The ease of dehydration of alcohols is: 3° alcohol > 2° alcohol > 1° alcohol.

It means, tertiary alcohols are dehydrated more readily than secondary alcohols which in turn are more readily dehydrated than primary alcohols.

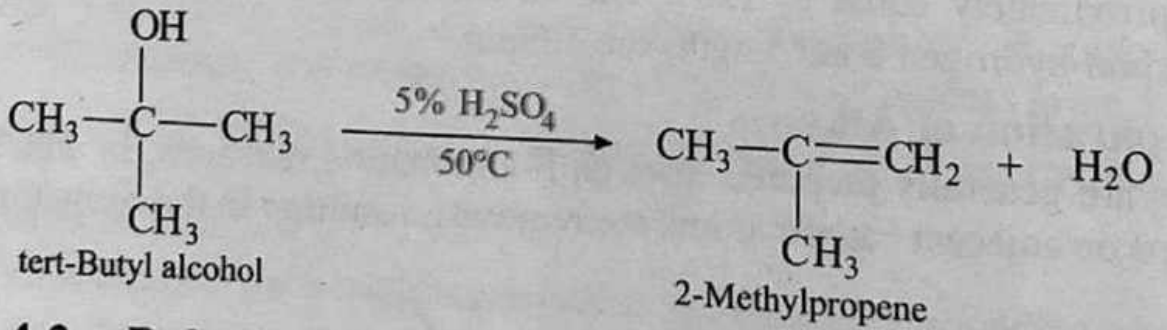
i) Dehydration of primary alcohol (ethyl alcohol) needs concentrated sulphuric acid and a temperature of 170-180°C.



ii) Dehydration of secondary alcohol needs 75% H_2SO_4 and a temperature of 100-140°C.



iii) Dehydration of tertiary alcohol (tert-butyl alcohol) needs 5% H_2SO_4 and a temperature of 50°C.



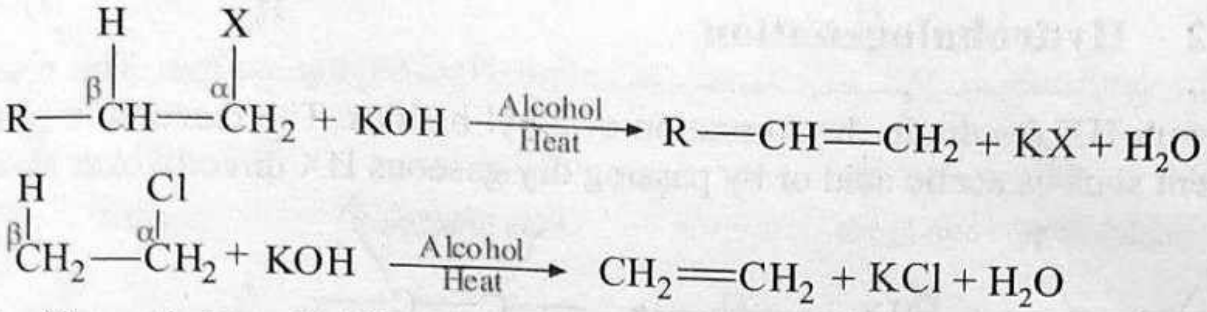
tert-Butyl alcohol

2-Methylpropene

16.5.4.2 Dehydrohalogenation of Alkyl Halides

Removal of HX from adjacent carbon atoms of alkyl halide by heating with alcoholic KOH is called dehydrohalogenation of alkyl halide. The *X* is removed from α-carbon and *H* is removed from β-carbon.

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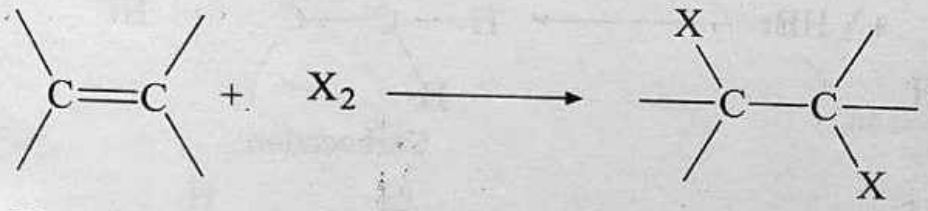


16.5.5 Reactivity of Alkenes

Alkenes are more reactive than alkanes due to presence of π-bond. A π-bond is formed by parallel overlaping of p-orbitals. The π-electrons of double bond are therefore located much farther from the carbon nuclei and are thus less firmly bound to them. This makes π-bond a weak bond as compared to sigma bond. Therefore it breaks much more easily by the attack of electrophilic reagent.

16.5.6 Reactions of Alkenes

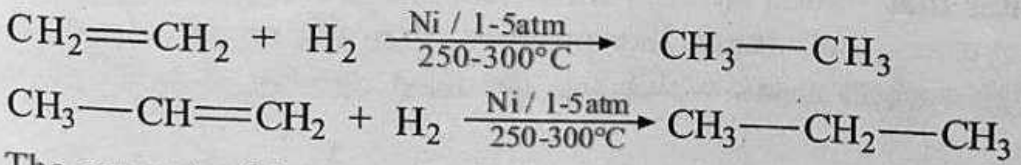
The most important reactions of alkenes are the addition reactions. Additions reactions are those reactions in which two molecules combine to form a single molecule of product. During addition reactions, a double bond of alkene is changed to a single bond.



The common addition reactions of alkenes are given below:

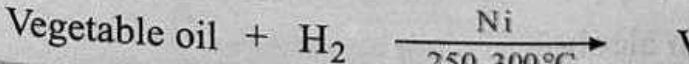
16.5.6.1 Catalytic Hydrogenation

The reaction in which hydrogen is added to an alkene in the presence of catalyst such as platinum, nickel, or palladium and at moderate pressure of 1 to 5 atmosphere to give a saturated hydrocarbon (alkane) is known as catalytic hydrogenation of alkene.



The amount of heat evolved when one mole of an alkene is hydrogenated is called heat of hydrogenation. The heat of hydrogenation of most alkene is 120kJ/mol for each double bond present in a molecule.

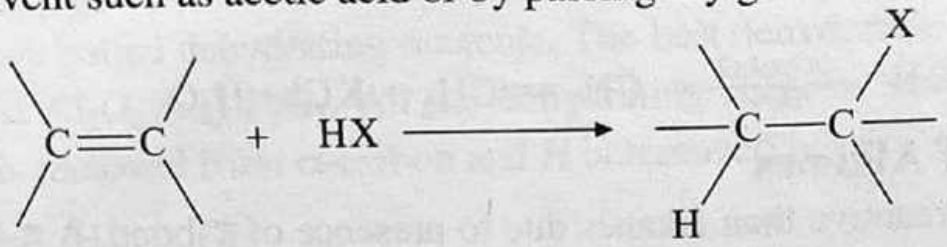
The process of catalytic hydrogenation is used in industry for the manufacture of vegetable ghee from vegetable oil.



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16.5.6.2 Hydrohalogenation

The addition of HX to alkenes is called Hydrohalogenation. The reaction of alkenes with HX results in the formation of alkyl halides. The reaction is carried out in a solvent such as acetic acid or by passing dry gaseous HX directly over an alkene.



Alkene Alkyl Halide

$$CH_2{=}CH_2 + HBr \longrightarrow CH_3{-}CH_2{-}Br$$

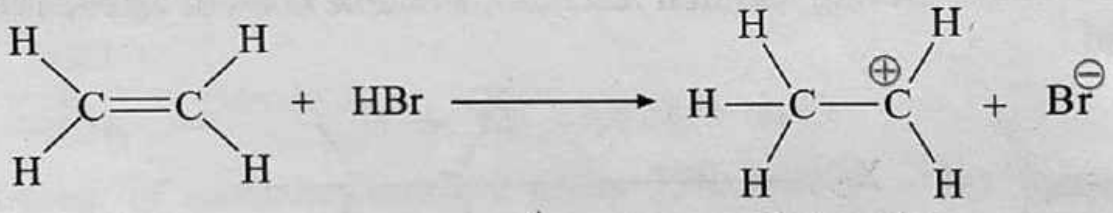
Ethene Ethyl bromide

The order of reactivity of HX is: HI > HBr > HCl

Mechanism of Reaction

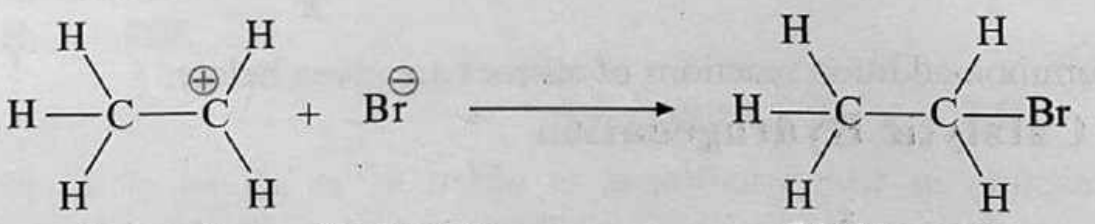
Consider the addition of HBr to ethene. It involves two steps:

Step 1:



Ethene Carbocation

Step 2:

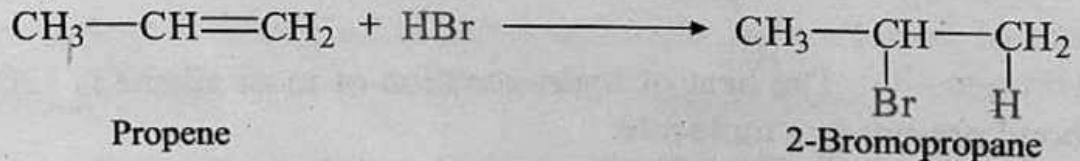


Carbocation Nucleophile Ethyl bromide

Markovnikov's Rule

This rule states that "when an unsymmetrical molecule (polar reagent) such as HX is added to unsymmetrical alkene like propene, then the negative part of adding molecule goes to that carbon atom, which has the least number of hydrogen atoms."

For example:



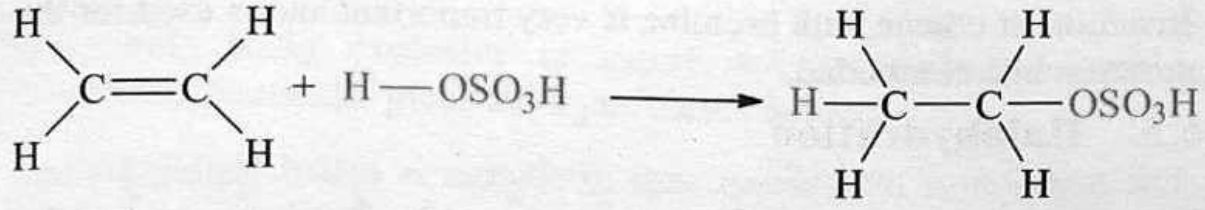
Propene 2-Bromopropane

16.5.6.3 Hydration

The addition of water molecule is called hydration. Alkenes react with H_2O in the presence of H_2SO_4 at 100°C to form alcohol.

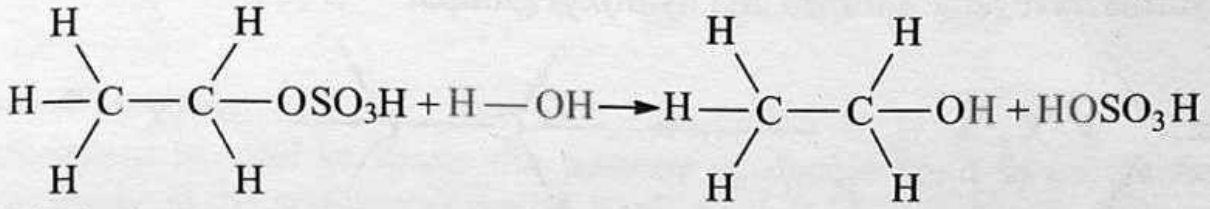
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Step 1:



Ethene Sulphuric acid Ethyl hydrogensulphate

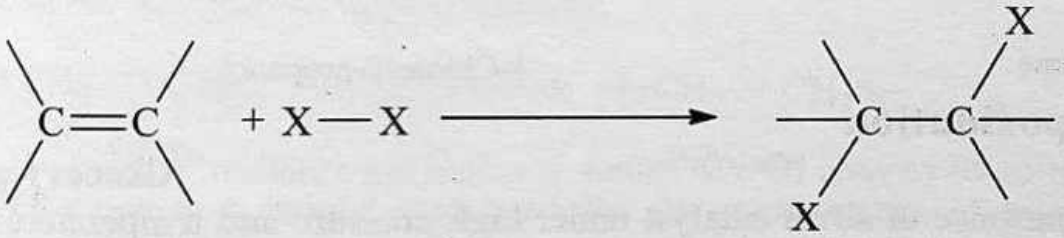
Step 2:



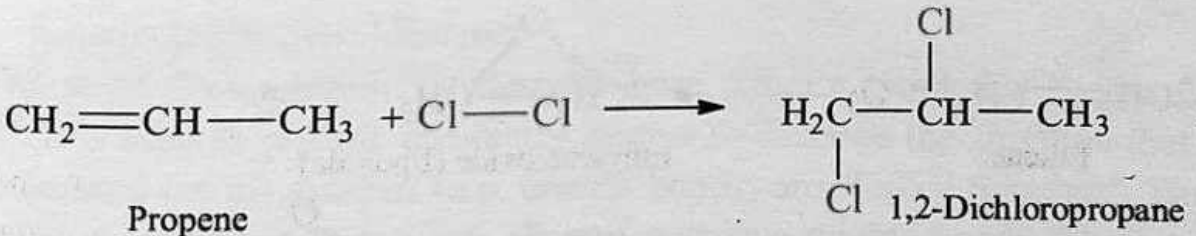
Ethyl hydrogensulphate Ethyl alcohol

16.5.6.4 Halogenation

The addition of halogens such as chorine (Cl_2) and bromine (Br_2) to alkenes is called halogenation. **Alkenes react readily with Cl_2 or Br_2, in an inert solvent such as CCl_4, in dark to form vicinal dihalides.**



Alkene Dihaloalkane

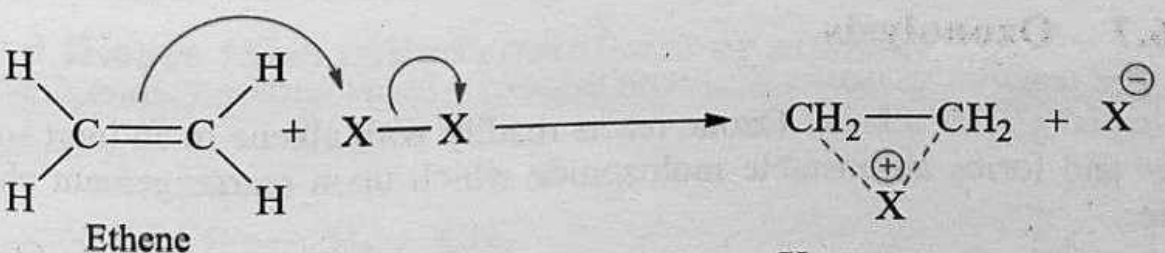


Propene 1,2-Dichloropropane

Mechanism of Reaction

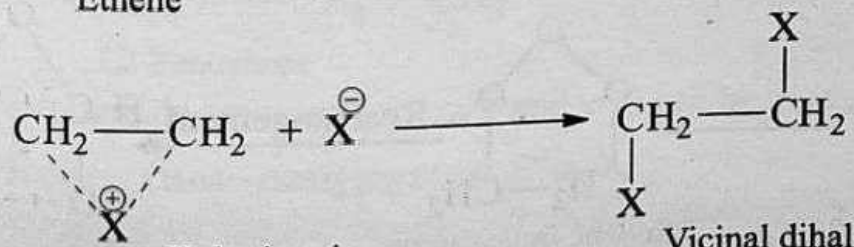
The addition of X_2 to ethene occurs in two steps:

Step 1:



Ethene

Step 2:



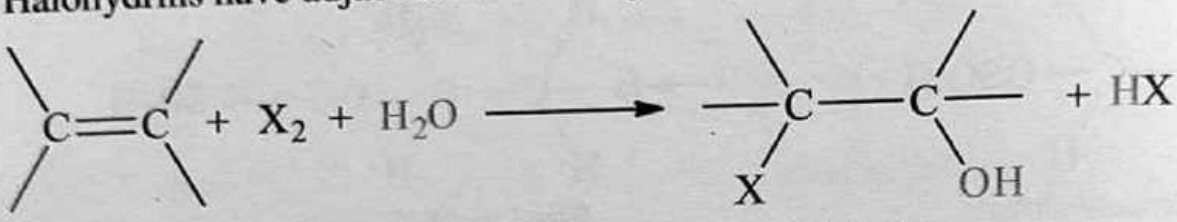
Holonium ion Vicinal dihalide

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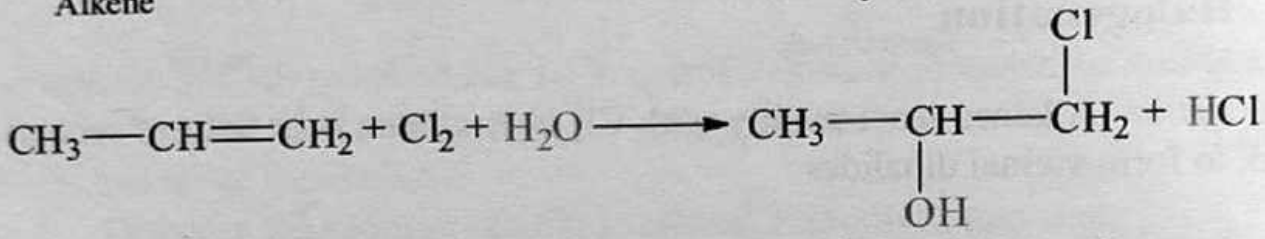
Reaction of ethene with bromine is very important and is used for the detection of unsaturation in a compound.

16.5.6.5 Halohydration

The addition of hypohalous acid to alkenes is called Halohydration. Aqueous solutions of halogens such as Cl_2 and Br_2 react with alkenes to produce halohydrins. Halohydrins have adjacent halo and hydroxyl groups.



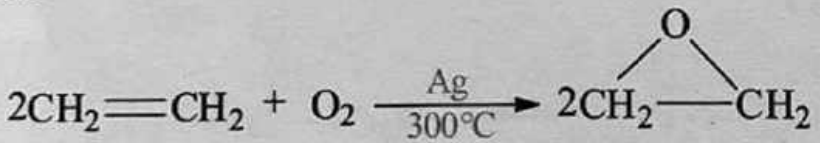
Alkene — Halohydrin



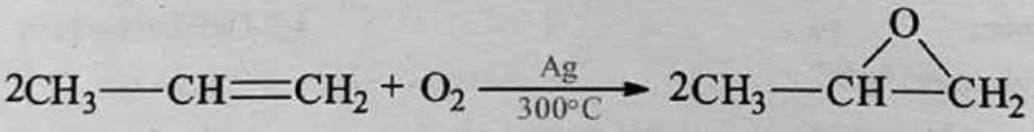
Propene — 1-Chloro-2-propanol

16.5.6.6 Epoxidation

The addition of oxygen (O_2) to alkene is called epoxidation. Alkenes react with oxygen in the presence of silver catalyst under high pressure and temperature to give epoxides.



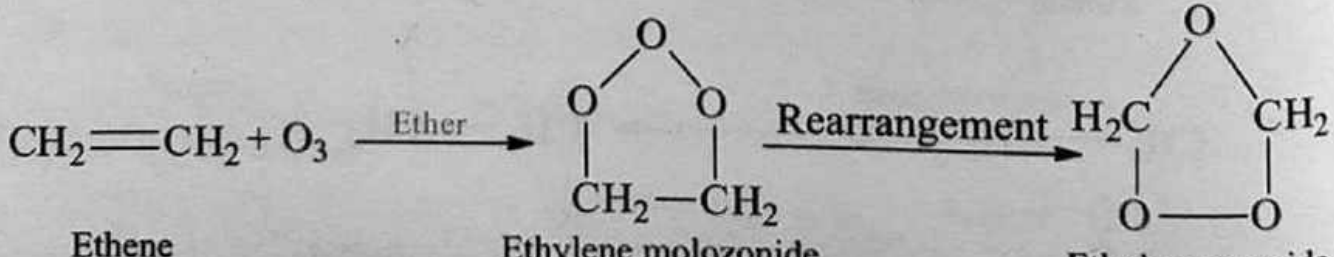
Ethene — Ethylene oxide (Epoxide)



Propene — Propylene oxide

16.5.6.7 Ozonolysis

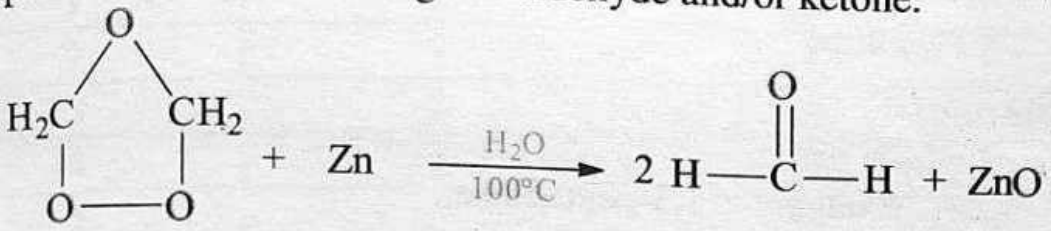
The reaction of ozone (O_3) with alkene to break carbon-carbon double bond is called ozonolysis of alkene. Ozone reacts readily with alkene in an inert solvent such as ether and forms an unstable molozonide which upon rearrangement changes into ozonide.



Ethene — Ethylene molozonide — Ethylene ozonide

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The ozonide being explosive in nature are not isolated. Ozonide upon decomposition with zinc/water gives aldehyde and/or ketone.



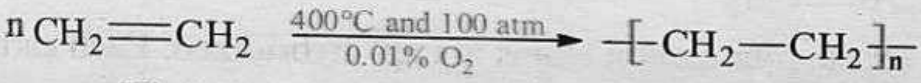
Ethylene ozonide

Formaldehyde

Ozonolysis is used to locate the position of double bond in an alkene. The molecules cleaves at the position of double bond.

16.5.6.8 Polymerization

The process by which small molecules (called monomers) combine together to form large molecules (called polymers) is known as polymerization. **Ethylene (an alkene) undergoes polymerization in the presence of catalyst at high temperature and pressure to form polythene or polyethylene.**



Ethene

Polythene

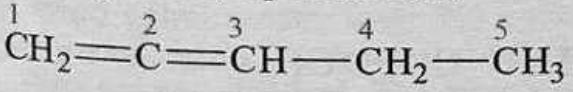
Polythene is a plastic and used for the manufacture of toys, bags, boxes, purses, carpet backing, buckets, rain coats, dustbins, shoes soles and pipe.

16.5.7 Conjugation in Alkenes

The word "*conjugation*" is derived from a Latin word that means "to link together". It is used in organic chemistry system to describe the situation that occurs when conjugated (or pi) systems (e.g. double bonds) are "linked together". The focus of this topic is on dienes. Dienes are alkenes with two double bonds. There are three different classes of dienes that depends on closeness of the pi bonds. They are cumulated, conjugated, or isolated.

Cumulated Dienes (also called *cumulenes* or *allenes*)

The dienes in which the two double bonds are adjacent are called cumulated dienes. Example is 1,2-pentadiene.



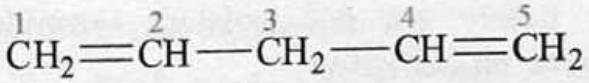
1,2-Pentadiene

The compounds are relatively rare and will not be discussed here in this topic.

Isolated Dienes (non-conjugated dienes)

The dienes in which the double bonds are separated by more than one single bonds are called isolated dienes. Example is 1,4-pentadiene.

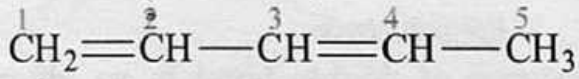
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1,4-Pentadiene

Conjugated Dienes

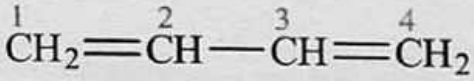
The dienes in which the double bonds are separated by one single bond are called conjugated dienes. Example is 1,3-pentadiene.



1,3-Pentadiene

Conjugation

Conjugation takes place whenever p-orbitals overlap on three or more adjacent atoms. The common conjugated system is 1,3-diens. The simplest example of conjugated diene is 1,3-butadiene.

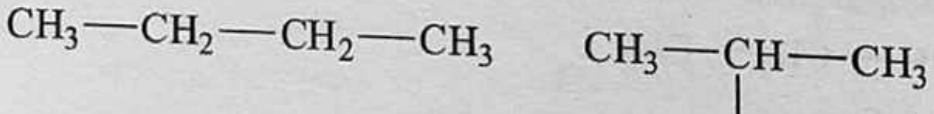


In 1,3-butadiene, all the four carbon atoms are sp^2 hybridized. Each carbon has pure p-orbital with unpaired electrons. The four pure p-orbitals on adjacent carbon atoms make 1,3-butadiene a conjugated system.

A molecule which has three or more pure p-orbitals on adjacent atoms allows p-orbitals to overlap and electrons to delocalize over the whole molecule. When p-orbitals overlap, the electron density in each of the pi bonds is spread out over all the four atoms of the molecule, thus lowering the energy of the molecule and making it more stable. Conjugation makes 1,3-butadiene (conjugated diene) different from 1,4-pentadiene (an isolated diene). The pi bonds in 1,4-pentadiene are separated by more than one sigma bonds and are too far apart to be conjugated.

16.6 Isomerism

The compounds having same molecular formula but different structural formulas are called isomers and the phenomenon is called isomerism. For example, n-butane and isobutane are isomers; they have same molecular formula (C_4H_{10}) but different structures.



n-Butane Isobutane

Isomers have different physical, chemical and biological properties.

Number of Isomers depend upon the number of carbon atoms. The number of isomers increases with the increase of carbon atoms.

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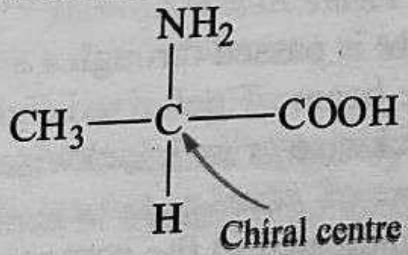
Table 16.7 : Number of Isomers of Alkanes

No. of C-atoms	No. of Isomers	No. of C-atoms	No. of Isomers
1	1	11	159
2	1	12	355
3	1	13	802
4	2	14	1858
5	3	15	4347
6	4	16	10359
7	9	17	24894
8	18	18	60523
9	35	19	148284
10	75	20	366319

There are two main types of isomerism: *constitutional isomerism* and *stereoisomerism.*

16.6.1 Chiral Centres and Carbon based Chiral Centres

Tetrahedral atoms usually carbon atoms that have four different substituents are called chiral centres (or sometimes stereogenic centres). A molecule that contains a chiral centre will be chiral and the molecules that does not contain a chiral centre will be achiral. Molecules with a single chiral centre are always chiral and the molecules with two or more chiral centres, may or may not be chiral. For example, alanine (an amino acid) contains a carbon atom with four different substituents; this carbon atom is chiral centre, and the molecule itself is chiral.



The four different groups bonded to chiral centre are: CH_3, H, COOH and NH_2.

Keep in Mind

The word chiral comes from the Greek word *cheir*, which means "hand." Your left and right hands are chiral i.e. they are not identical. The mirror image of chiral object is not the same as an image of the object itself. A hand is chiral because when you look at your right hand in a mirror, you see not a right hand but a left hand. Left and right hands are mirror images that do not superimpose on each other.



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16.6.2 Optical Activity

Ordinary light consists of waves vibrating in many different planes. When it is passed through polarizer (Nicol prism or Polaroid lens), the light vibrates in one plane only. This light which vibrates in one plane only is called plane polarized light.

The compounds having the ability to rotate the plane of polarized light in either clockwise or anticlockwise direction are called optically active and the property of rotating the plane of polarized light of compounds is called optical activity.

Optical activity in a compound is measured by means of Polarimeter.

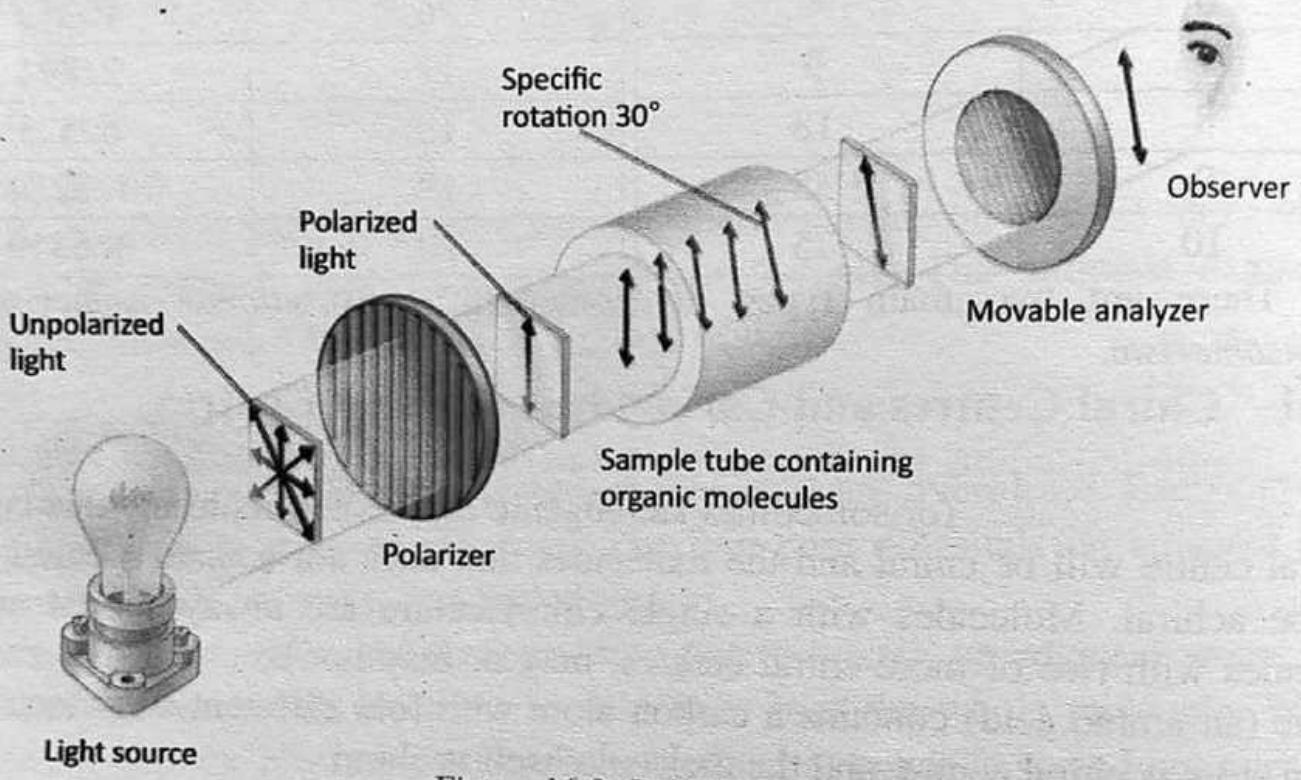


Figure 16.3: Polarimeter

When plane polarized light is passed through a solution of chiral compound (an optically active compound), the beam of polarized light is rotated through a certain number of degrees, either in clockwise or anticlockwise direction. The compound that rotates the plane of polarization of plane-polarized light in clockwise direction is called dextrorotatory. It can be indicated in the compound's name by the prefix lower case ***d*** or (+). The compound that rotates the plane of polarization of plane-polarized light in anticlockwise direction is called levorotatory. It can be indicated in the compound's name by the prefix lowercase ***l*** or (–). *Dextro* and *levo* are Latin prefixes. The word "Dextro" means "to the right" and the word "levo" means "to the left." Sometimes lowercase d and ***l*** are used rather than (+) and (–).

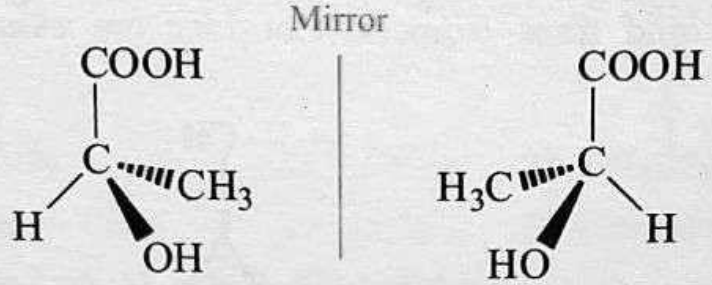
16.6.3 Optical Isomers

The optically active compounds having same molecular formulas, structural formulas but differing in their interaction towards plane polarized light are called optical isomers and the phenomenon is known as optical isomerism. Optical isomers have same physical and chemical properties.

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Optical Isomers of Lactic Acid

The two optically active forms of lactic acid (+) and (–) are similar in physical and chemical properties but differ only in their behaviour toward plane polarized light. The (+) lactic acid is dextrorotatory whereas (–) lactic acid is levorotatory. The (+) lactic acid is the mirror image of the (–) lactic acid.



(+) Lactic Acid (–) Lactic Acid

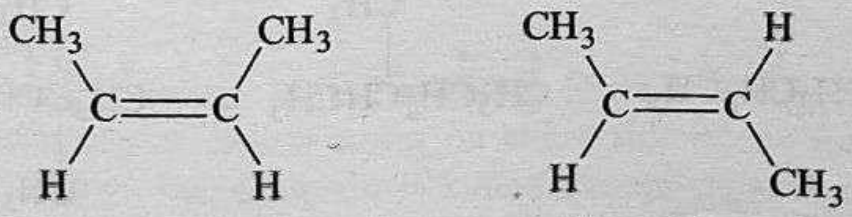
The mixture of equal amounts of (+) lactic acid and (–) lactic acid i.e. (±) lactic acid (called racemic mixture or racemate) rotate plane-polarized light to an equal extent but in opposite directions, the rotations cancel, and no rotation is observed.

16.6.4 Stereoisomers (Configurational Isomers)

The compounds having same molecular and structural formulas but differ in the arrangement of atoms or groups in space are called stereoisomers and the phenomenon is called stereoisomerism. There are two types of stereoisomers: geometric isomers and optical isomers.

16.6.4.1 Geometrical Isomers (Cis-Trans Isomers)

Compounds having same molecular and structural formulas but restricted rotation are called geometric isomers and the phenomenon is called geometric isomerism. Restricted rotation can be caused either by a carbon-carbon double bonds or by a carbon-carbon single bonds in cyclic compounds. The cis isomer (Latin, cisoid = same side) has similar groups on the same side of carbon-carbon double bond and the trans isomer (Latin, transoid = opposite side) has the similar groups on opposite sides of the carbon-carbon double bond. For example, the cis isomer of 2-butene has hydrogen atoms on the same side of the double bond whereas the trans isomer has the hydrogen atoms on opposite sides of the double bond.

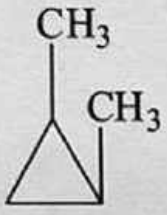


Cis-2-butene Trans-2-butene

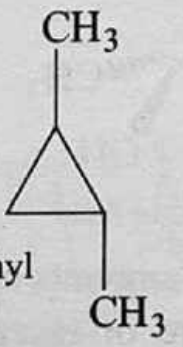
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Cis and trans isomers are two different compounds and have different physical and chemical properties. It is found that *trans* isomers are more stable than the corresponding *cis* isomers. This is because, in the cis isomer, the bulky (big) groups are on the same side of the double bond. The repulsion of bulky groups makes the cis isomer less stable than trans isomer.

Cyclic compounds that have two substituents bonded to two different carbon atoms also have cis and trans isomers. Consider the example of 1,2-dimethyl-cyclopropane.



Cis-1,2-dimethyl cyclopropane



Trans-1,2-dimethyl cyclopropane

The cis isomer has its methyl groups on the same side of the ring, whereas the trans isomer has its methyl groups on opposite sides of the ring.

Conditions for Geometric Isomers

i) The geometric isomers must have a double bond.

ii) There must be two different atoms or groups bonded to each carbon atom of the double bond.

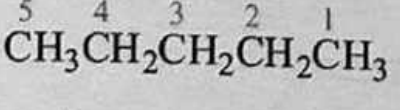
16.6.5 Constitutional isomers (Structural Isomers)

The compounds having same molecular formula but different structural formulas are called constitutional isomers and the phenomenon is called constitutional isomerism. Structural isomers differ in the arrangement of atoms within the molecule.

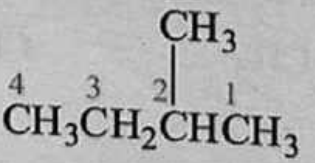
Constitutional isomers are further divided into five types namely, chain isomers, position isomers, functional group isomers, metamers and tautomers.

16.6.5.1 Chain Isomers (Skeleton Isomers)

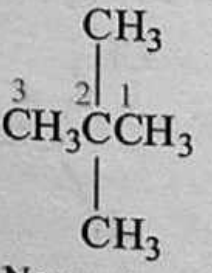
The compounds having same molecular formula but different carbon chains (or skeletons) are called chain isomers and the phenomenon is called chain isomerism. For example, the chain isomers of pentane has the same molecular formula (C_5H_{12}) but they have different chains of carbon atoms.



n-Pentane



Isopentane



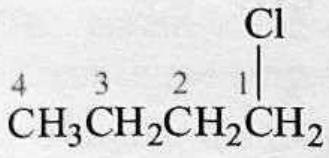
Neopentane

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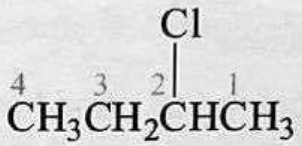
The compound n-pentane has five carbon chain, isopentane has four carbon chain and neopentane has three carbon chain.

16.6.5.2 Position Isomers

The compounds having same molecular formula but different positions of the same functional group are called position isomers and the phenomenon is called position isomerism. **Examples of position isomers are the following:**

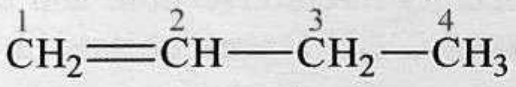


1-Chlorobutane

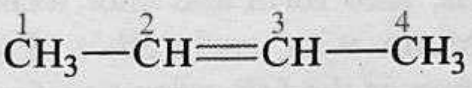


2-Chlorobutane

The compounds, 1-chlorobutane and 2-chlorobutane, have same molecular formula (C_4H_9Cl) but different positions of chlorine atoms (functional groups).



1-Butene

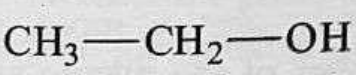


2-Butene

The compounds, 1-butene and 2-butene, have same molecular formula (C_4H_8) but different positions of double bonds (functional group).

16.6.5.3 Functional Group Isomers (Functional Isomers)

The compounds having same molecular formula but differ in the nature of functional groups are called functional group isomers and the phenomenon is known as functional group isomerism. **For example, ethyl alcohol and dimethyl ether have same molecular formula (C_2H_6O) but different functional groups.**

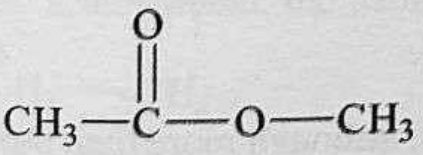


Ethyl alcohol

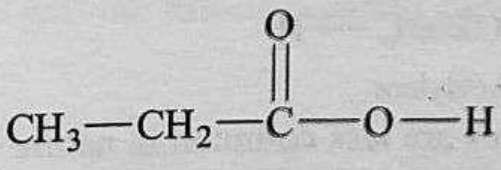


Dimethyl ether

Similarly, methyl acetate and propionic acid have same molecular formula ($C_3H_6O_2$) but different functional groups.



Methyl acetate

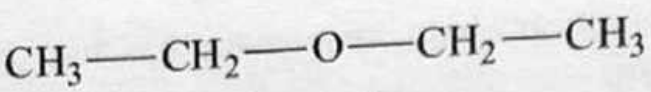


Propionic acid

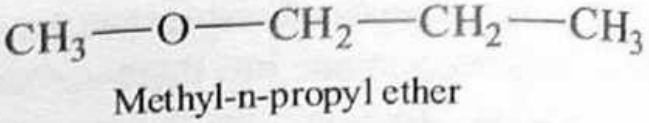
16.6.5.4 Metamers

The compounds having same molecular formula and functional group but differ in the distribution of carbon atoms on either side of the functional group are called metamers and the phenomenon is called metamerism. **For example, diethyl ether and methyl-n-propyl ether are metamers.**

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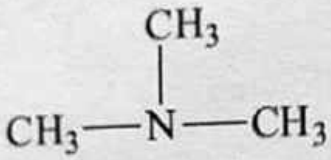


Diethyl ether

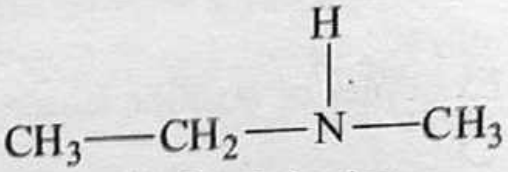


Methyl-n-propyl ether

Similarly, trimethylamine and ethylmethylamine are metamers.



Trimethylamine

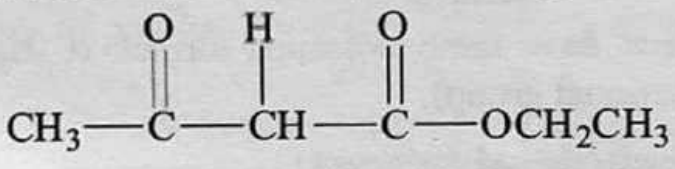


Ethylmethylamine

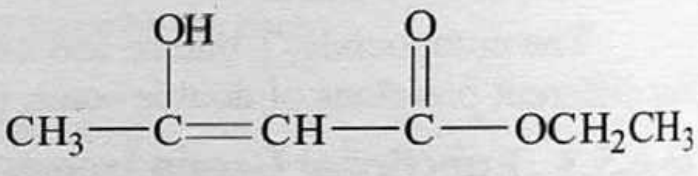
Metamers belong to same homologous series.

16.6.5.5 Tautomers

The two forms of same compound, which differ in the position of the protons and electrons are called tautomers and the phenomenon is called tautomerism. The two forms, that is, keto form and enol form are readily interconvertible and exist in dynamic equilibrium with each other. For example, ethyl acetoacetate is in an equilibrium mixture of the following two forms:



Keto-Form (93% at 25°C)



Enol-Form (7% at 25°C)

Usually the 'keto' form of the compound is more stable, but in some cases the 'enol' form can be more stable.

16.7 Alkynes

Alkynes are unsaturated hydrocarbons which contain one or more carbon-carbon triple bonds in their structures. The simplest member of the alkyne series is ethyne, commonly called acetylene. The common name of alkynes is acetylenes, after the simplest member, acetylene. They have the general formula C_nH_{2n-2}, where n = 2, 3, 4, 5.... The structure for acetylene is:



Acetylene

Alkynes are less common in nature than alkenes, although more than thousand different alkynes have been isolated from natural sources. They are produced during cracking of petroleum.

16.7.1 Nomenclature

Alkynes are named in the same way as alkenes. The IUPAC name of an alkyne is obtained by replacing the ending "ane" of the corresponding alkane with "yne." For example, CH≡CH is called ethyne and $CH_3C{\equiv}CH$ is called propyne. When there

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are two or more possible location for the triple bond in a molecule, its position is shown by a number. The IUPAC rules for naming alkynes are similar to those used for naming alkenes.

Step 1. Select the longest chain of carbon atoms that contains the triple bond and name it.

$$CH_3—C\equiv C—CH_3$$

The parent name of the compound is butyne. It means that there are four carbon atoms in the longest chain.

Step 2. Number the longest chain of carbon atoms from that end which is closer to the triple bond. Alkynes with two or three carbon atoms do not need numbers.

$$\begin{array}{l} \overset{6}{C}H_3—\overset{5}{C}H_2 \\ \qquad\quad | \\ CH_3—\overset{4}{C}H—\overset{3}{C}\equiv\overset{2}{C}—\overset{1}{C}H_3 \end{array}$$

Step 3. Indicate the position of the triple bond by the lower numbered carbon atom bound by the triple bond.

$$\begin{array}{l} \overset{6}{C}H_3—\overset{5}{C}H_2 \\ \qquad\quad | \\ CH_3—\overset{4}{C}H—\overset{3}{C}\equiv\overset{2}{C}—\overset{1}{C}H_3 \end{array}$$

The triple bond is present between carbon 2 and 3, so the name of compound is 2-hexyne.

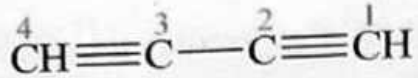
Step 4. Indicate the position of the substituent by the number of that carbon to which it is attached and name it in a manner similar to alkanes. The name of substituent is stated before the name of the longest continuous chain of carbon atoms that contains the triple bond, together with a number to designate the carbon to which the substituent is attached. Note that if a compound's name contains both a triple bond suffix and a substituent, the triple bond suffix gets the lowest possible number.

$$\begin{array}{l} \overset{6}{C}H_3—\overset{5}{C}H_2 \\ \qquad\quad | \\ CH_3—\overset{4}{C}H—\overset{3}{C}\equiv\overset{2}{C}—\overset{1}{C}H_3 \end{array}$$

The methyl group is located at carbon 4 and the name of compound is 4-methyl-2-hexyne.

Step 5. If an alkyne has two or more triple bonds, the "ne" of the corresponding alkane is replaced with "diyne," "triyne," "tetrayne," and so on depending upon the number of triple bonds present in the parent alkyne.

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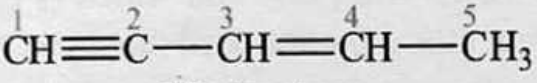
The compound has two triple bonds and the name of compound is 1,3-butadiyne or buta-1,3-diyne.

Alkenyne

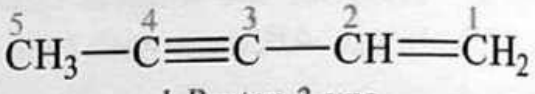
Alkenynes are hydrocarbons which have both double and triple bonds.

Nomenclature

Step 1. If double and triple bonds are present at different positions from respective ends, then preference in numbering will be given to that end which is closer to double or triple bond.

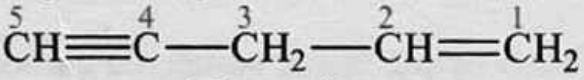


3-Penten-1-yne



1-Penten-3-yne

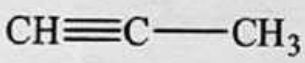
Step 2. If double and triple bonds are present at same positions, then preference in numbering will be given to double bond.

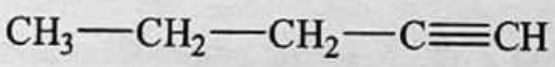


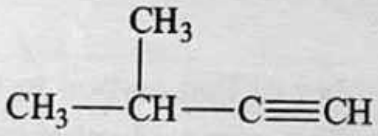
1-Penten-4-yne

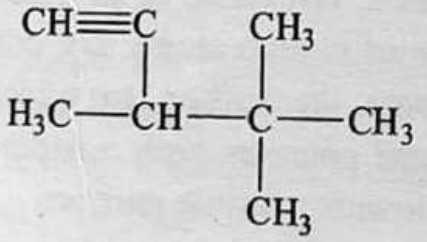
Practice Exercise - 1

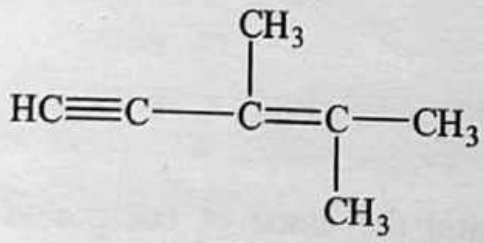
Give the IUPAC name for each of the following:

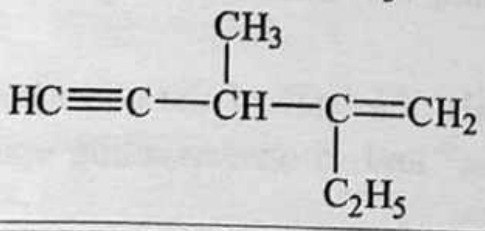
i) 

ii) 

iii) 

iv) 

v) 

vi) 

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Practice Exercise - 2

Draw the structure for each of the following:

i) 2-Butyne
ii) Pent-2-yne
iii) 1,3-Butadiyne
iv) 3-Methyl-1-butyne
v) 4-Methyl-2-pentyne
vi) Penta-1,3-diyne
vii) Hexa-2,4-diyne
viii) Octa-2,4,6-triyne
ix) 3-Hexen-1-yne
x) 1-Hexen-4-yne

16.7.2 Relative Stability of Alkynes

Alkynes are more stable than alkenes because of smaller bond length of triple bond. The stability of alkynes also depend upon:

i) The Position of Triple Bond

The internal alkynes (alkynes with triple bond located elsewhere along the chain, other than the end of the chain) are more stable than terminal alkynes (alkynes with triple bond located at the end of the chain). For example, 2-pentyne is more stable than 1-pentyne.

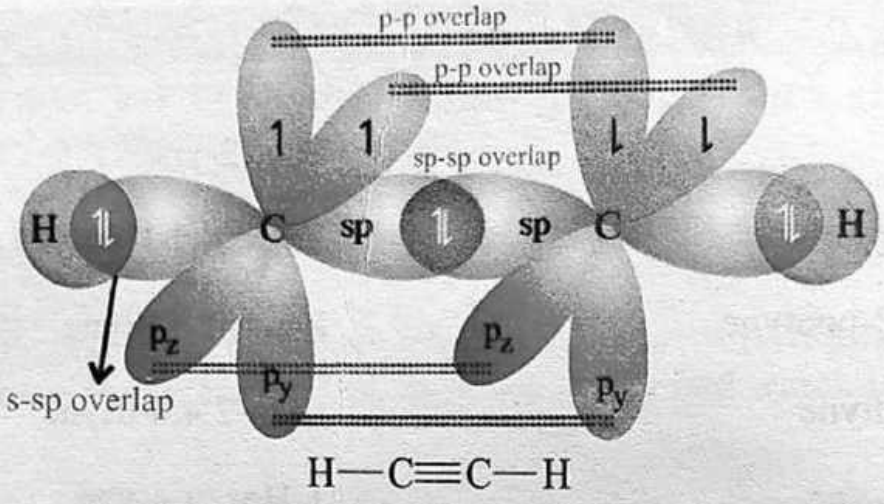
ii) The Number of Substituents

Branched alkynes are more stable than unbranched alkynes. For example, 2,5-dimethyl-3-hexyne is more stable than 3-hexyne.

16.7.3 Structure of Alkynes

Acetylene (an alkyne) has carbon-carbon triple bond. The triple bond of acetylene consists of one sigma bond and two pi bonds. The two carbon atoms linked through pi bonds are *sp* hybridized. Thus, each carbon has two *sp* hybrid orbitals and two pure *p*-orbitals. One of the two *sp* hybrid orbitals of each carbon atom overlaps with half-filled *s* orbital of hydrogen atom to form C—H sigma bonds. The other *sp* hybrid orbital of one carbon atom overlaps with *sp* hybrid orbital of the other carbon atom to form C—C sigma bond. The remaining two pure *p*-orbitals form two pi bonds between two carbon atoms through sidewise overlapping. Acetylene has linear shape with bond angles of 180°. The carbon-carbon triple bond length is 120pm and carbon-hydrogen bond lengths are 106pm.

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H—C≡C—H

Figure 16.4: Acetylene (C_2H_2) Molecule

16.7.4 Physical Properties

i) The first three members of alkynes are gases, next eight members are liquids and higher members are solids.

ii) Alkynes are colourless and odourless except acetylene which has a garlic like smell.

iii) They are generally non-polar and are soluble in non-polar solvents like ether, benzene, CCl_4, etc.

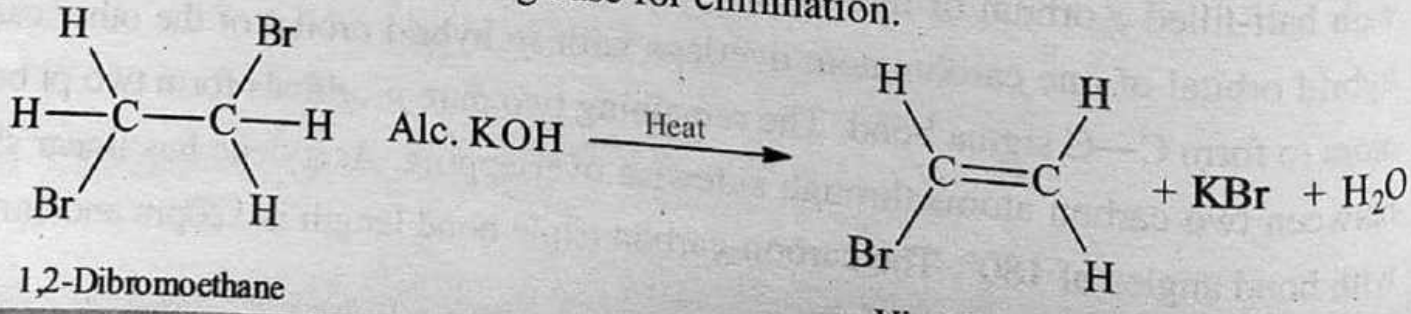
iv) Their melting points, boiling points and densities increase gradually with the increase in molecular masses.

16.7.5 Preparation of Alkynes

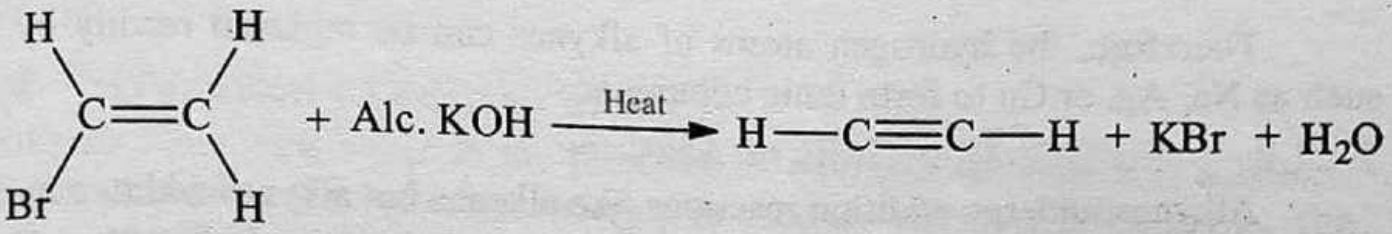
Alkynes are prepared by the elimination of atoms (or group of atoms) from the adjacent carbon atoms.

16.7.5.1 Dehydrohalogenation of Dihalides (Removal of HX)

Alkynes are prepared by heating vicinal dihalide with alcoholic KOH. It is a two-step reaction. The removal of first HX results in the formation of vinyl halide and the removal of second HX result in the formation of alkyne. The removal of second HX is difficult and requires a strong base for elimination.



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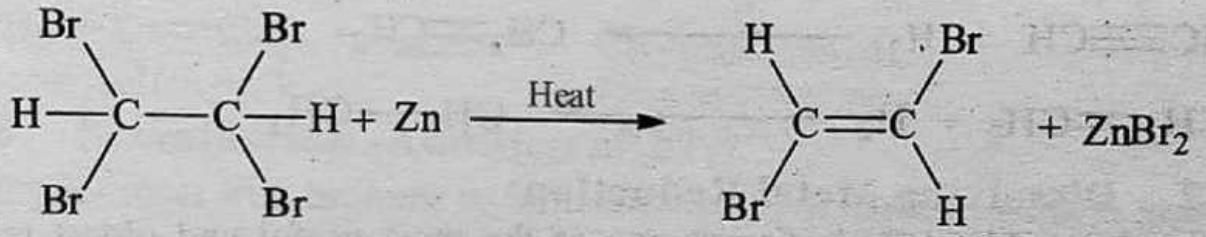
Vinylbromide

Acetylene

This method is useful for the preparation of alkynes because the vicinal dihalides are readily prepared from alkenes by the addition of halogens.

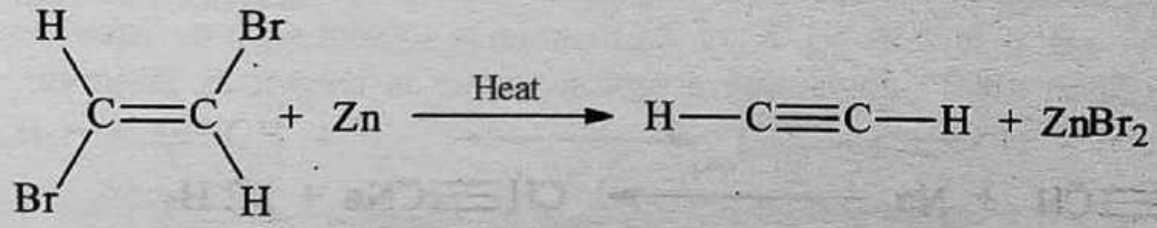
16.7.5.2 Dehalogenation of Tetrahalides

Alkynes are prepared by heating vicinal tetrahalides with zinc dust in ethanol. The reaction occurs in two steps.



1,1,2,2-Tetrabromoethane

1,2-Dibromoethene



1,2-Dibromoethene

Acetylene

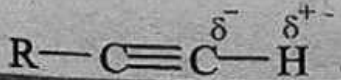
This method is not used for the preparation of alkynes because the tetrahalides are themselves prepared by the halogenation of alkynes.

16.7.6 Reactivity of Alkynes

Alkynes contain a carbon-carbon triple bond. One of them is a sigma bond and the other two are pi bonds. The electron density between the carbon atoms is very high which draws atoms very close to each other. Hence, the electrons of the triple bond are less exposed than the electrons of the double bond. Thus alkynes are less reactive towards electrophilic reagents as compared to alkenes.

16.7.7 Acidity of Terminal Alkynes

In alkynes, the triply bonded carbon atom is *sp* hybridized. In terminal alkynes, the *sp* hybridized carbon is highly electronegative and so it is strongly electron withdrawing. This makes the attached hydrogen atom slightly acidic.



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Therefore, the hydrogen atoms of alkynes can be replaced readily by metals such as Na, Ag, or Cu to form ionic compounds.

16.7.8 Addition Reactions of Alkynes

Alkynes undergo addition reactions like alkenes but alkynes add two molecules of reagent instead of one. The reaction takes place in two steps. In first step, the triple bond of alkyne is converted to double bond. In the second step, the double bond is converted to single bond.

16.7.8.1 Hydrogenation (Addition of H_2)

Alkynes react with hydrogen gas in the presence of finely divided metal catalyst such as Ni, Pt or Pd at or above room temperature. The reaction occurs in two steps. The initial product is an alkene and the final product is an alkane.

$$HC{\equiv}CH + H_2 \xrightarrow[250\text{-}300^\circ C]{Ni} CH_2{=}CH_2$$

$$CH_2{=}CH_2 + H_2 \xrightarrow[250\text{-}300^\circ C]{Ni} CH_3{-}CH_3$$

16.7.8.2 Dissolving Metal Reduction

Dissolving Metal Reduction is one of the most useful and oldest reduction methods. Reduction of organic compounds using the solution of strongly electropositive metal such as Na, K, or Zn in an inert solvent such as liquid ammonia or tetrahydrofuran (THF) containing a proton source is known as dissolving metal reduction.

$$\underset{\text{Acetylene}}{HC{\equiv}CH} + Na \xrightarrow{Liq.\ NH_3} \underset{\text{Sodium acetylide}}{CH{\equiv}CNa} + 1/2\ H_2$$

Sodium acetylides can be used to convert lower alkynes to higher alkynes.

$$HC{\equiv}CNa + CH_3I \longrightarrow CH{\equiv}C{-}CH_3 + NaI$$

In the above two reactions, the 'H_2' is added as $2e^-$ and $2H^+$.

16.7.8.3 Hydrohalogenation

Alkynes react with halogen acids (HX) to produce dihaloalkanes. Addition of halogen acids follows Markovnikov's rule. Halogen atom adds to the carbon that has the lesser number of hydrogen atoms. The addition of HX occurs in two steps.

$$CH_3{-}C{\equiv}CH + HBr \longrightarrow CH_3{-}\overset{\overset{Br}{|}}{C}{=}CH_2$$

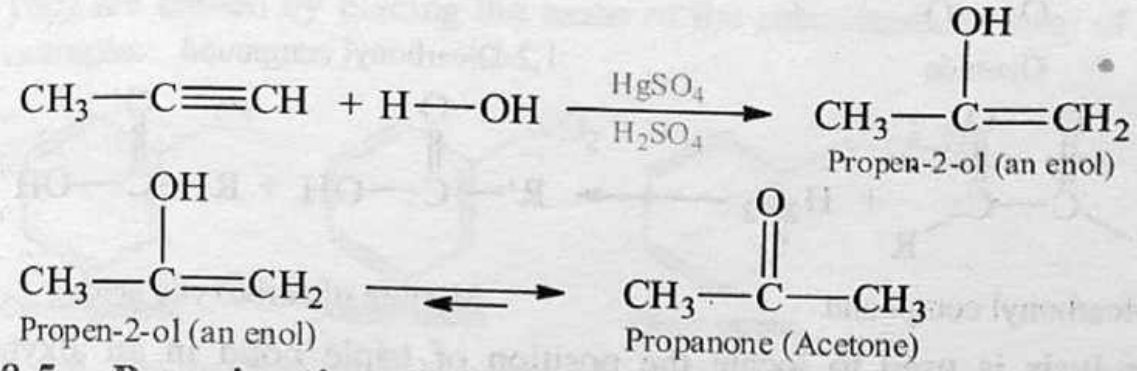
$$CH_3{-}\overset{\overset{Br}{|}}{C}{=}CH_2 + HBr \longrightarrow CH_3{-}\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}{-}CH_3$$

The order of reactivity for HX is: HI>HBr>HCl>HF

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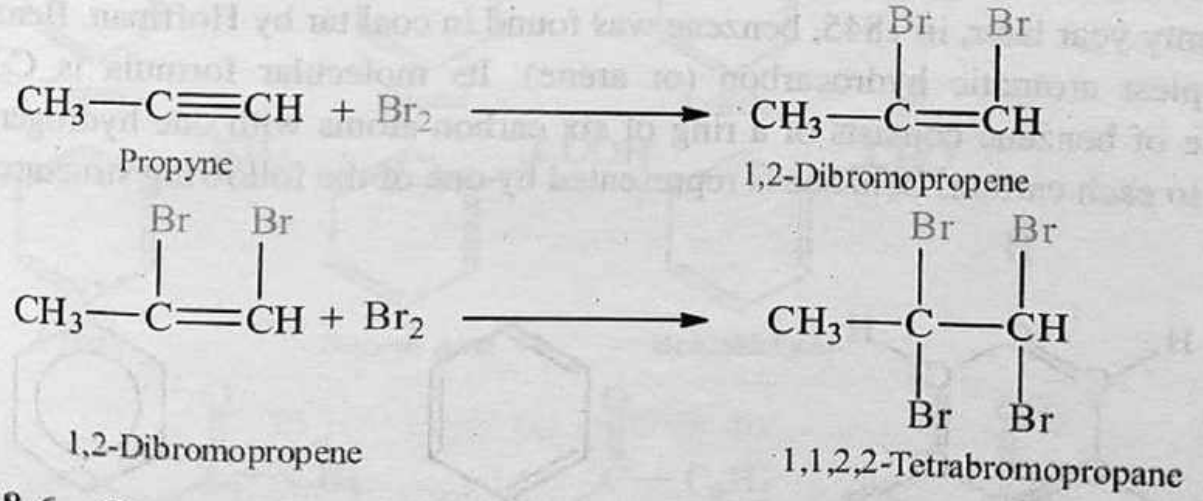
16.7.8.4 Hydration (Addition of H_2O)

Alkynes react with water in the presence of mercuric sulphate and sulphuric acid to form unstable enols which rearranges to produce carbonyl compounds. The product is an aldehyde in the case of acetylene and a ketone in the case of all other alkynes. The addition of water follows Markovnikov's rule.



16.7.8.5 Bromination (Addition of Br_2)

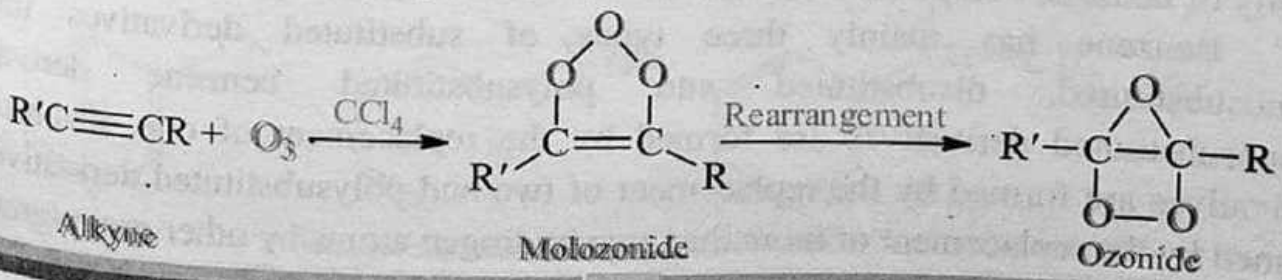
Alkynes react with bromine to form dibromides or tetrabromides. If bromine is in smaller amount, then dibromides are formed. If bromine is in larger amount, then tetrabromides are formed.



16.7.8.6 Ozonolysis (Addition of O_3)

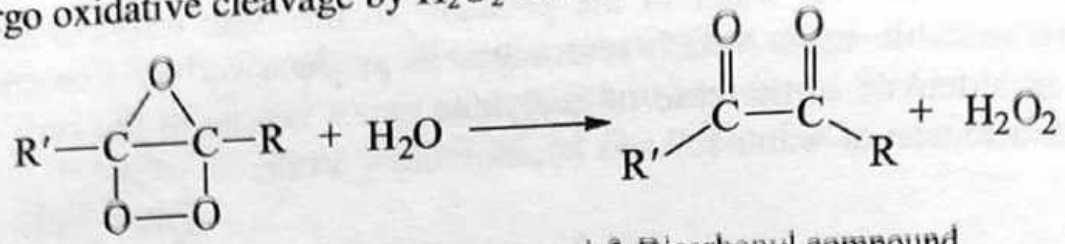
The reaction of ozone (O_3) with alkynes to break carbon-carbon triple bond is called ozonolysis of alkynes. The reaction of ozone with alkynes occurs in two steps:

i) Ozone adds to alkynes across the carbon-carbon π-bond to form molozonides. The molozonides rearrange to form ozonides.



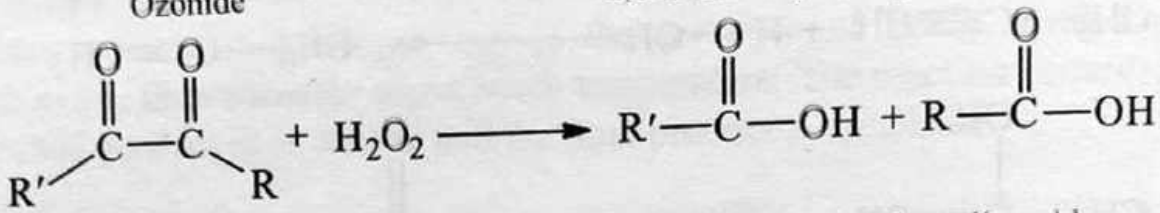
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ii) The ozonides are hydrolysed by water to form 1,2-dicarbonyl compounds which undergo oxidative cleavage by H_2O_2 to form carboxylic acid mixture.



Ozonide

1,2-Dicarbonyl compound



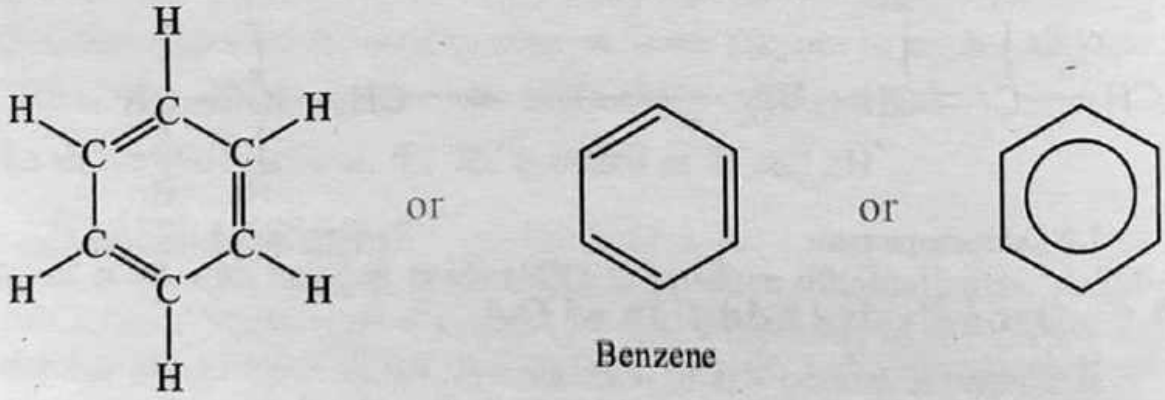
1,2-Dicarbonyl compound

Mixture of carboxylic acids

Ozonolysis is used to locate the position of triple bond in an alkyne. The molecules cleaves at the position of triple bond.

16.8 Benzene and Substituted Benzenes

Michael Faraday, an English scientist, in 1825 isolated benzene from the whale oil. Twenty year later, in 1845, benzene was found in coal tar by Hoffman. Benzene is the simplest aromatic hydrocarbon (or arene). Its molecular formula is C_6H_6. A molecule of benzene consists of a ring of six carbon atoms with one hydrogen atom bonded to each carbon. Benzene is represented by one of the following structures:



Benzene

The organic compounds that contain benzene ring are called aromatic compounds. Because many compounds containing benzene had fragrant odours, the family of benzene compounds became known as aromatic compounds.

Benzene has mainly three types of substituted derivatives that is monosubstituted, disubstituted and polysubstituted benzene derivatives. Monosubstituted derivatives are formed by the replacement of one, disubstituted derivatives are formed by the replacement of two and polysubstituted derivatives are formed by the replacement of more than two hydrogen atoms by other group/groups.

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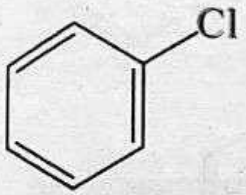
16.8.1 Nomenclature

The nomenclature of aromatic hydrocarbons is complex than aliphatic hydrocarbons.

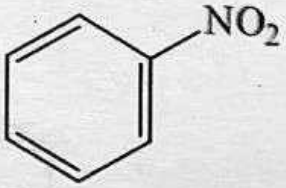
16.8.1.1 Monosubstituted Benzene Derivatives

The IUPAC rules for naming monosubstituted benzene derivatives are:

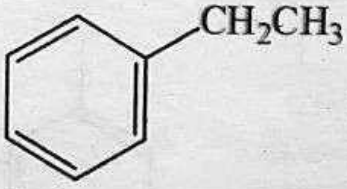
i) They are named by placing the name of the substituent in front of benzene. For example:



Chlorobenzene

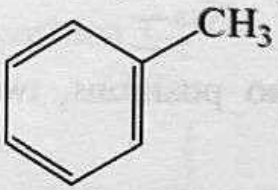


Nitrobenzene

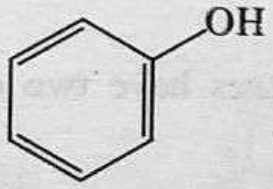


Ethylbenzene

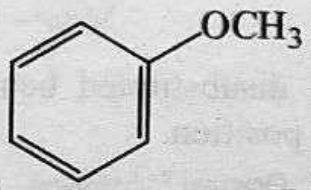
ii) Some monosubstituted benzene derivatives have common names that are accepted by IUPAC. Such names have to be memorized.



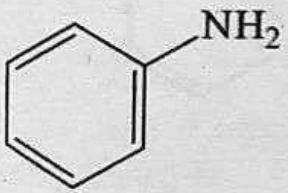
Toluene



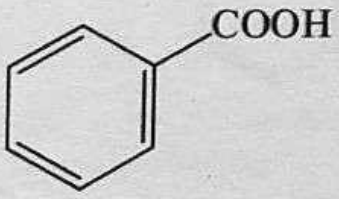
Phenol



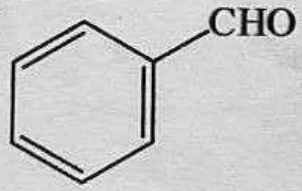
Anisole



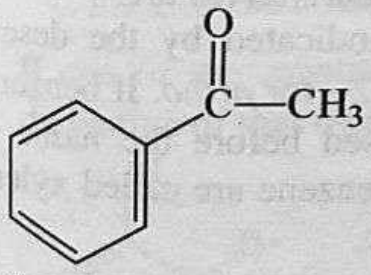
Aniline



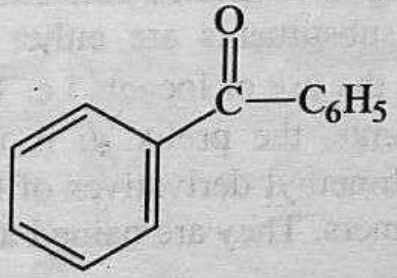
Benzoic Acid



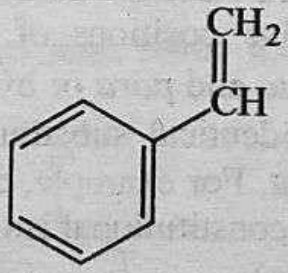
Benzaldehyde



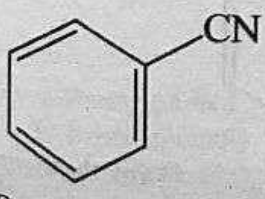
Acetophenone



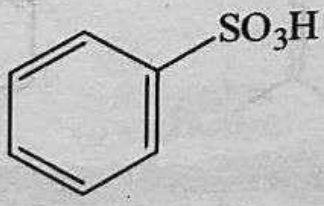
Benzophenone



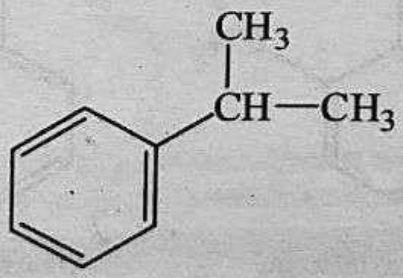
Styrene



Benzonitrile



Benzenesulphonic acid

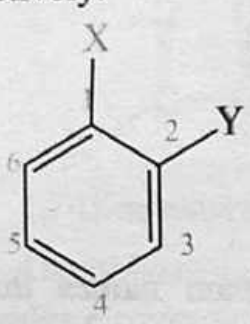


Cumene

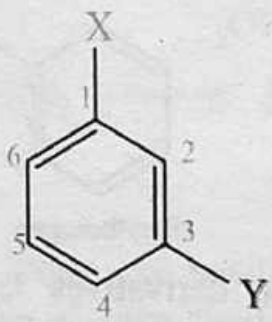
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16.8.1.2 Disubstituted Benzene Derivatives

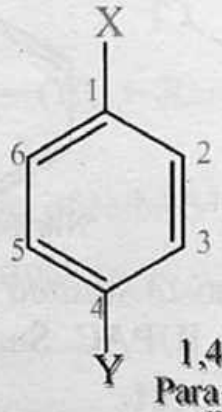
There are three different isomers for disubstituted benzene derivatives. Their structures have substitution at 1,2–; 1,3–; and 1,4– positions. They are designated by prefixes *ortho*, *meta* and *para*. 1,2– is equivalent to ortho (Greek, correct or straight), 1,3– is equivalent to meta (Greek, between, in the middle), and 1,4– is equivalent to para (Greek, beyond). *Ortho*, *meta* and *para* are also abbreviated as *o*–, *m*– and *p*– respectively.



1,2–
Ortho–
o–



1,3–
Meta–
m–



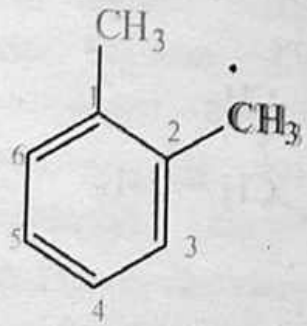
1,4–
Para–
p–

Notice that the disubstituted benzenes have two ortho positions, two meta positions and one para position.

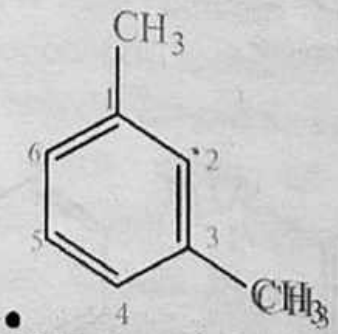


The IUPAC rules for naming disubstituted benzene derivatives are:

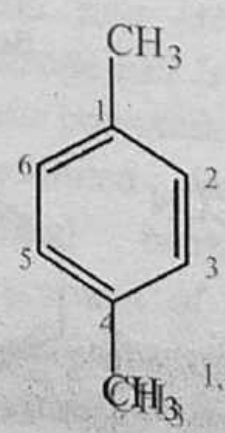
i) The relative positions of substituents are either indicated by the descriptors *ortho*, *meta* and *para* or by the use of locants i.e. 1,2– for *ortho*. If benzene ring has two identical substituents, the prefix *di* is used before the name of the substituent. For example, dimethyl derivatives of benzene are called xylene and has three constitutional isomers. They are named as:



1,2 Dimethylbenzene
(*o* Xylene)



1,3 Dimethylbenzene
(*m* Xylene)

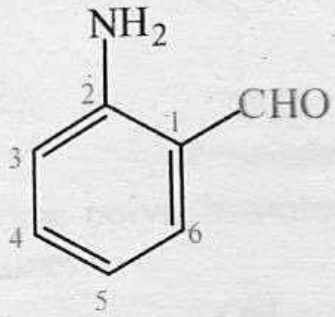


1,4 Dimethylbenzene
(*p* Xylene)

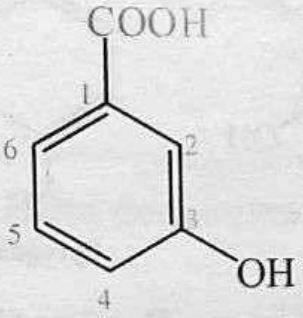
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ii) If benzene ring contains two different substituents, the position one is given to the group of high priority. The order of the priority of the groups is as: –COOH, –CN, –CHO, $-COCH_3$, –OH, $-NH_2$, –OR, –R

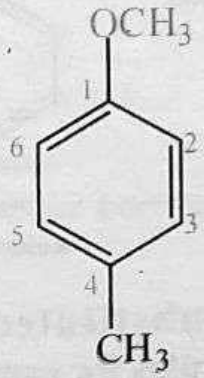
Examples are:



2-Aminobenzaldehyde
(*o*-Aminobenzaldehyde)

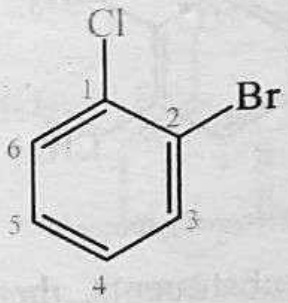


3-Hydroxybenzoic acid
(*m*-Hydroxybenzoic acid)

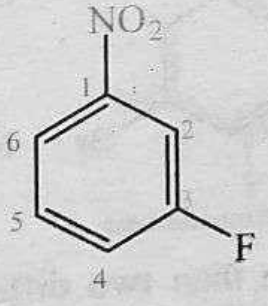


4-Methylanisole
(*p*-Methylanisole)

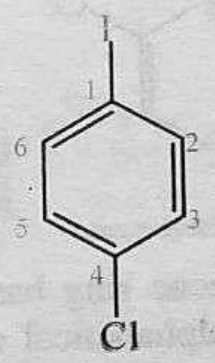
iii) If benzene has two different substituents without priority order, then they are named in alphabetical order. The last name substituent is assumed to be in position 1.



2-Bromochlorobenzene
(*o*-Bromochlorobenzene)

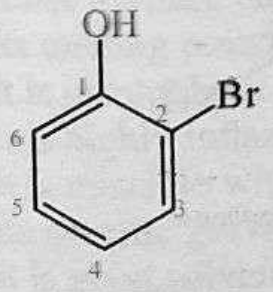


3-Fluoronitrobenzene
(*m*-Fluoronitrobenzene)

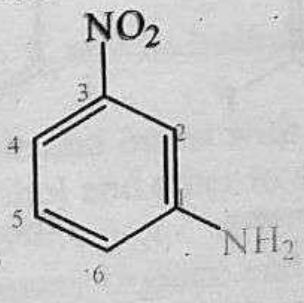


4-Chloroiodobenzene
(*p*-Chloroiodobenzene)

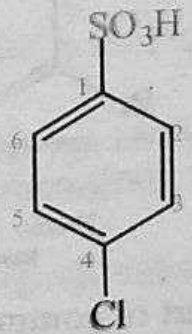
iv) If one of the substituent is part of a common root, name the compound as a derivative of that monosubstituted benzene.



2-Bromophenol
(*o*-Bromophenol)



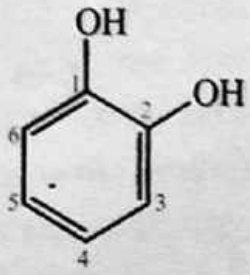
3-Nitroaniline
(*m*-Nitroaniline)



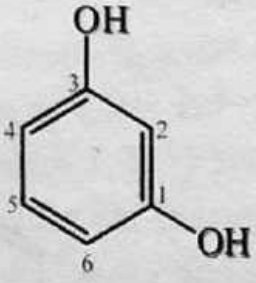
4-Chlorobenzenesulphonic acid
(*p*-Chlorobenzenesulphonic acid)

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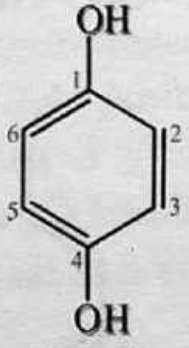
v) Some disubstituted benzene derivatives are better known by their common names.



Catechol



Resorcinol

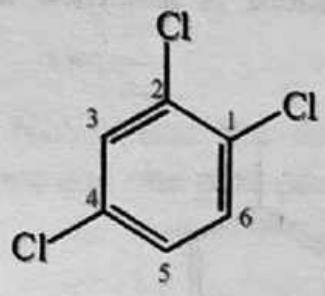


Hyroquinone

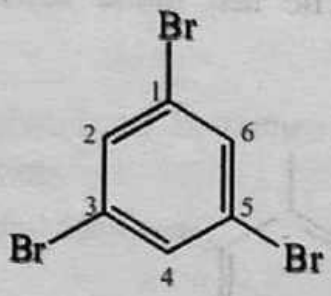
16.8.1.3 Polysubstituted Benzene Derivatives

The IUPAC rules for naming polysubstituted benzene derivatives are:

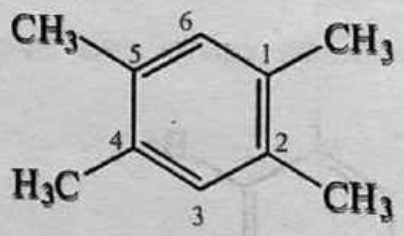
i) When benzene ring has more than two identical substituents, the prefix *tri* is used for three, *tetra* for four, *penta* for five and *hexa* for six before the name of the substituents. Assign the lowest possible numbers to the substituents.



1,2,4-Trichlorobenzene

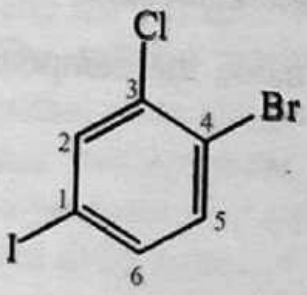


1,3,5-Tribromobenzene

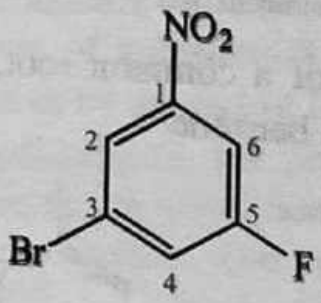


1,2,4,5-Tetramethylbenzene

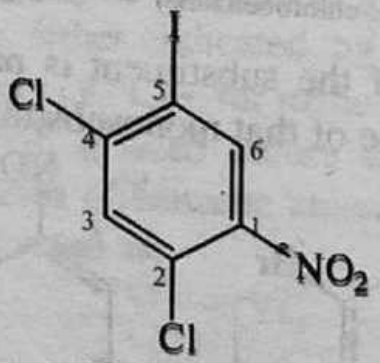
ii) When benzene ring has more than two different substituents, then they are named in alphabetical order. The last name substituent is assumed to be in position 1.



4-Bromo-3-chloroiodo benzene



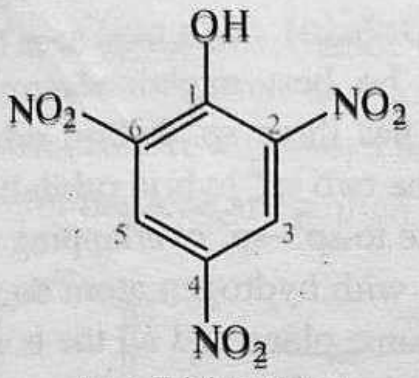
3-Bromo-5-fluoronitro benzene



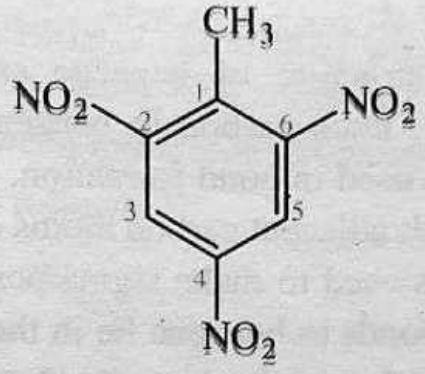
2,4-Dichloro-5-iodonitro benzene

iii) If substituents are part of common roots, name the compound as a derivative of that monosubstituted benzene. The substituent that includes the common root is assumed to be in position 1.

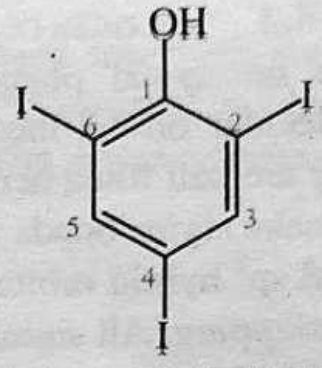
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2,4,6-Trinitrophenol

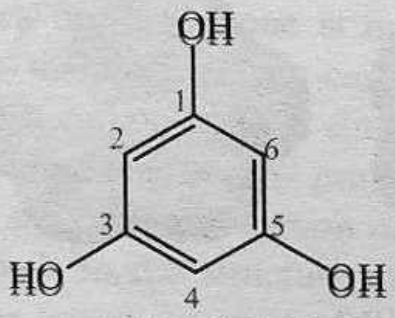


2,4,6-Trinitrotoluene

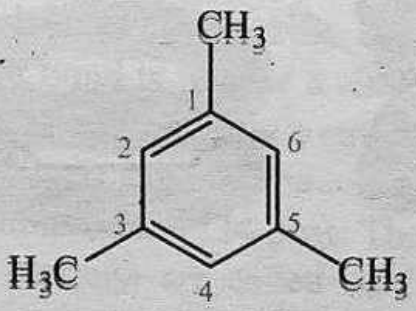


2,4,6-Triiodophenol

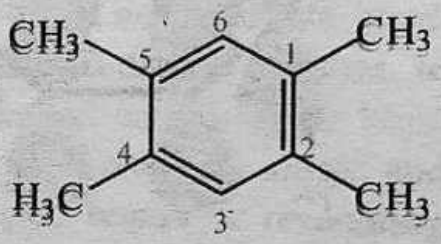
iv) Some polysubstituted benzene derivatives are better known by their common names.



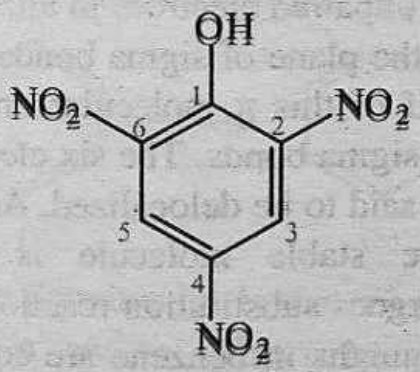
Phloroglucinol



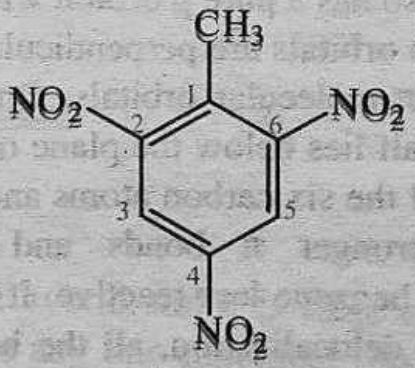
Mesitylene



Durene



Picric acid



TNT

16.8.2 Physical Properties of Benzene

i) Benzene is a colourless liquid and has peculiar smell.
ii) It has burning taste.
iii) Its melting point is 5.5°C and its boiling point is 80.1°C.
iv) It is insoluble in water.
v) It is highly inflammable and burns with luminous and smoky flame.
vi) It is miscible with alcohol and ether in all proportions.
vii) Its specific gravity is 0.884 g/cm^3 at 15°C.
viii) It is good solvent for many organic and inorganic substances such as fats, resins, sulphur, phosphorus, and iodine.
ix) Its vapours are highly toxic which on inhalation produce loss of consciousness. In long run, its vapours destroy the red and white blood cells.

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16.8.3 Structure of Benzene (Molecular Orbital Aspects)

The hexagonal planar structure of benzene can be best explained in terms of molecular orbital theory. Each carbon in benzene has three sp^2 hybrid orbitals and they are half filled hence used in bond formation. The two sp^2 hybrid orbitals are used to make sigma bonds with adjacent carbon atoms due to sp^2–sp^2 overlapping while the third sp^2 hybrid orbital is used to make sigma bond with hydrogen atom due to sp^2–s overlapping. All sigma bonds in benzene lie in the same plane and all the bond angles are of 120°. This confirm the regular hexagonal structure of benzene.

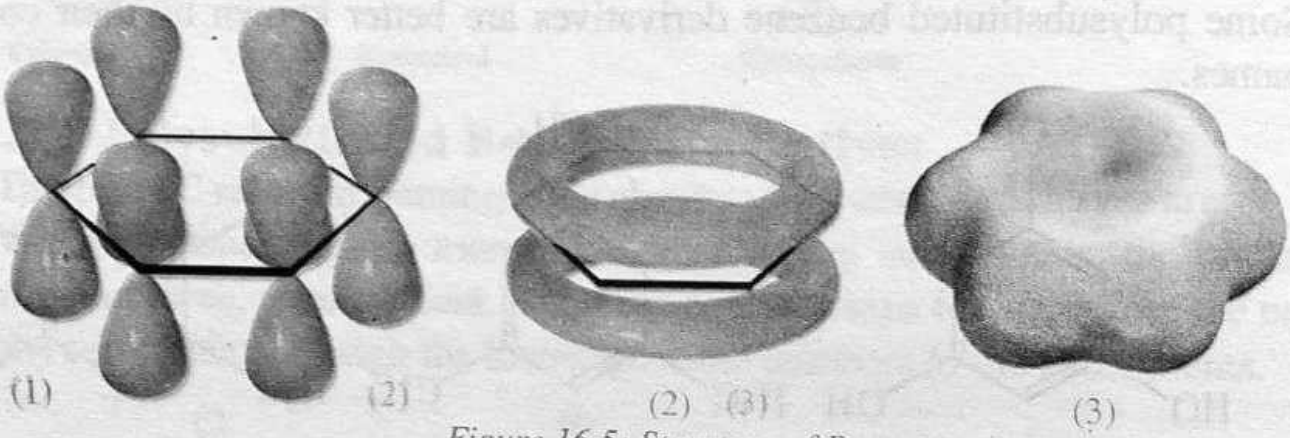


Figure 16.5: Structure of Benzene

Each carbon also has a pure p orbital with an unpaired electron. In all, there are six p orbitals. These p orbitals are perpendicular to the plane of sigma bonds. The six pure p orbitals form π-molecular orbitals. One half of this π molecular orbital lies above and the other half lies below the plane of the sigma bonds. The six electrons of the p orbitals cover all the six carbon atoms and are said to be delocalized. As a result of delocalization, stronger π bonds and more stable molecule is formed. Delocalization makes benzene less reactive. It undergoes substitution reactions rather than addition. Due to delocalization, all the bond lengths in benzene are equal. The delocalization of six π electrons is shown by a circle in the ring.

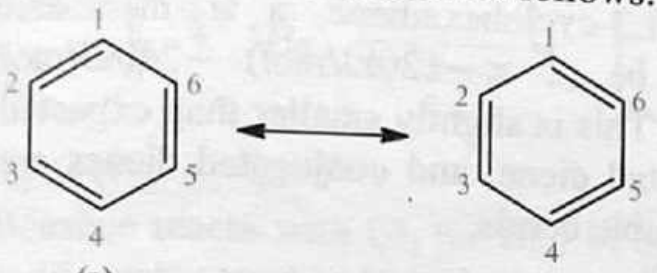
16.8.4 Resonance, Resonance Energy and Stabilization

16.8.4.1 Resonance

The resonance is another term that is used for delocalization. The process in which two or more structures are written for a compound which differ only in the arrangement of electrons is called resonance. The different structures obtained are called resonance structures. They are also known as contributing structures or canonical structures. The resonance theory gave the correct description for the structure of benzene. It states that whenever a molecule is represented by two or more structures any one of the structure alone is not able to explain the characteristics of the molecule on the whole. The actual structure in such cases is a hybrid of all the resonance structures. These resonance structures are hypothetical and exist only in

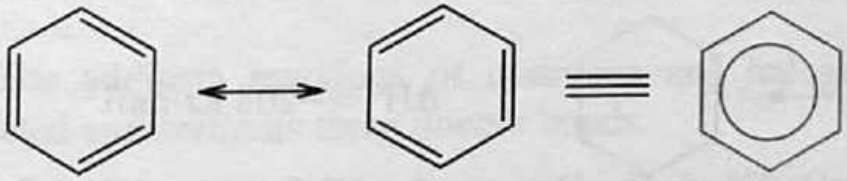
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theory. These structures cannot be isolated. In writing resonance structures we are allowed to move electrons and not the atoms. The resonance is represented by placing a double headed arrow (⟷) between resonance structures. The major contributing structures for benzene are written as follows:



(a) (b)

Each drawing alone is inadequate to describe the structure of benzene. The problem is that each carbon-carbon bond is neither a single bond nor a double bond. Each carbon-carbon bond is single in one resonance structure and double in other, so the actual bond length (139 pm) is intermediate between a carbon-carbon single bond (153 pm) and a carbon-carbon double bond (134 pm). The three alternate single and double bonds in the structure of benzene are called conjugate bonds or resonating bonds. The actual structure of benzene may be represented as a hybrid of the above two (a and b) resonance structures.



(a) (b) (c)

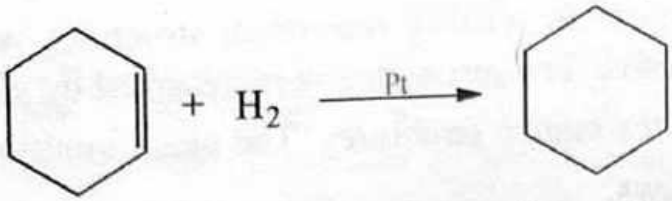
The drawing 'c' is the resonance hybrid and it is more stable than resonance structures 'a' and 'b'. This is because in any one canonical form the π-electrons are localized while in the hybrid the π-electrons are delocalized over six atoms of the benzene ring.

16.8.4.2 Resonance Energy and Stability of Benzene

The difference between the energy of the actual molecule (a resonance hybrid) and the most stable resonance structure is called resonance energy. It is also known as delocalization energy. Resonance energy can be used to explain unusual stability and lack of reactivity toward addition of benzene. Resonance energy can be determined by the difference between the calculated and experimental heats of hydrogenation of the compound. Consider the following thermochemical results to see the unusual stability of benzene.

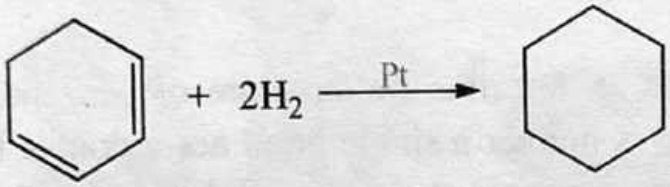
The heat of hydrogenation for cyclohexene, a six-membered ring containing one double bond, is found to be −120kJ/mol.

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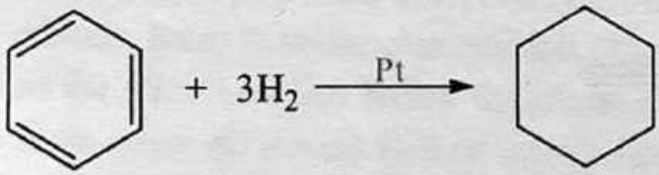
$\Delta H° = -120$ kJ/mol

The heat of hydrogenation for 1,3-cyclohexadiene, a six-membered ring containing two double bonds, should be (2 × −120kJ/mol) −240kJ/mol. The observed value, however, is −232kJ/mol. This is slightly smaller than expected value because 1,3-cyclohexadiene is a conjugated diene, and conjugated dienes are more stable than two isolated carbon-carbon double bonds.



$\Delta H° = -232$ kJ/mol

The heat of hydrogenation of 1,3,5-cyclohexatriene (benzene), a six-membered ring containing three double bonds, should be (3 × −120 kJ/mol) −360kJ/mol. The observed heat of hydrogenation, however, is only −208 kJ/mol. The observed value is 152 kJ/mol less than expected value. This difference between the amount of observed heat of hydrogenation and that of calculated heat of hydrogenation is called the resonance energy of the compound (benzene).



$\Delta H° = -208$ kJ/mol

Benzene is, therefore, said to be resonance stabilized by an amount of 152 kJ/mol, which is known as resonance energy. Now it becomes clear that the process of resonance makes benzene more stable than the other unsaturated hydrocarbons.

16.8.5 Reactivity and Reactions of Benzene

Benzene is highly unsaturated and has six π-electrons delocalized in six p orbitals. But it does not undergo addition reactions as happily as other unsaturated hydrocarbons such as alkenes and alkynes. This is because the loosely π-electrons in alkenes and alkynes are localized but in benzene are delocalized. In alkenes and alkynes the π-electrons are easily available for different addition reactions while, in benzene, the π-electrons are not easily available. Therefore, benzene is less reactive than alkenes and alkynes towards electrophilic addition reactions. The most common reactions of benzene are electrophilic substitution reactions.

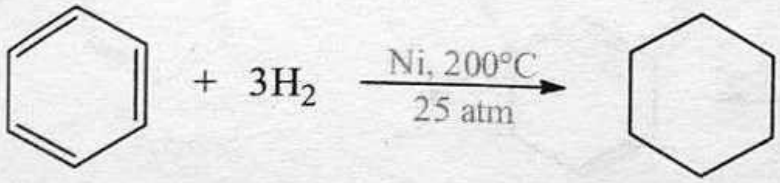
16.8.5.1 Addition Reactions

There are two types of addition reactions: addition of hydrogen and addition of halogens.

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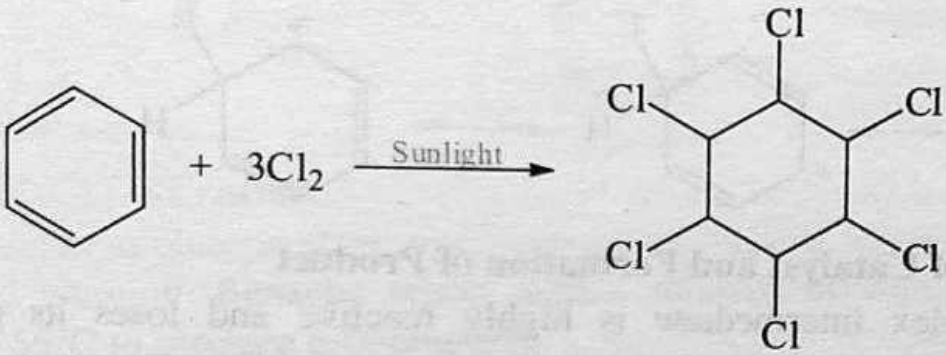
ition of Hydrogen (Catalytic Hydrogenation)

Benzene reacts with hydrogen in the presence of catalyst like Pt, Pd and Ni at temperature and pressure to produce cyclohexane.



tion of Halogens

Benzene reacts with Cl_2 (or Br_2) in the presence of sunlight to form benzene chloride and is used as insecticide.



Reaction of F_2 with benzene is vigorous and reaction of I_2 with benzene is very

The addition reactions of hydrogen and halogens indicate that benzene is urated and contains three double bonds.

.5.2 Electrophilic Aromatic Substitution Reactions

5.2.1 General Introduction

The most important reactions of benzene are electrophilic substitution ions. In these reactions, one of the hydrogen atom (proton) of the benzene ring is ced by an electrophile. The electrophilic substitution reactions carried out in the nce of Lewis acid catalyst such as FeX_3 or AlX_3 that help in generation of ophile. The electrophile will either be a positive ion, or the slightly positive end olar molecule.

eral Mechanism

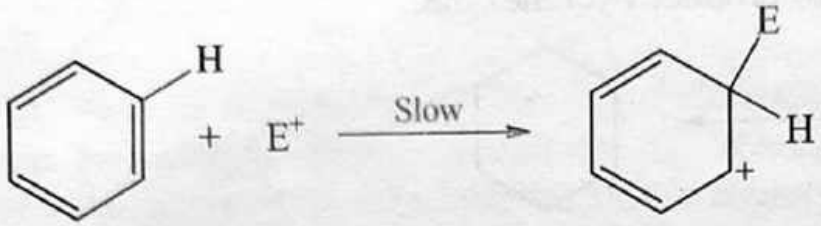
The electrophilic aromatic substitution reaction generally involves two-steps:

1: Formation of Arenium Ion

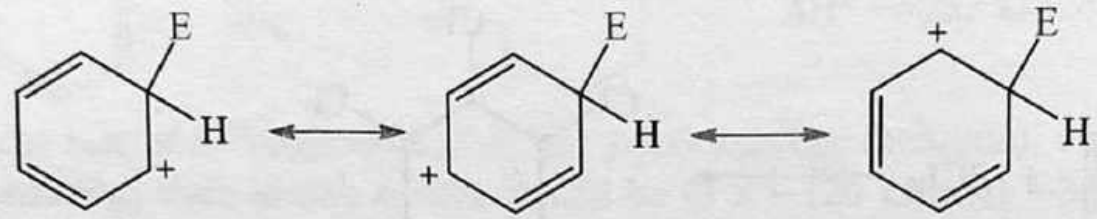
The electrophile attacks the π-electrons of the benzene ring to form a σ-bond one of the carbon atoms of the benzene ring, generating a positively charged mediate (cyclohexadienyl carbocation) known as Arenium ion or sigma complex. sigma complex is not aromatic because the carbon that forms a bond to the ophile becomes sp^3 hybridized and it has no *p*-orbital. Now only five carbon

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atoms of the ring are sp^2 hybridized and has *p*-orbitals. Hence, the sigma complex does not possess a continuous system of overlapping *p*-orbitals.

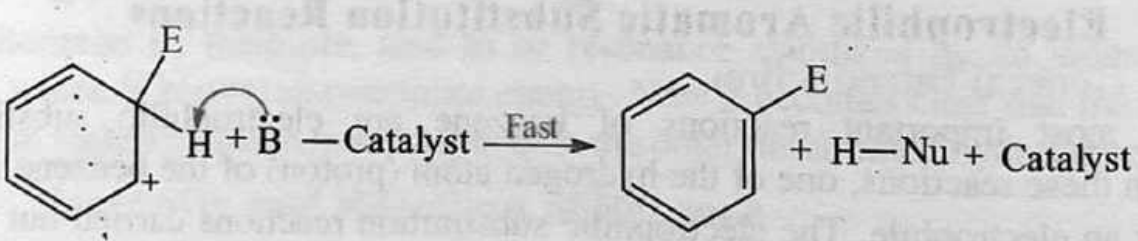


The positive charge is effectively distributed over three carbon atoms by resonance which makes it partially stable.



Step 2: Regeneration of Catalyst and Formation of Product

The sigma complex intermediate is highly reactive and loses its proton from sp^3 hybridized carbon to a Lewis base. The electrons that held the proton (hydrogen) move into the ring to restore its aromaticity. Remember that the proton is always removed from the carbon that has formed the new bond with the electrophile.



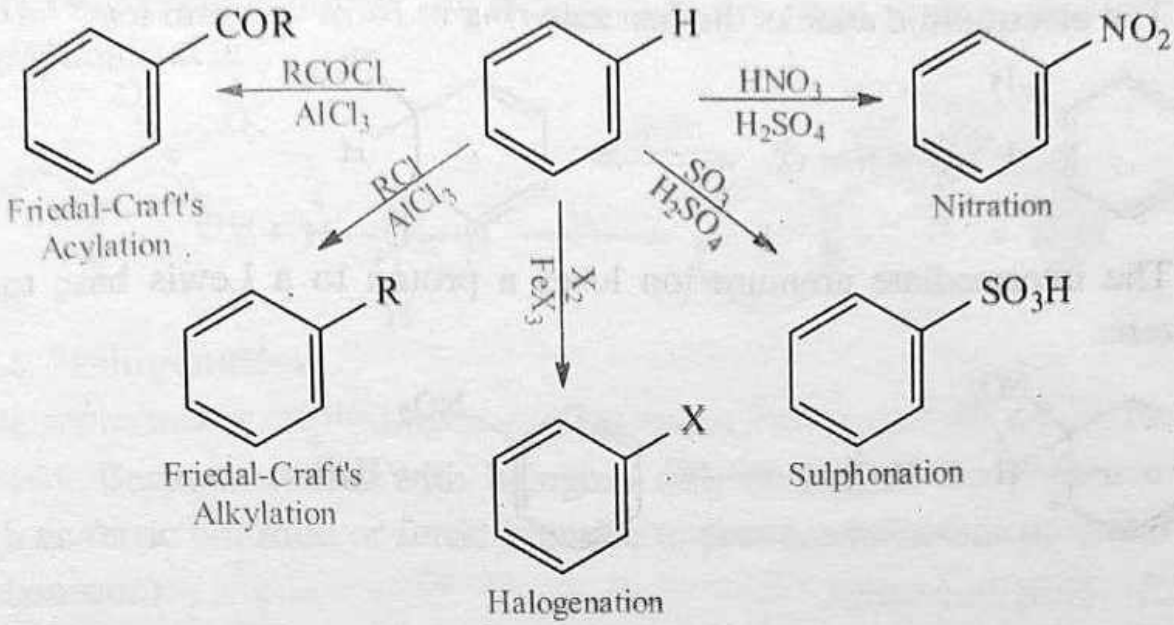
Keep in Mind

The first step is rate determining step and is relatively slow. This step consumes energy because an aromatic compound is being converted into a much less stable non-aromatic intermediate.

The second step is fast because the aromaticity of the benzene ring is restored.

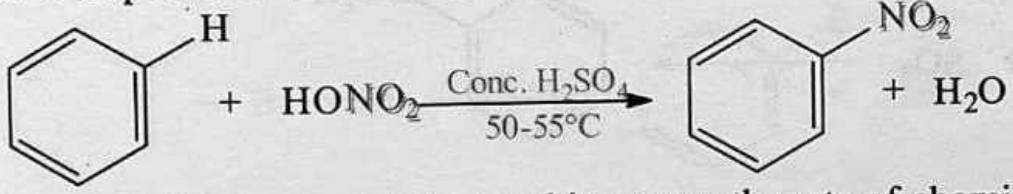
The five most useful electrophilic aromatic substitution reactions are nitration, sulphonation, halogenation, Friedel-Craft's alkylation and Friedel-Craft's acylation.

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16.8.5.2.2 Nitration

The replacement of hydrogen of an organic compound by a nitro group is called nitration. **Benzene reacts with a mixture of conc. HNO_3 and conc. H_2SO_4 at 50-55°C to produce nitrobenzene.**

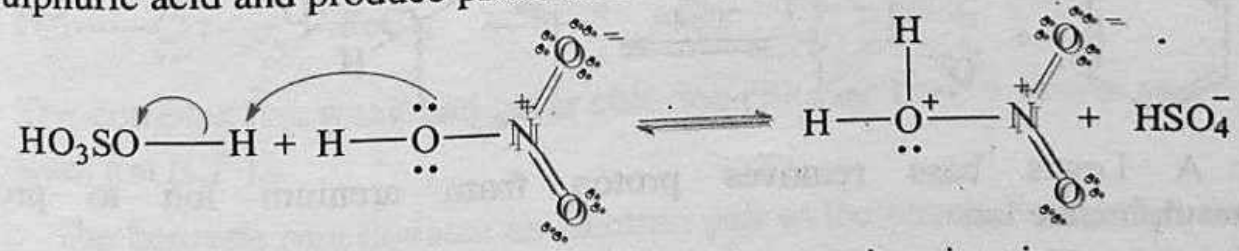


Conc. H_2SO_4 acts a catalyst and increases the rate of chemical reaction by increasing the concentration of the electrophile, NO_2^+ (the nitronium ion).

Mechanism

The electrophile (NO_2^+) is produced from the acid-base reaction that occurs between HNO_3 and H_2SO_4.

Step 1: Nitric acid acts as a base to accept a proton (hydrogen ion) from the stronger acid, sulphuric acid and produce protonated nitric acid.

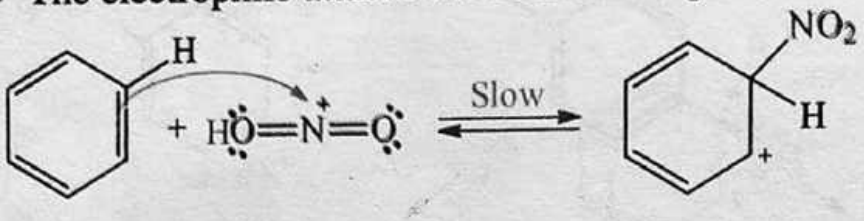


Step 2: Now protonated nitric acid dissociate to form a nitronium ion.

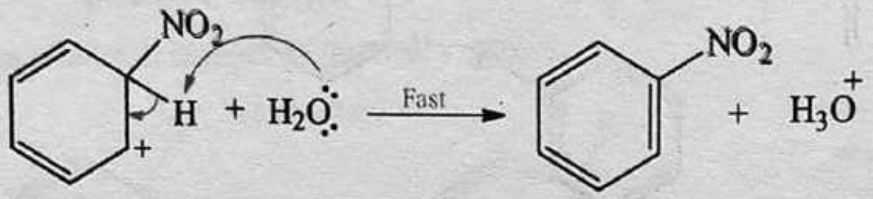


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Step 3: The electrophile attacks the benzene ring to form arenium ion.

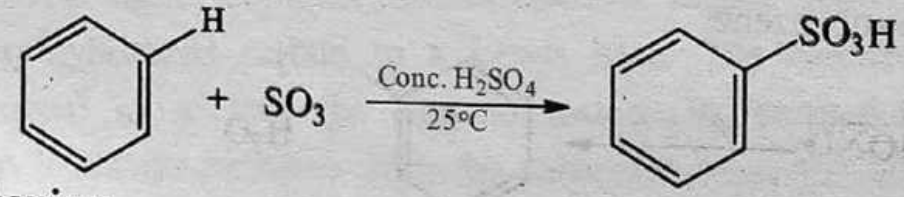


Step 4: The intermediate arenium ion loses a proton to a Lewis base to produce nitrobenzene.



16.8.5.2.3 Sulphonation

The replacement of hydrogen of an organic compound by a sulphonic acid ($-SO_3H$) group is called sulphonation. **Benzene reacts with fuming sulphuric acid ($H_2SO_4 + SO_3$) at room temperature to give benzenesulphonic acid.**

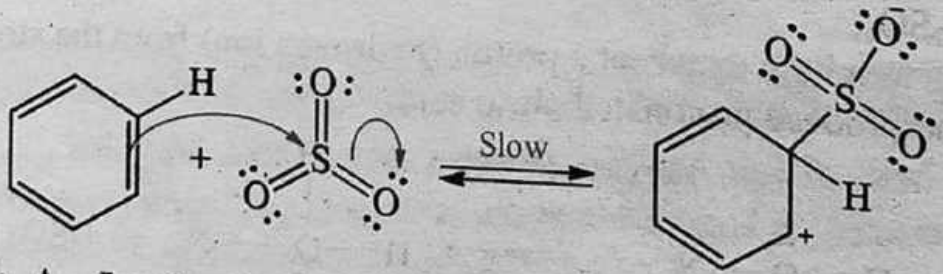


Mechanism

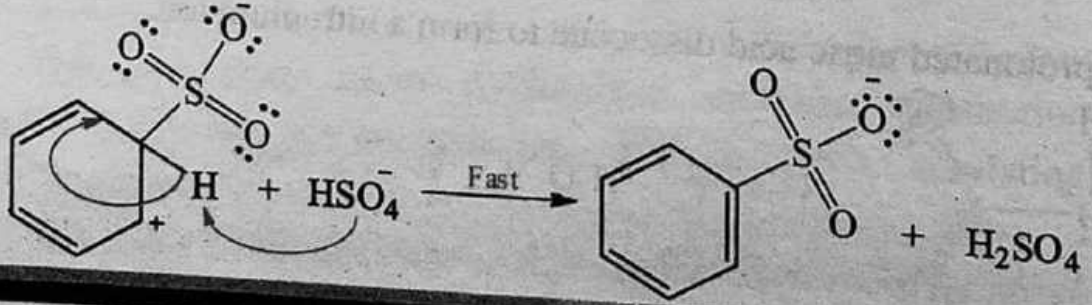
Step 1: The sulphuric acid ionizes in water to produce hydrogen sulphate and hydronium ions.

$$H_2SO_4 + H_2O \longrightarrow HSO_4^- + H_3O^+$$

Step 2: The electrophile attacks the benzene ring to form arenium ion.

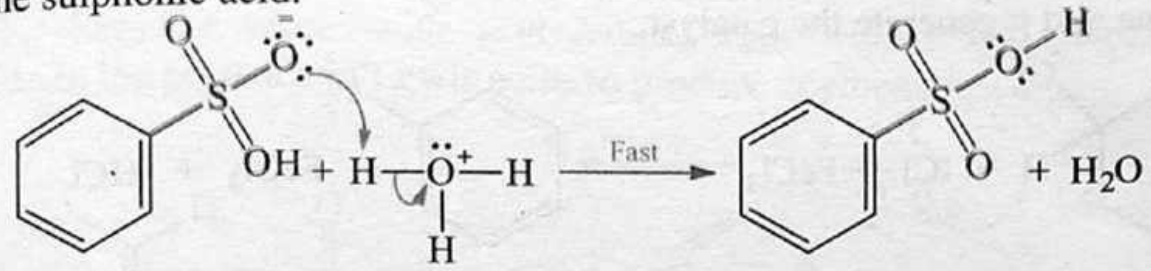


Step 3: A Lewis base removes proton from arenium ion to produce benzenesulphonate ion.



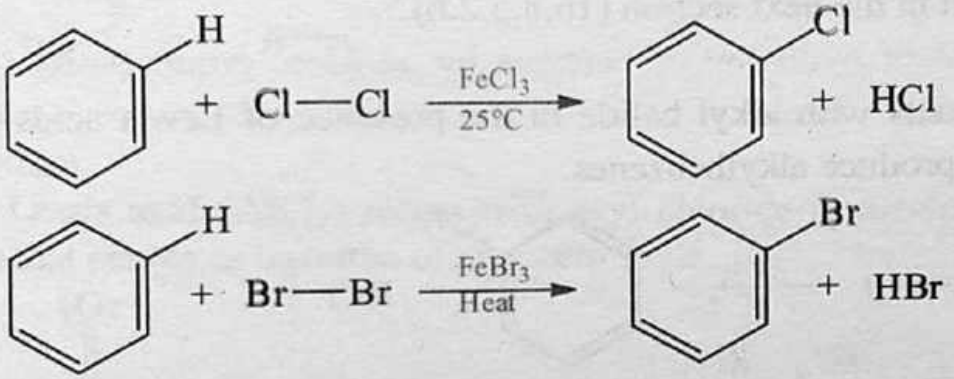
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Step 4: The benzenesulphonate ion accepts a proton form hydronium ion to produce benzene sulphonic acid.



16.8.5.2.4 Halogenation

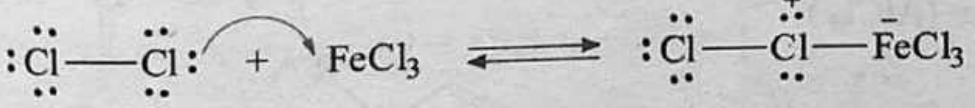
The replacement of hydrogen of an organic compound by a halogen is called halogenation. Benzene reacts with halogens (Cl_2 or Br_2) in the presence of Lewis acids such as ferric chloride or ferric bromide to produce halobenzene (chlorobenzene or bromobenzene).



The reactions of iodine and fluorine are not synthetically useful because the reaction of iodine with benzene is too slow and that of fluorine is too fast.

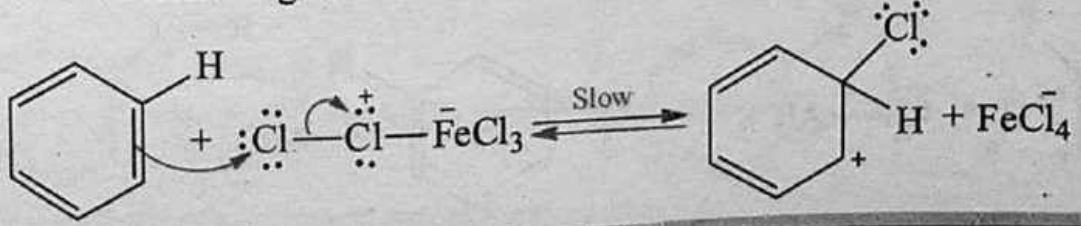
Mechanism

Step 1: Chlorine reacts with $FeCl_3$ to produce a Lewis acid-base complex (electrophile).



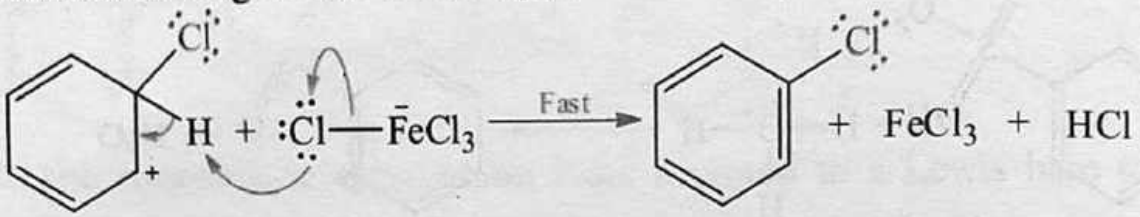
The complex has weak and polar chlorine-chlorine bond and acts as a source of chloronium ion (Cl^+).

Step 2: The benzene ring donates an electron pair to the terminal chlorine, forming a new carbon-chlorine sigma bond and forms an arenium ion along with a base ($FeCl_4^-$).



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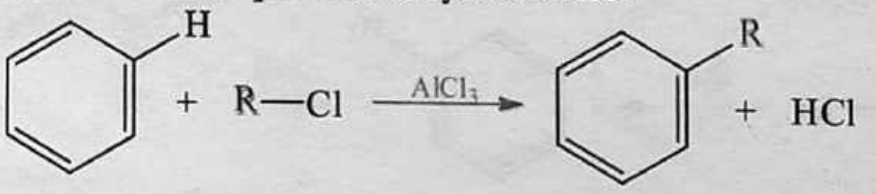
Step 3: A base ($FeCl_4^-$) removes the proton from the arenium ion to from chlorobenzene and regenerate the catalyst.



16.8.5.2.5 Friedel-Crafts Alkylation

Charles Friedel, a French chemist, and James Crafts, an American chemist, discovered new methods for the preparation of alkylbenzenes and acylbenzenes in 1877. Because of this, these reactions are known as Friedel-Crafts alkylation and acylation reactions. We are going to study the Friedel-Crafts alkylation here and Friedel-Crafts acylation in the next section (16.8.5.2.6).

The replacement of hydrogen of benzene by an alkyl group (—R) is called alkylation. **Benzene reacts with alkyl halide in the presence of Lewis acids such as aluminium chloride to produce alkylbenzenes.**

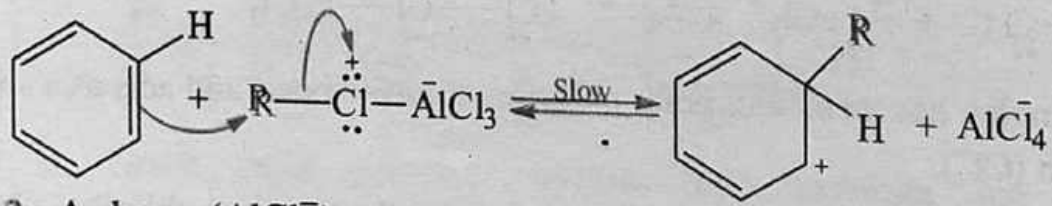


Mechanism

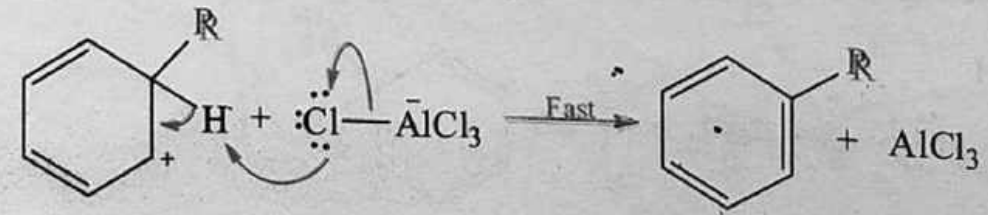
Step 1: Lewis acid ($AlCl_3$) reacts with alkyl chloride to produce a Lewis acid-base complex that serves as a source of an electrophile.



Step 2: The benzene ring donates an electron pair to the alkyl group, forming the arenium ion and a base ($AlCl_4^-$).



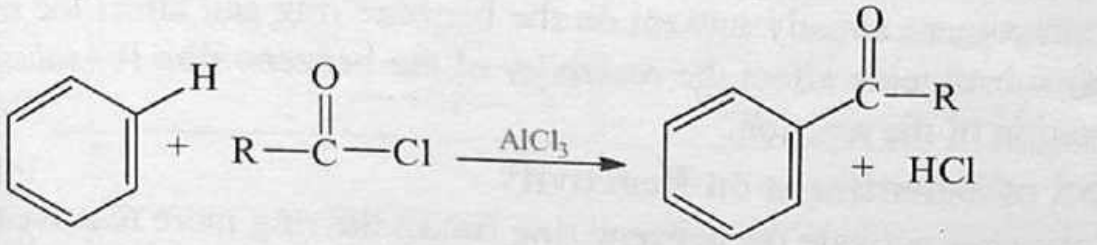
Step 3: A base ($AlCl_4^-$) removes the proton from the arenium ion to from alkylbenzene and regenerate the catalyst.

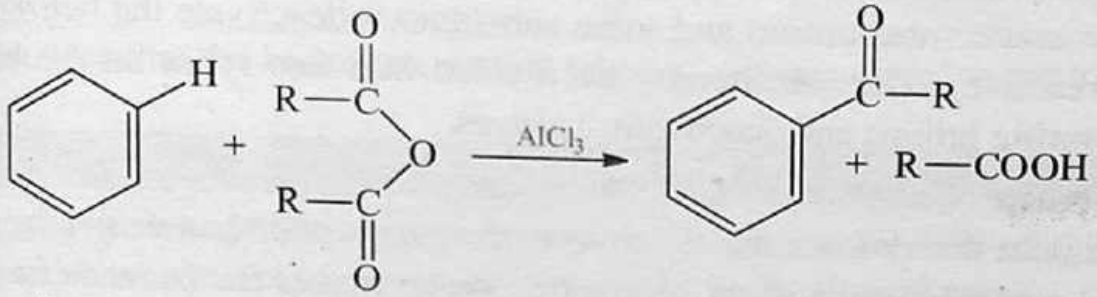


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16.8.5.2.6 Friedel-Crafts Acylation

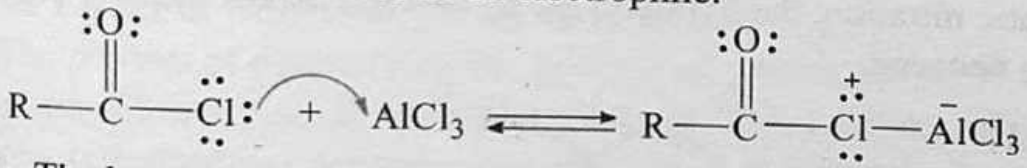
The replacement of hydrogen of benzene by an acyl group (—COR) is called acylation. Benzene reacts with acyl halides (also called acid halides) or acid anhydride in the presence of Lewis acids to produce acylbenzene.



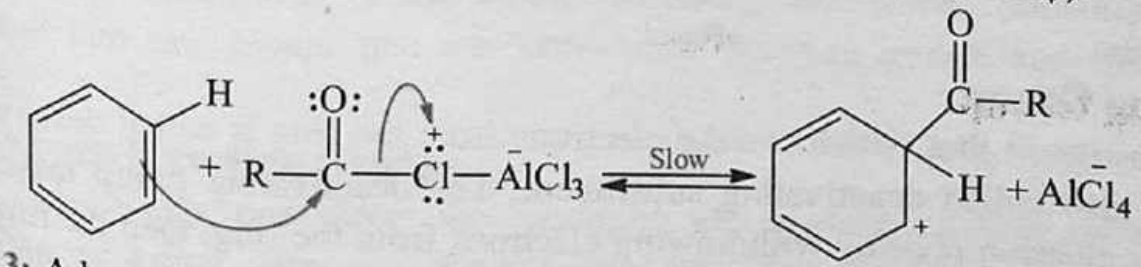


Mechanism

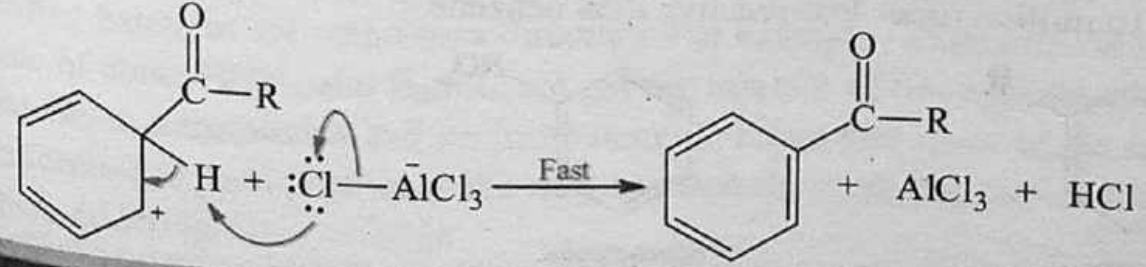
Step 1: Lewis acid ($AlCl_3$) reacts with acyl chloride to produce a Lewis acid-base complex that serves as a source of an electrophile.



Step 2: The benzene ring donates an electron pair to the carbon of carbonyl group of Lewis acid-base complex, forming the arenium ion and a base ($AlCl_4^-$).



Step 3: A base ($FeCl_4^-$) removes the proton from the arenium ion to from acylbenzene and regenerate the catalyst.



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16.8.5.2.7 Substituent Effects on Benzene Ring

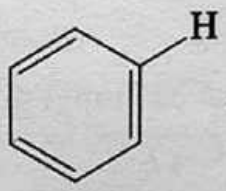
Only one product can produced when an electrophilic substitution takes place on benzene. It is because all the available sites of benzene ring are equivalent. But what would happen if we were to carry out a reaction on a benzene ring that already has a substituent? A substituent already present on the benzene ring can affect the reaction in two ways: (a) substituents affect the reactivity of the benzene ring (b) substituents affect the orientation of the reaction.

A) The Effect of Substituent on Reactivity

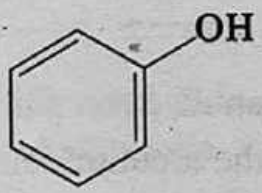
Some substituents activate the benzene ring (make the ring more reactive toward electrophilic aromatic substitution) and some substituents deactivate the benzene ring (make it less reactive). The substituents are divided into two types on the basis of reactivity: activating groups and deactivating groups.

Activating Group

A substituent that donates the electrons to the ring is called an activating group. It is also called activating substituent. Activating group makes the benzene ring more electron rich by donating electrons to the ring, then the ring will be more reactive towards electrophilic aromatic substitution and the reaction will occur faster. For example, in aromatic nitration, the hydroxyl group (—OH) makes the ring 1000 times more reactive than benzene.



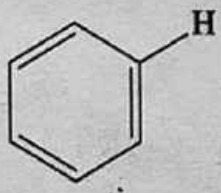
Benzene



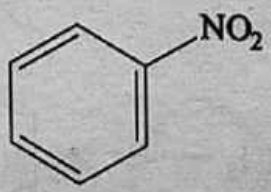
Phenol

Deactivating Group

A substituent that withdraws the electrons from the ring is called deactivating group. It is also called deactivating substituent. The deactivating group makes the benzene ring electron poor by withdrawing electrons from the ring, then the ring will be less reactive towards electrophilic aromatic substitution and the reaction will occur slower. For example, in aromatic nitration, the nitro group (—NO_2) makes the ring more than 10 million times less reactive than benzene.



Benzene



Nitrobenzene

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Table 16.8: Activating and Deactivating Groups

Activating Groups			Deactivating Groups		
Strong	**Moderate**	**Weak**	**Strong**	**Moderate**	**Weak**
$-\ddot{\underset{\cdot\cdot}{O}}:^-$	$-\ddot{N}COR$	$-R$	$-NO_2$	$-COCl$	$-X$
$-\ddot{N}R_2$	$-\ddot{O}COR$	$-C_6H_5$	$-\overset{+}{N}R_3$	$-COOH$	
$-\ddot{N}H_2$		$-CH=CR_2$	$-SO_3H$	$-COOR$	
$-\ddot{O}H$			$-CN$	$-COR$	
$-\ddot{O}R$			$-CF_3$	$-CHO$	

Notices that the hydrogen atom is taken as a standard and is regarded as having no effect.

Keep in Mind

Activating groups are alkyl groups, phenyl groups or they have an atom esp. N or O atom with a lone pair of electrons attached directly to the benzene ring.
Deactivating groups are either halogens or they have an atom with full or partial positive charge attached to the benzene ring.

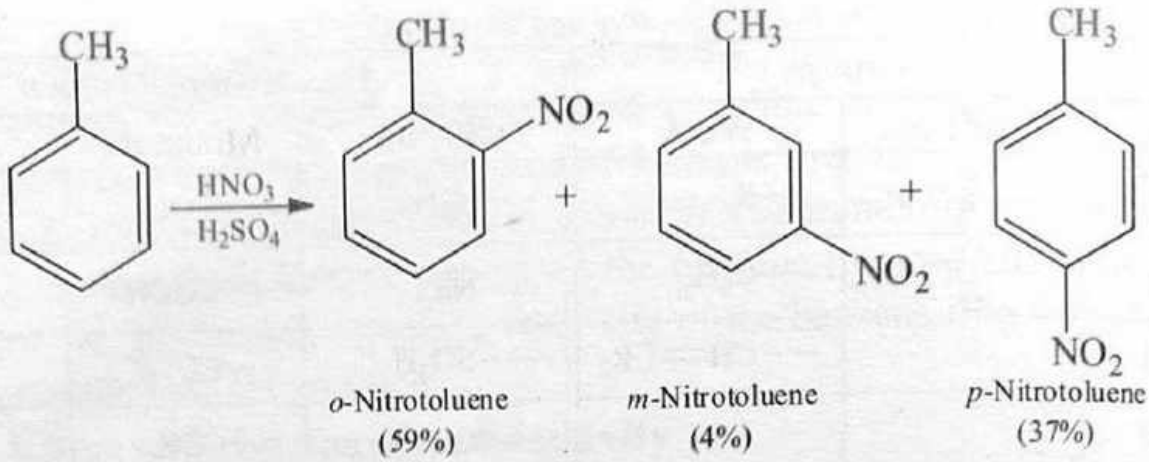
B) The Effect of Substituents on Orientation

The process of determining the position of second incoming substituent on the monosubstituted benzene is called orientation. The position of second incoming substituent (electrophile) depends upon the nature of first substituent already present on the benzene ring. Because the first substituent activates or deactivates the benzene ring and provides a site for the second incoming substituent. Substituents can be classified into two groups that are: ortho-para directing groups and meta directing groups.

Ortho-para Directing Groups

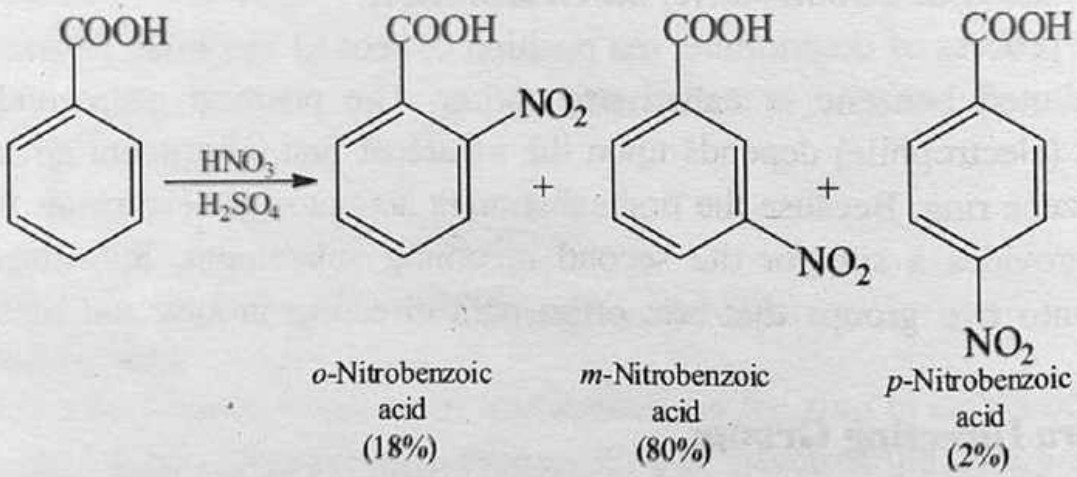
Substituents that direct the incoming electrophile towards ortho and para positions are called ortho-para directing groups. They are electron releasing groups and activates primarily the ortho and para positions. Hence, the attack of electrophile may occur at ortho and para positions. All activating substituents and the weakly deactivating halogens are ortho-para directors. For example, when toluene reacts with a mixture of conc. HNO_3 and H_2SO_4, we get the mixture of three products that are o-nitrotoluene, m-nitrotoluene and p-nitrotoluene. We find that most of the substitution occur at ortho and para positions. We may say that the methyl group of toluene is an ortho-para directing.

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Meta Directing Groups

Substituents that direct the incoming electrophile towards meta positions are called meta directing groups. They are electron withdrawing groups and deactivates primarily the ortho and para positions. Hence, the attack of electrophile may occur at metapositions. All moderately and strongly deactivating substituents are metadirectors. For example, when benzoic acid reacts with a mixture of conc. HNO_3 and H_2SO_4 at 100°C, we get the mixture of about 80% of the m-nitrobenzoic acid, 18% o-nitrobenzoic acid and 2% p-nitrobenzoic acid. We find that most of the substitution occurs at meta positions. We may say that the carboxyl group of benzoic acid is metadirecting.



Keep in Mind

Monosubstituted benzenes that give mainly ortho and para products usually react faster than benzene. Monosubstituted benzenes that give mainly meta product always react more slowly than benzene.

16.8.5.2.8 Formation of Polysubstituted Benzenes

The substitution pattern of electrophilic substitution reactions can be controlled by the substituent group already present on the benzene ring other than hydrogen. The activating group such as methyl, hydroxyl, and methoxy on a benzene ring directs the

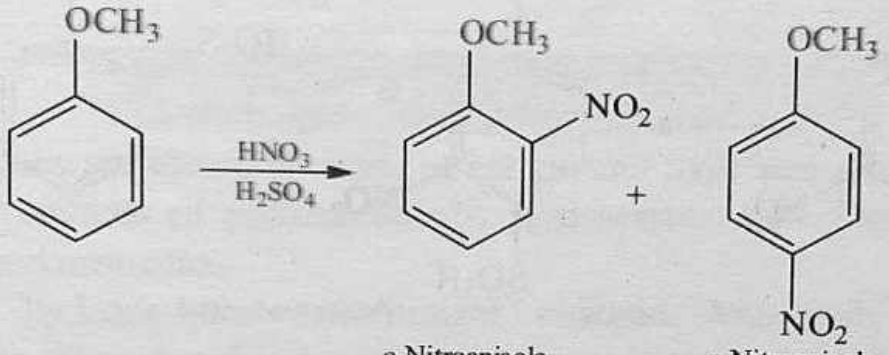
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electrophile to ortho and para positions of the ring whereas the deactivating groups such as nitro, carboxyl and aldehyde except halogens directs the electrophile to meta positions. If there is competition between ortho-para and meta directing groups, ortho-para directing groups predominate.

Formation of Disubstituted Benzenes

The position of the second substituent depends upon the nature of the first substituents already bonded to the ring.

Consider the example of nitration of anisole. The methoxy group of phenol is electron releasing group and is ortho-para director. It sends the second substituent (electrophile) mostly to the ortho and para positions.



o-Nitroanisole *p*-Nitroanisole

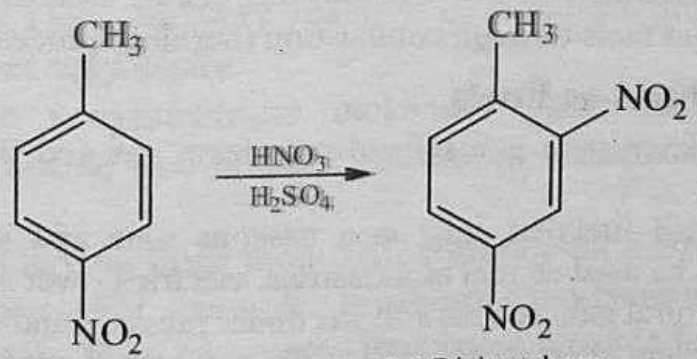
(Major Products)

The ortho and para products can be separated by several methods because they have different physical properties.

Formation of Trisubstituted Benzenes

The position of third substituent depends upon the nature of both the substituents that are already bonded to the benzene ring.

Example 1: If the two substituents direct the new substituent to same positions, then neither group will dominate. Consider the example of nitration of p-nitrotoluene. It has two substituents: the methyl group and nitro group. The methyl group in p-nitrotoluene is ortho-para director and the nitro group is meta director.

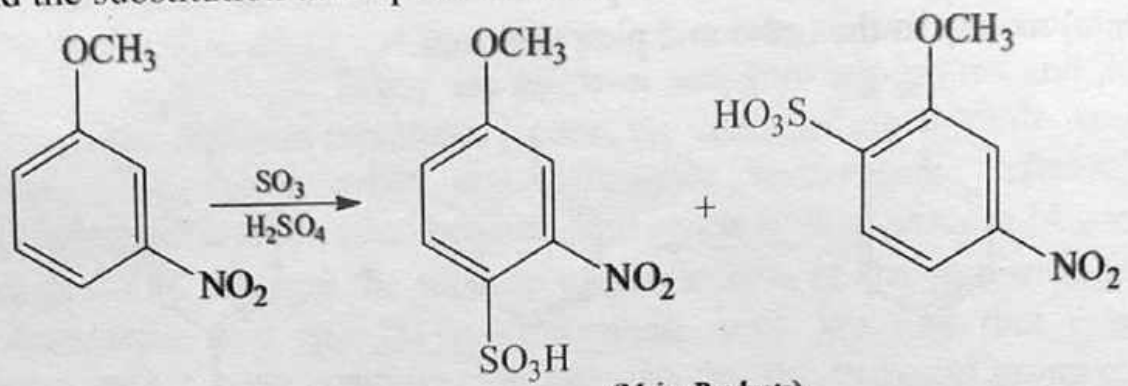


p-Nitrotoluene 2,4-Dinitrotoluene

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In this example, the methyl group directs the incoming substituent to the ortho positions only because the para position is already blocked and the nitro group directs the incoming substituent to the meta position to the nitro group. In this example, both the methyl group and nitro group direct the incoming substituent to the same positions. Since the two positions are identical and only one product is formed.

Example 2: If the two substituents direct the new substituent to different positions, the more powerful group predominates. Consider the example of m-nitroanisole. The methoxy group in m-nitroanisole is a stronger activating group as compared to nitro group, and the substitution takes place ortho and para to the methoxy group.



(Major Products)

The isomer with sulphonic acid group (—SO_3H) between the —OCH_3 and —NO_2 is a very minor product because of steric hindrance.

Society, Technology and Science

Importance of Various Hydrocarbons as Fuels for the Future Energy Needs

Fuels are naturally occurring combustible substances that act as a source of heat energy or raw materials for the chemical industry. Hydrocarbons (compounds of hydrogen and carbon) are mainly used as fuels. Fuels include from methane to higher hydrocarbons containing seventeen carbon atoms. Some of the important hydrocarbons that are used as fuels are LPG, natural gas, gasoline, kerosene oil, and diesel. The higher hydrocarbons having more than seventeen carbon atoms are present in heavy oil fractions. They can be cracked to get gasoline and other hydrocarbons that can be used as fuel in various sectors. Energy is obtained from fuels through combustion (burning) process.

Uses of Hydrocarbons as Fuels

LPG (liquefied petroleum gas) is a refined petroleum gas and is used as camping and domestic fuel.

Natural Gas is a fossil fuel that exist in a gaseous state and is composed mainly of methane (CH_4). It can be used as fuel in industries, electric power stations and homes.

CNG (compressed natural gas) is a natural gas under pressure and can be used as cheaper, greener and more efficient alternative to the traditional petrol and diesel fuels for vehicles.

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Gasoline is used as a fuel for cars, motorbikes, trucks, boats and other transport vehicles.
Kerosene oil is widely used to power jet engines of aeroplanes and some rocket engines. It is used to fuel lamps and lanterns because it has low explosion hazard and burns relatively cleanly. It is also used in stoves for cooking.
Diesel is used as a fuel for trucks, buses, tractors, tanks and central heating systems. It is also used in diesel engine generators to generate electricity.
Coal is not hydrocarbon. It is made up almost entirely of carbon. It is mainly used in power generation. It is also used as household fuel for cooking and heating.
Fuel oil is derived from crude petroleum either as a distillate or a residue at the oil refinery and is the most widely used liquid fuel for power generation and ships. Fuel oil has more than sixteen carbon atoms.
Paraffin wax is an alkane with approximately 25 carbon atoms, and is used as fuel for candles.

Summary of Facts and Concepts

- Hydrocarbons are the compounds of carbon and hydrogen atoms only. They are the major sources of petrochemicals. Hydrocarbons are broadly classified as aliphatic and aromatic.
- Aliphatic hydrocarbons are straight chained, branched or non-aromatic compounds. They may be classified as saturated or unsaturated.
- Saturated hydrocarbons contain carbon-carbon single bonds. They are also known as alkanes or paraffins. They have no functional groups. They have general formula C_nH_{2n+2}.
- Alkanes react with halogens by free radical mechanism to produce alkyl halides. The mechanism occurs in three steps: (i) initiation (ii) propagation and (iii)termination.
- Complete oxidation of alkanes give carbon dioxide, water vapours and energy.
- Unsaturated hydrocarbons contain one or more carbon-carbon multiple bonds. They are further divided into alkenes and alkynes.
- Alkenes are unsaturated hydrocarbons, which contain one or more carbon-carbon double bonds. They are also known as olefins. They have general formula C_nH_{2n}. They are very reactive compounds and undergo electrophilic addition reactions very easily.
- Addition of an unsymmetrical molecule (polar reagent) such as HX to unsymmetrical alkene like propene, occurs in accordance with Markovnikov's rule.
- The compounds having same molecular formula but different structural formulas are called isomers. For example, n-pentane, iso-pentane and neo-pentane are isomers of pentane. They have same molecular formula but different structures.

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- Alkynes are unsaturated hydrocarbons, which contain one or more carbon-carbon triple bonds. They have general formula C_nH_{2n-2}. They are produced during cracking of petroleum.
- Alkynes undergo addition reactions like alkenes but alkynes add two molecules of reagent instead of one. They occur in two steps.
- Terminal alkynes contain weakly acidic hydrogen, hence the hydrogen atoms of alkynes can be replaced readily by metals such as Na, Ag, or Cu to form ionic compounds.
- Hydrocarbons which have at least one benzene ring in their structures are called aromatic hydrocarbons. The term "aromatic" is derived from the Greek word "aroma" meaning fragrant.
- The molecule of benzene consists of a ring of six carbon atoms with one hydrogen atom bonded to each carbon. Benzene was discovered by Michael Faraday in 1825.
- Resonance is the process in which two or more structures are written for a compound which differ only in the arrangement of electrons. The resonance is represented by placing a double headed arrow ($\longleftrightarrow$) between resonance structures.
- The difference between the energy of the actual molecule (a resonance hybrid) and the most stable resonance structure is called resonance energy. The resonance energy of benzene is 152 kJ/mol. The process of resonance makes benzene more stable than the other unsaturated hydrocarbons.
- Benzene is less reactive than alkenes and alkynes towards electrophilic addition reactions. The most common reactions of benzene are electrophilic substitution reactions.
- Some substituents activate the benzene ring while some others deactivate the benzene ring. On the basis of reactivity, the substituents are divided into two types: activating groups and deactivating groups.

Multiple Choice Questions

Q. Select one answer from the given choices for each question:

i) The compounds of carbon and hydrogen in which all the four valencies of carbon are fully satisfied are termed as:

(a) Alkanes (b) Alkenes
(c) Alkynes (d) Alkanols

ii) Acetylene is the example of:

(a) Alkane (b) Alkene
(c) Alkyne (d) Enyne

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iii) The addition of unsymmetrical reagent to an unsymmertical alkene follows the rule:

(a) Pauli's exclusion principle (b) Hund's rule

(c) Auf bau principle (d) Markownikov's rule

iv) The geometry of alkanes is:

(a) Linear (b) Triangular

(c) Tetrahedral (d) Octahedral

v) Alkanes are colourless and odourless liquids when they have:

(a) Less than five carbons (b) Five to seventeen carbons

(c) One to seventeen carbons (d) More than seventeen carbons

vi) The isomers of a compound have same:

(a) Physical properties (b) Chemical properties

(c) Structural formulas (d) Molecular masses

vii) Which type of substitution reaction occurs in benzene easily?

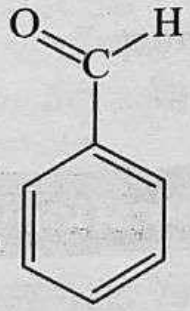
(a) Electrophilic substitution reaction

(b) Nucleophilic substitution reaction

(c) Both occurs simultaneously

(d) None of the reaction takes place

viii) The substituent (—CHO) as shown attach to benzene ring is said to be:



(a) Activator to the ring

(b) Deactivator to the ring

(c) It does nothing to the ring

(d) It is just a functional group

ix) The given two compounds are ..... of each other



(a) Skeletal isomers (b) Metameres

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(c) Tautomers (d) Positional isomers

x) Two optical isomers such as (+) lactic acid and (−) lactic acid, have:

(a) Same physical and chemical properties
(b) Same physical but different chemical properties
(c) Different physical but same chemical properties
(d) Same behavior towards plane of polarized light

Short Answer Questions

Q.1. Why alkanes are less reactive than alkenes?
Q.2. Why alkenes are more reactive than alkynes?
Q.3. Why benzene is less reactive than alkenes?
Q.4. Explain why cis-alkenes are generally less stable than their trans-isomers
Q.5. Why a substituent directs an incoming electrophile to a particular position?
Q.6. Define radical, homolytic fission and heterolytic fission.
Q.7. Give the order of reactivity of alkanes, alkenes, alkynes and benzene.
Q.8. Why alkynes are acidic in nature?
Q.9. What is electrophilic substitution of benzene?
Q.10. Why benzene does undergo electrophilic substitution reaction?
Q.11. Why benzene does not undergo electrophilic addition?
Q.12. Why benzene acts as a nucleophile?
Q.13. What are activating and deactivating groups?
Q.14. Is nitro group activating or deactivating?

Long Answer Questions

Q.1. What are hydrocarbons? How are they classified? Give an example of each type.
Q.2. Define nomenclature. Give historical background of common and IUPAC systems.
Q.3. Explain nomenclature of straight chain and branched chain alkanes
Q.4. Describe the nomenclature of cycloalkanes.
Q.5. Explain structure, relative stability and reactivity of alkanes.
Q.6. Explain structure, relative stability and reactivity of cycloalkanes.
Q.7. Write down the physical properties of alkanes and cycloalkanes.
Q.8. Give an overview of the radical substitution reactions.
Q.9. Explain the reaction mechanism of free radical.

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Q.10. Describe the oxidation of organic compounds.
Q.11. What are alkenes? Explain the nomenclature of alkenes.
Q.12. Describe the relative stability, structure and reactivity of alkenes.
Q.13. Write down the methods for the preparation of alkenes in detail.
Q.14. What are the physical and chemical properties of alkenes? Explain.
Q.15. Describe the concept of conjugation in alkenes. Your focus should be on dienes.
Q.16. What is isomerism? Explain different types of isomerism.
Q.17. What are alkynes? Explain the nomenclature of alkynes.
Q.18. Explain relative stability, structure and reactivity of alkynes.
Q.19. Give the general methods for the preparation of alkynes.
Q.20. Write down the physical properties of alkynes.
Q.21. What do you know about addition reactions of alkyne? Explain.
Q.22. Define benzene and give its classification.
Q.23. Explain the nomenclature of aromatic hydrocarbons.
Q.24. Explain the structure of benzene in terms of molecular orbital theory.
Q.25. What is resonance? Explain the important aspects of resonance with reference to benzene.
Q.26. Define the term resonance energy and discuss the stability of benzene.
Q.27. Draw the structures for the following hydrocarbons:

i) 2-Methylhexane
ii) 3-Methylheptane
iii) 4-Ethyl-3-methylheptane
iv) 2,2,4-trimethylhexane
v) 4-Ethyl-2-methylhexane
vi) 3-Ethyl-3-methylhexane
vii) 2,3-dimethylbutane
viii) 2,3,4-trimethlylpentane
ix) 3-ethyl-2,2-dimethylpentane
x) 5-ethyl-2,6-dimethyloctane
xi) Methylcyclopentane
xii) Ethylcyclohexane
xiii) 1-ethyl-2-methylcyclopentane
xiv) 1,1,2- trimethylcyclopentane

Q.28. Write the structural formulas of the following compounds:

i) 3-hexene
ii) 2,3-heptadiene
iii) Hepta-2,4-diyne
iv) 1,3-dimethylcyclohexane
v) TNT
vi) Picric acid

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2.29. Give the IUPAC names of the following compounds:

i) $CH_3CH_2CH_3$

ii) $CH_3(CH_2)_2CH_3$

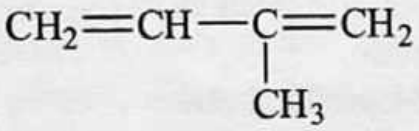
iii) $CH_3CH(CH_3)_2$

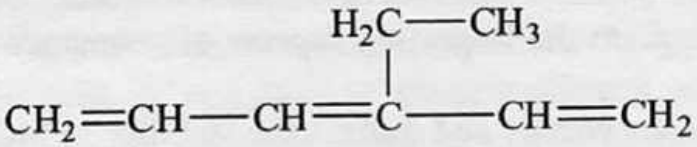
iv) $(CH_3)_3CCH_2CH_3$

v) $CH_3CH(CH_3)CH_2CH_3$

vi) $CH_3—CH=CH_2$

vii) $CH_2=CH—CH=CH_2$

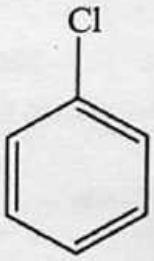
viii)


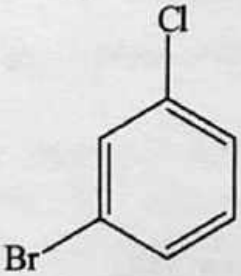
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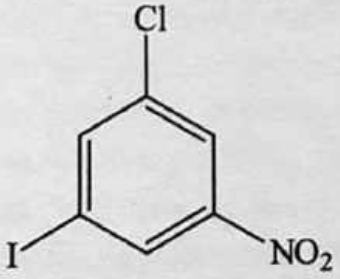
x) $CH_3—C\equiv C—CH_3$

xi) $CH_3—C\equiv C—CH_2—C\equiv CH$

xii) $CH\equiv C—CH=CH_2$

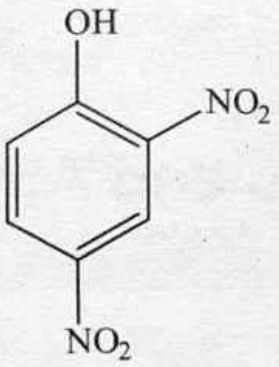
xiii)


xiv)


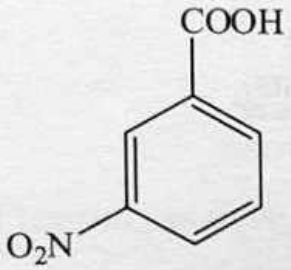
xv)


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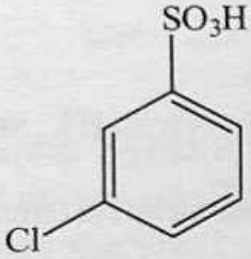
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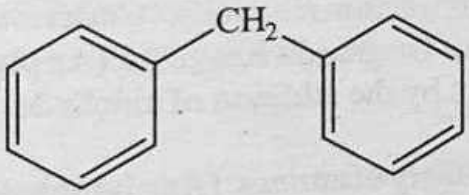
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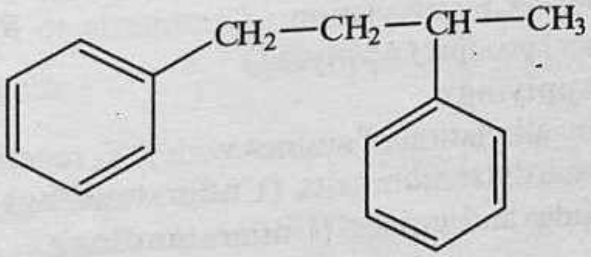
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Chapter 17

Alkyl Halides and Amines

Major Concepts

17.1 Alkyl Halides
17.2 Organometallic Compounds (Grignard's Reagents)
17.3 Amines

Learning Outcomes:

Students will be able to:

- Name alkyl halides using IUPAC system. **(Applying)**
- Discuss the structure and reactivity of RX. **(Applying)**
- Describe the preparation of RX by the reaction of alcohols with HX, $SOCl_2$ and PX_3 and by radical halogenation of alkanes. **(Applying)**
- Describe the mechanism and types of nucleophilicsubstitution reactions. **(Understanding)**
- Describe the mechanism and types of elimination reactions. **(Understanding)**
- Describe the preparation and reactivity of Grignard's Reagents. **(Applying)**
- Discuss chemistry of Grignard's reagent by the addition of aldehydes, ketones, esters and carbon dioxide. **(Understanding)**
- Discuss nomenclature, structure and basicity of amines. **(Applying)**
- Describe the preparation of amines by alkylation of ammonia to RX and reduction of nitriles, nitro and amide functional groups. **(Applying)**
- Discuss reactivity of amines. **(Applying)**
- Describe chemistry of amines by alkylation of amines with RX, reactions with aldehydes, ketones, preparation of amides and diazonium salts. **(Understanding)**
- Describe isomerism in alkyl halides and amines. **(Understanding)**

Introduction

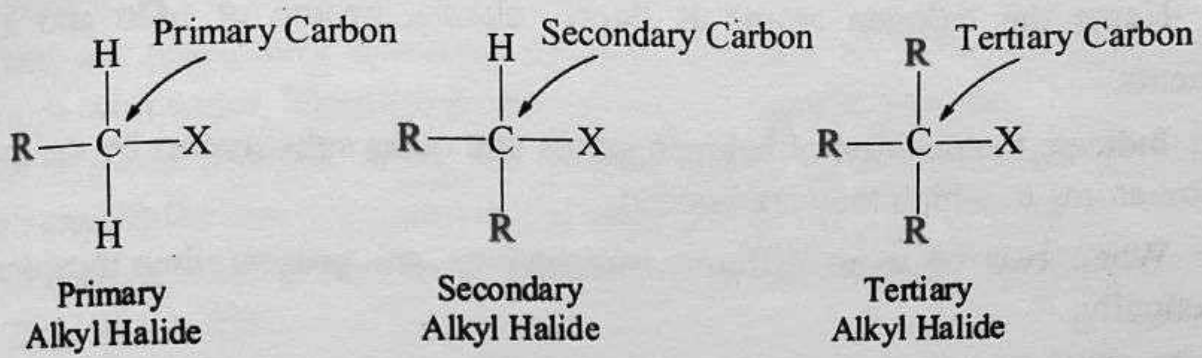
Alkyl halides are one of the most important types of reactants in nucleophilic substitution reactions. In this chapter, we consider the properties and reactions of alkyl halides and then study the two of the most important types of reactions in organic chemistry, namely the substitution and elimination reactions. In this chapter, we also discuss the basicity and properties of amines.

17.1 Alkyl Halides

Alkyl halides are organic compounds containing a halogen atom covalently bonded to one of the saturated carbon atoms of an alkyl group. They are termed as, in

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the IUPAC system of nomenclature, haloalkanes. They are classified as primary (1°), secondary (2°) or tertiary (3°) alkyl halides depending upon whether the halogen atom is directly bonded to primary, secondary or tertiary carbon atom.



Primary Alkyl Halide | **Secondary Alkyl Halide** | **Tertiary Alkyl Halide**

Their general formula is $C_nH_{2n+1}X$, where X = F, Cl, Br, or I.

17.1.1 Nomenclature of Alkyl Halides

There are two systems for naming alkyl halides that is common system and IUPAC system.

17.1.1.1 Common System

The common names of alkyl halides are two word names. Common names are constructed by naming the alkyl group first and then the halide as fluoride, chloride, bromide and iodide. These names are useful only for simple alkyl halides. Examples are:

CCl_4

Carbon **tetrachloride**

$CHCl_3$

Chloroform

CH_2Cl_2

Methylene **chloride**

$CH_3—Cl$

Methyl **chloride**

$\overset{2}{C}H_3—\overset{1}{C}H_2—F$

Ethyl **fluoride**

$\overset{3}{C}H_3—\overset{2}{C}H_2—\overset{1}{C}H_2—I$

n-Propyl **iodide**

$\overset{3}{C}H_3—\overset{2}{\underset{\displaystyle Cl}{C}}H—\overset{1}{C}H_3$

Isopropyl **chloride**

$(CH_3)_3CBr$

Tert.butyl **bromide**

17.1.1.2 IUPAC System

In this system, alkyl halides are considered as halogen derivatives of corresponding alkane and are named as ***haloalkanes***. The IUPAC names of alkyl halides are one-word names. The rules for naming alkyl halides are:

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Step 1: Select the longest continuous chain of carbon atoms containing the halogen atom.

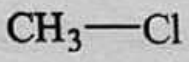
Step 2: Number the carbon chain from that end which is nearer to halogen atom.

Step 3: Name the halogen atoms as fluoro, chloro, bromo or iodo and all other substituents.

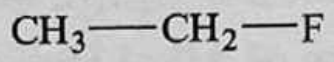
Step 4: Indicate the position of halogen atoms and other substituents by the number of carbon atoms to which they are bonded.

Step 5: When two or more different substituents are present, then they are named alphabetically.

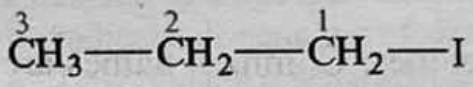
Examples are:



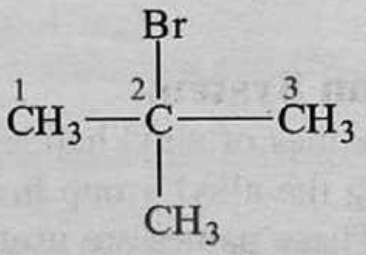
Chloromethane



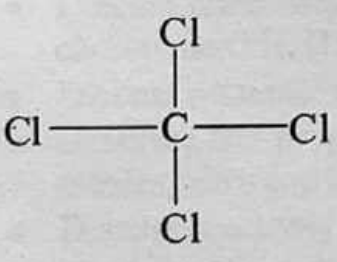
Fluoroethane



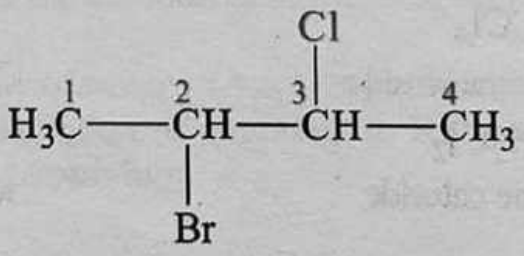
1-Iodopropane



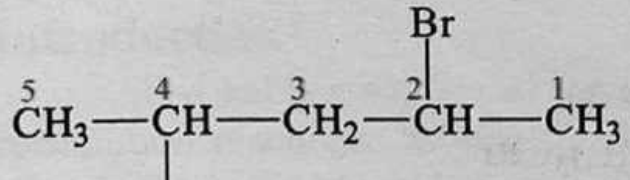
2-Bromo-2-methylpropane



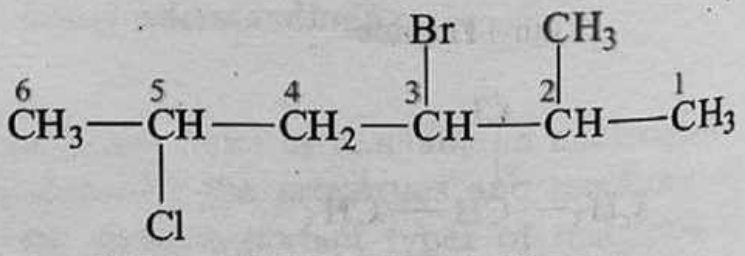
Tetrachloromethane



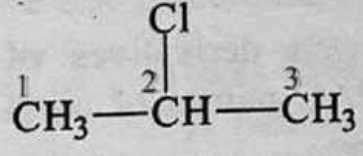
2-Bromo-3-chlorobutane



2,4-Dibromopentane



3-Bromo-5-chloro-2-methylhexane



2-Chloropropane

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17.1.2 Physical Properties of Alkyl Halides

i) Lower alkyl halides such as CH_3Cl, CH_3Br, CH_3F and CH_3CH_2Cl are gases at room temperature. The alkyl halides up to C_{18} are colourless liquids and those further than C_{18} are colourless solids.

ii) They are practically insoluble in water because they do not form hydrogen bonds with water. They are readily soluble in organic solvents.

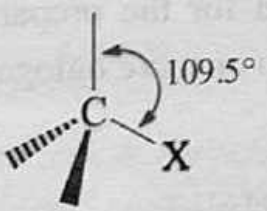
iii) For a given halogen atom, the boiling points of alkyl halides increase with increase in the size (or mass) of the alkyl group.

iv) For a given alkyl group, the boiling points of alkyl halides are in the order: **RI > RBr > RCl > RF**

v) For a given halogen atom, the density of alkyl halides decrease with increase in the size (or mass) of the alkyl group.

17.1.3 Structure of Alkyl Halides

Let us consider the example of simple alkyl halide (i.e. methyl chloride). The carbon atom to which the halogen is bonded is sp^3 hybridized. The halogen (chlorine) atom has one half-filled *p* orbital. The carbon-halogen σ-bond is formed by head to head overlap of one sp^3 hybrid orbital of carbon and one half-filled p orbital of halogen atom. The carbon-hydrogen σ-bond is formed by head to head overlap of one sp^3 hybrid orbital of carbon and half-filled *s* orbital of hydrogen atom.



The $H\hat{C}H$ and $H\hat{C}X$ bond angles are nearly 109.5°. The arrangement of atoms or groups around the carbon atom is usually tetrahedral.

17.1.4 Preparation of Alkyl Halides

Alkyl halides are prepared by the methods given below:

17.1.4.1 Reaction of Alcohols with Hydrogen Halides

Alkyl halides are prepared by the reaction of alcohol with hydrogen halides in the presence of dehydrating agent such as anhydrous $ZnCl_2$.

$$CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$$

The order of reactivity of hydrogen halides is: HI > HBr > HCl

The order of reactivity of alcohols is: 3° > 2° > 1°

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17.1.4.2 Reaction of Alcohols with other Halogenating Agent ($SOCl_2$, PX_3)

Reaction of Alcohols with Thionyl Halides

Alkyl halides are prepared by heating alcohols with thionyl halides in the presence of pyridine.

$$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3CH_2Cl + SO_2 + HCl$$

This is the best method for the preparation of alkyl halides because both the products (SO_2 and HCl) are in gaseous state and can be removed easily.

Reaction of Alcohols with Phosphorus Halides (PX_3)

Alkyl halides are prepared by the reaction of alcohols with phosphorous halides.

$$3\,CH_3CH_2OH + PCl_3 \longrightarrow 3\,CH_3CH_2Cl + H_3PO_3$$

17.1.4.3 Radical Halogenation of Alkanes

Alkyl halides are prepared by the reaction of alkanes with halogens in the presence of diffused sun light or UV light.

$$CH_3CH_3 + Cl_2 \xrightarrow{\text{UV Light}} CH_3CH_2Cl + HCl$$

This is not a good method for the preparation of alkyl halides because the halogen derivatives containing two or more halogen atoms are also formed along with alkyl halides.

17.1.5 Reactivity of Alkyl Halides

Alkyl halides are very reactive compounds. The extent of reactivity depends upon two factors: (i) bond polarity of carbon-halogen bond (ii) bond energy of carbon-halogen bond.

17.1.5.1 Bond Polarity of Carbon-Halogen Bond

The halogen atom in alkyl halides is more electronegative than carbon. Because of this, the molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to carbon. Greater the electronegativity difference (ΔEN) of carbon and halogen atoms, greater would be the polarity of C—X bond. Greater the polarity, greater would be the bond strength and lesser would be the reactivity of RX.

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Table 17.1: Dipole Moment of Halomethanes

Halomethane	Electronegativity of Halogen	EN Difference between C and X	Dipole moment (in Debye unit)
CH_3F	3.98	3.98–2.50 = 1.48	1.85
CH_3Cl	3.00	3.00–2.50 = 0.50	1.87
CH_3Br	2.96	2.96–2.50 = 0.46	1.81
CH_3I	2.56	2.56–2.50 = 0.06	1.62

17.1.5.2 Bond Energy of Carbon-Halogen Bond

Bond energy is the measure of bond strength. Greater the bond energy, greater would be the bond strength and lesser would be the reactivity of C—X bond.

Table 17.2: Bond Energy of C—X Bonds

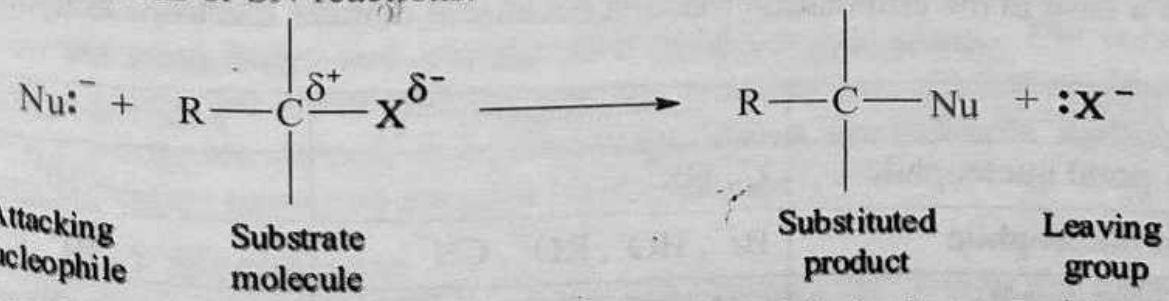
Bond	Bond Energy (kJ/mol)
C—F	467
C—Cl	346
C—Br	290
C—I	228

The order of reactivity of alkyl halides is: RI > RBr > RCl > RF

17.1.6 Nucleophilic Substitution Reactions

17.1.6.1 General Introduction

The reactions in which an electron rich nucleophile replaces another nucleophile (leaving group) to form a new molecule are called nucleophilic substitution reactions or SN-reactions.



In nucleophilic substitution reactions, the nucleophile is always Lewis base and it may be neutral or negatively charged. The substrate is frequently an alkyl halide and the leaving group is a halide ion. The partial positive carbon atom of alkyl halides acts as an electrophile and has ability to accept a pair of electrons from attacking

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nucleophile. In this way, a new bond is formed between the nucleophile and carbon of alkyl halide.

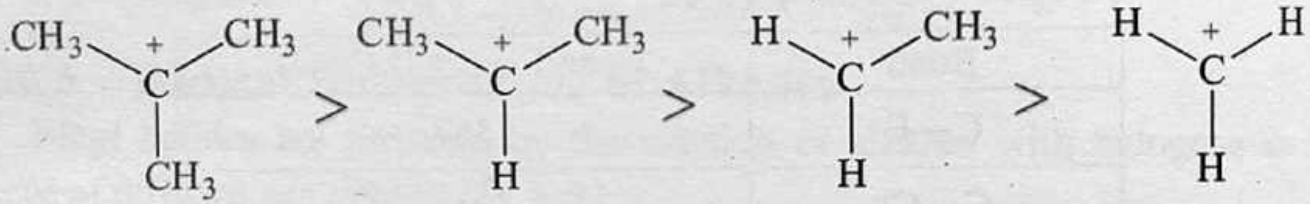
The S_N reactions occur by S_N1 mechanism or by S_N2 mechanism.

17.1.6.2 Important Concepts

Carbocations and Their Stability

Carbocations are very reactive unstable electron deficient species. Anything which donates electron density to the electron deficient centre will help to stabilize them.

Alkyl groups are weak electron donating groups and thus stabilize nearby carbocations. In general, more substituted carbocations are more stable. This means that tertiary carbocations are more stable than secondary which in turn are more stable than primary. In other words, tertiary carbocations are the most stable and the methyl carbocation is the least stable. The overall order of stability is given below:



Tertiary carbocation > Secondary carbocation > Primary carbocation > Methyl carbocation

Nucleophile and Base

Both nucleophiles and Lewis bases are electron pair donor species. Then what is the difference between a nucleophile and a base?

Base is a specie that donates an electron pair to hydrogen (a proton) and nucleophile is a specie that donates an electron pair to an atom other than hydrogen particularly carbon atom. A nucleophile can also be called a base when this donation happens towards a hydrogen ion (a proton). For example, the hydroxide ion acts as a nucleophile in the substitution reaction because it donates electrons to carbon but it acts as a base in the elimination reaction because it donates electrons to hydrogen.

Table 17.3: Some Common Nucleophiles and their Nucleophilicity

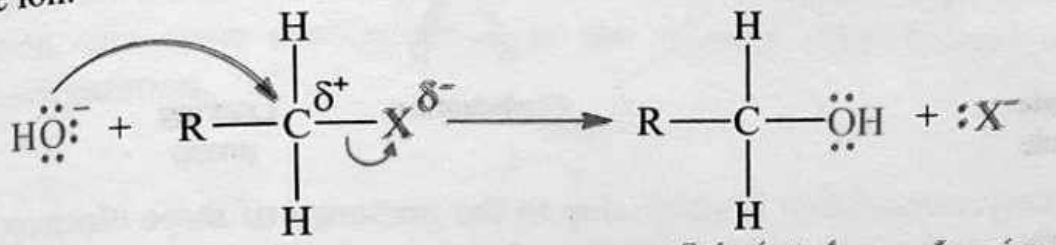
Reactivity Class	Nucleophile	Relative Reactivity
Very good nucleophile	I^-, HS^-	$> 10^5$
Good nucleophile	Br^-, HO^-, RO^-, CN^-	10^4
Fair nucleophile	NH_3, Cl^-, F^-	10^3
Weak nucleophile	H_2O, ROH	10^0
Very weak nucleophile	RCOOH	10^{-2}

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Substrate and Leaving Group

The substrate may be defined as: the carbon containing compound on which substitution takes place. It is the reactant to which the nucleophile became bonded and from which the leaving groups departed.

The leaving groups may be defined as: the species that depart from substrate and take a pair of electrons with them. Consider the reaction of alkyl halide with hydroxide ion.



In this reaction, the alkyl halide is a substrate molecule and halide ion is a leaving group. The bond between carbon and leaving group is polar because the leaving group is more electronegative than carbon. The leaving group has partial negative charge and the carbon has partial positive charge. Thus the carbon acts as an electrophile and is reactive towards nucleophile.

Table 17.4: Some Common Leaving Groups

Class	Leaving Group
Good leaving groups	I^-, Br^-, Cl^-, H_2O
Moderate leaving groups	HS^-, CN^-, NH_3
Poor leaving groups	F^-, HO^-, RO^-
Very poor leaving groups	NH_2^-, H^-, R^-

The best leaving groups are those that become the most stable ions after they depart. The best leaving groups are weakly basic molecules or ions. For example, halide ions are weak bases and are therefore good leaving groups. Conversely, the poor leaving groups are those that become the unstable ions after they depart. The poor leaving groups are strongly basic molecules or ions. For example, hydroxide and amide ions are strong bases and are poor leaving groups.

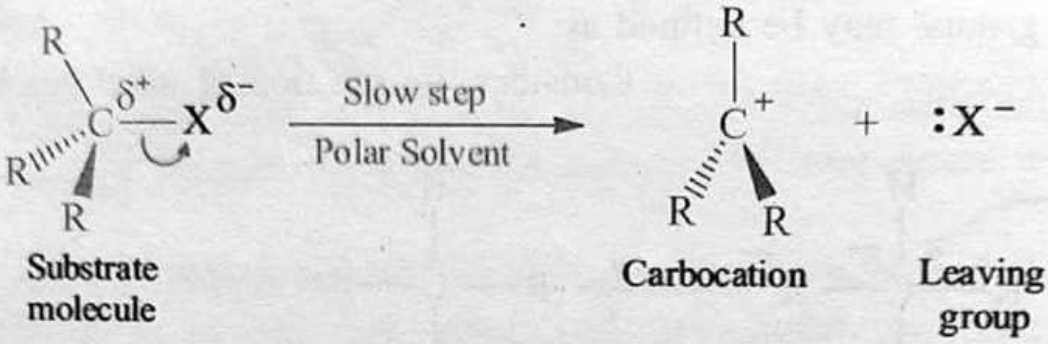
17.1.6.3 S_N1 Mechanism

In the designation S_N1, "S" stands for *substitution*, "N" stands for *nucleophilic* and "1" stands for *unimolecular*. Unimolecular means that only one molecule is involved in the rate-determining step. In this mechanism, the breaking of bond between carbon and the leaving group is fully completed before bond making with the

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nucleophile starts. Consider the reaction of *tertiary* alkyl halide with nucleophile. The reaction occurs in two steps.

Step 1: The *tert*-alkyl halide ionizes to produce a planar carbocation and a leaving group.

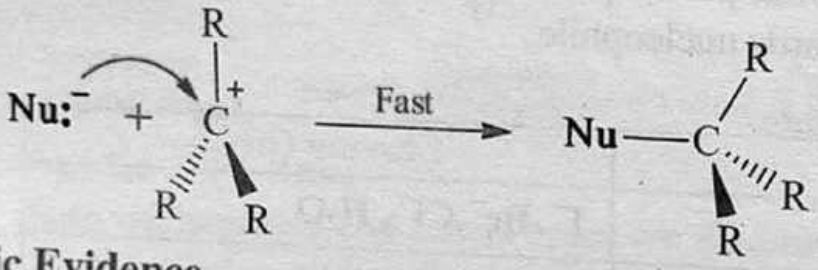


The tertiary carbocation is stable due to the presence of three electron donating alkyl groups. The order of stability of carbocation is as:

3° carbocation > 2° carbocation > 1° carbocation > CH_3^+

This step of reaction is the rate determining step. Since this step involves the breakage of covalent bond so it is a slow step.

Step 2: The nucleophile attacks the planar carbocation to produce *tert.*alkyl product. Since the second step involves the combination of cations and anions, so it is fast.



Kinetic Evidence

The rate law for the reaction is:

Rate ∝ $[R_3CX]$

Rate = $k[R_3CX]$

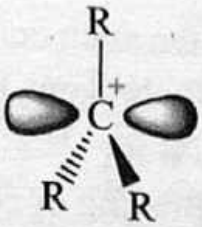
Where **'k'** is the rate constant.

The rate of reaction depends only on the concentration of the substrate, *tert.*alkyl halide but it does not depend on the concentration of the nucleophile. Doubling the concentration of the *tert.*alkyl halide doubles the rate of the reaction, but changing the concentration of the nucleophile has no effect on its rate. This rate equation is first order overall.

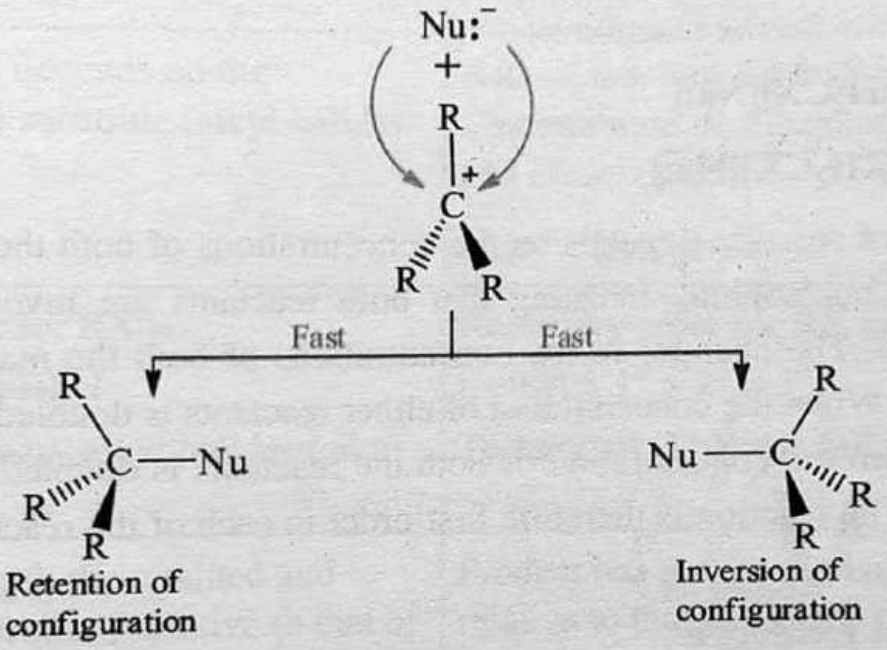
Stereochemical Evidence

Positively charged carbon of carbocation intermediate is sp^2 hybridized and has one pure *p* orbital with two lobes. The three substituent's bonded to positively charged carbon are in the same plane. The empty unhybridized *p*- orbital on carbon perpendicular to the plane of molecule with one lobe on each side of the plane.

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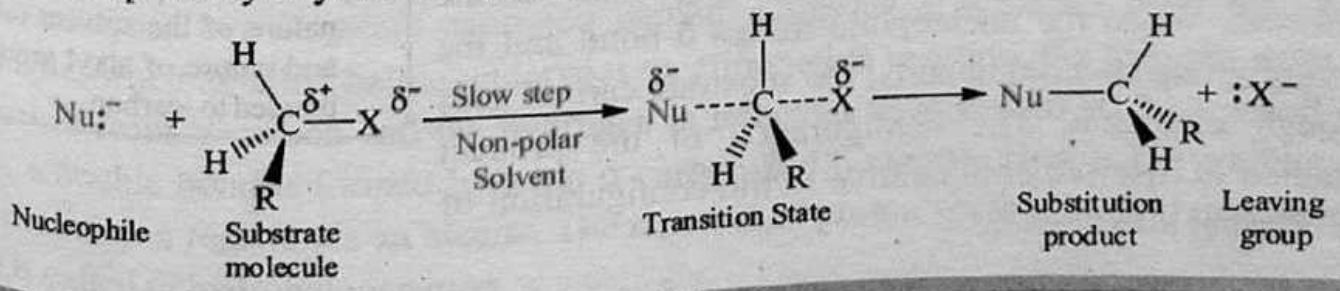
In the second step of the S_N1 mechanism, the nucleophile can attack the carbocation from either side of the plane, therefore some of the product has retained configuration (the same configuration as the reacting alkyl halide) and some has inverted configuration.



When complete inversion of configuration is observed in a substitution reaction, we realize that the mechanism is S_N2 but not S_N1.

17.1.6.4 S_N2 Mechanism

In the designation S_N2, "S" stands for *substitution*, "N" stands for *nucleophilic* and "2" stands for *bimolecular*. Bimolecular means that two molecules (both the alkyl halide and nucleophile) are involved in the rate-determining step. In this mechanism, the breaking of bond between carbon and the leaving group as well as the formation of bond between a nucleophile and an electrophile occur simultaneously. Consider the reaction of *primary*alkyl halide with nucleophile. The reaction occurs in one step.



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In transition state, the bond to the nucleophile is partially formed, and the bond to the leaving group (halide) is partially broken. The transition state has very short-lived existence.

This is slow step and rate determining or controlling step of reaction. Since two molecules are involved in rate determining step, hence it is called bimolecular reaction.

Kinetic Evidence

The rate law for the reaction is:

$$\text{Rate} \propto [RH_2CX][Nu:^-]$$

$$\text{Rate} = k[RH_2CX][Nu:^-]$$

The rate of reaction depends on the concentrations of both the substrate (alkyl halide) and the nucleophile, meaning that both reactants are involved in the rate determining step. The changes in the concentrations of both the reactants affect the rate of reaction. When the concentration of either reactants is doubled, the rate should be doubled. When the concentration of both the reactants is doubled, the rate should be quadruples. The reaction is therefore first order in each of the reactants and second orders overall.

Stereochemical Evidence

In primary alkyl halides, the electrophilic carbon is bonded with one alkyl group and two small hydrogen atoms. These two hydrogen atoms do not show steric hindrance due to smaller size and give way to attacking nucleophile to attack on electrophilic carbon from back side of leaving group. The nucleophile cannot attack on electrophilic carbon atom from front side of the leaving group. We may say that the leaving group blocks the approach of the nucleophile to the front side of the molecule. When the nucleophile makes a bond and the leaving group (halide) departs, the substrate carbon goes through inversion. The configuration of the product obtained is inverted comparative to the configuration of the reactant alkyl halide.

Keep in Mind

- **Methyl halide and primary alkyl halides undergo S_N2 reactions only.**
- **Tertiary alkyl halides undergo S_N1 reactions only.**
- **Secondary alkyl halides undergo both S_N1 and S_N2 reactions depending on the nature of the solvent used and nature of alkyl groups bonded to -carbon.**

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Table 17.5:Comparison of S_N1 and S_N2 Mechanisms

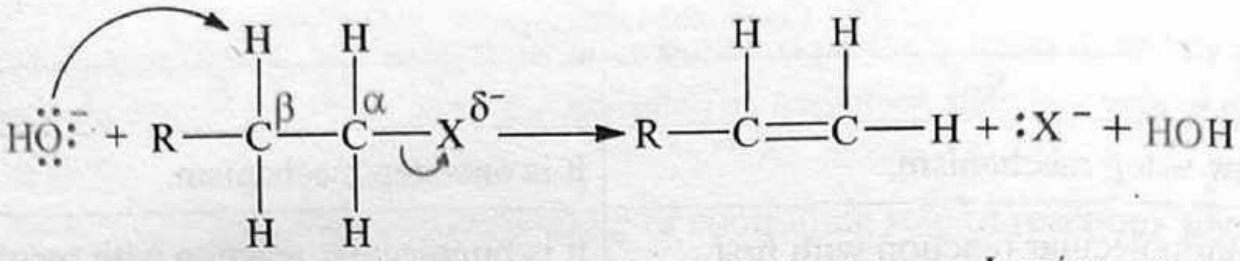
S_N1	S_N2
It is two-step mechanism.	It is one-step mechanism.
It is unimolecular reaction with first order kinetics.	It is bimolecular reaction with second order kinetics.
Reaction proceeds through the formation of carbocation.	Reaction proceeds through the formation of transition state.
Rate of reaction depends on the concentration of substrate (alkyl halide) only. Rate $\propto$ [RX]	Rate of reaction depends on the concentration of substrate (alkyl halide) and nucleophile. Rate $\propto$ [RX][Nu:]
Reactivity order for RX is: $3° > 2° > 1° >$ methyl Methyl and primary alkyl halides fail to react.	Reactivity order for RX is: methyl $> 1° > 2° > 3°$ Tertiary alkyl halides fail to react.
Products have both the retained and inverted configurations relative to that of the reactant (alkyl halide).	Product has the inverted configuration relative to that of the reactant (alkyl halide).
It is favoured by polar solvents.	It is favoured by non-polar solvents.
It is favoured by weaker nucleophiles.	It is favoured by stronger nucleophiles.

17.1.7 1,2-Elimination Reactions

17.1.7.1 Overview

In addition to S_N reactions, alkyl halides also undergo elimination reactions. An elimination reaction is a type of organic reaction in which two substituents are removed from two adjacent saturated carbon atoms of a substrate molecule. For example, when an alkyl halide undergoes an elimination reaction, the halogen atom is removed from α-carbon and the hydrogen is removed from β-carbon. As a result of this, a double bond is formed between α-carbon and β-carbon. Hence, the product of an elimination reaction is an alkene. The removal of proton (hydrogen ion) and halide ion is called dehydrohalogenation.

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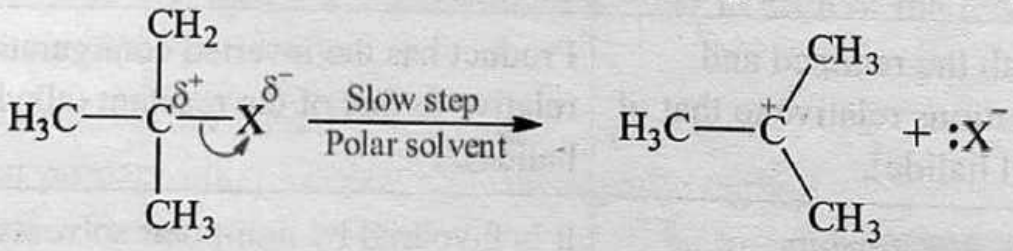
Base | Substrate molecule | Elimination product | Leaving group | Water

The most common bases used in elimination reactions are HO^-, RO^- and H_2N^-. There are two important mechanisms for elimination reactions viz. E2 and E1 just like for S_N reactions.

17.1.7.2 E1 Mechanism (Unimolecular Elimination)

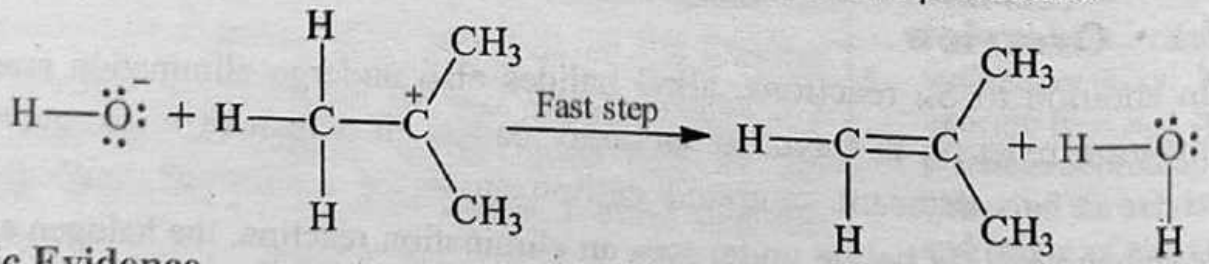
In the designation E1, "E" stands for *elimination* and "1" stands for *unimolecular*. Unimolecular means that only one molecule is involved in the rate-determining step. In this mechanism, the breaking of bond between carbon and the leaving group is fully completed before any reaction occurs with the base to lose a hydrogen. Consider the reaction of *tert*.alkyl halide with base. The reaction occurs in two steps.

Step 1: The *tert*-butyl halide undergoes ionization to produce a planar carbocation and a leaving group. The bond breaks between halogen atom and α-carbon atom.



This step of reaction is the rate determining step. Since this step involves the breakage of covalent bond so it is a slow step.

Step 2: The base (HO^-) removes a proton from one of the β-carbon and with the removal of halide ion, a new π-bond is formed between α and β-carbons.



Kinetic Evidence

The rate law for the reaction is:

$$\text{Rate} \propto [(CH_3)_3CX]$$

$$\text{Rate} = k[(CH_3)_3CX]$$

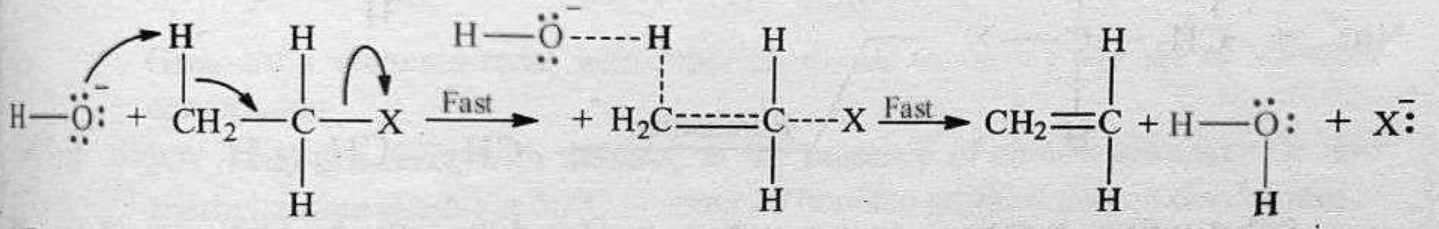
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Where 'k' is the rate constant.

The rate of reaction depends only on the concentration of the substrate, *tert*-butyl halide but it does not depend on the concentration of the base. This rate equation is first order overall.

17.1.7.3 E2 Mechanism (Bimolecular Elimination)

In the designation E2, "E" stands for *elimination* and "2" stands for *bimolecular*. Bimolecular means that both the alkyl halide and base are involved in the rate-determining step. In this mechanism, the breaking of bond between carbon and the leaving group as well as the reaction with the base to lose a proton (hydrogen) occurs simultaneously. Consider the reaction of *primary* alkyl halide with base. The reaction occurs in one step.



Base **Primary alkyl halide** **Transition State** **Ethene (an alkene)**

In the transition state, the bond of base to one of the β-hydrogen and the bond between α and β-carbon atoms are partially formed. On the other hand, the bond of β-hydrogen to carbon and the bond between α-carbon and leaving group is partially broken.

This is slow step and rate determining or controlling step of reaction. Since two molecules are involved in rate determining step, hence it is called bimolecular reaction.

Kinetic Evidence

The rate law for the reaction is:

Rate $\propto$ $[RH_2CX][\bar{O}H]$

Rate = $k[RH_2CX][\bar{O}H]$

Where **'k'** is the rate constant.

The rate of reaction depends on the concentrations of both the substrate (alkyl halide) and the base. The changes in the concentrations of both the reactants affect the rate of reaction. When the concentration of either reactants is doubled, the rate should be doubled. When the concentration of both the reactants is doubled, the rate should be quadruples. The reaction is therefore second order.

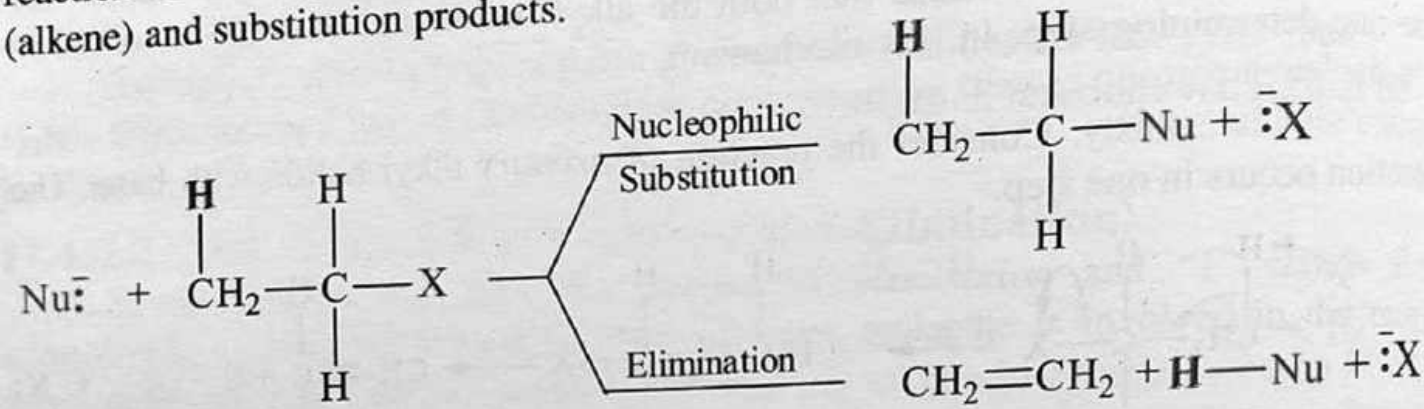
Keep in Mind

- **Primary alkyl halides undergo E2 reactions only.**
- **Secondary and Tertiary alkyl halides undergo both E1 and E2 reactions.**

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17.1.8 Substitution versus Elimination

All nucleophiles are possible bases and all bases are possible nucleophiles. Hence, the reactive part of both nucleophiles and bases is an unshared electron pair. Elimination reactions occur simultaneously with substitution reactions. There is always a competition between elimination and substitution reactions. For example, the reaction of nucleophile (base) with an alkyl halide produce mixture of elimination (alkene) and substitution products.



Substitution reaction occurs when nucleophile attacks on α-carbon. If nucleophile attacks on β-hydrogen, elimination reaction occurs. The ratio of products formed depends on the relative rates of the substitution and elimination reactions. The relative rates of elimination and substitution reactions are affected by the following factors:

i) Nature of Solvent

Polar solvents favour substitution reactions while non-polar solvents favour elimination reactions. In aqueous medium (more polar solvent), the main reaction will be substitution and elimination will be a side reaction. In alcoholic medium (less polar solvent), the main reaction will be elimination and substitution will be a side reaction.

ii) Nature of base

Strong bases favour elimination reactions. In the presence of strong base, the main reaction will be elimination and substitution reaction will be a side reaction.

iii) Effect of Temperature

An increase in temperature will favour elimination than substitution.

iv) Nature of Substrate

Crowding within the substrate favours elimination over substitution.

v) Nature of Alkyl Halide

Primary alkyl halides favour mainly substitution reactions while tertiary alkyl halides mainly favour elimination reactions. Secondary alkyl halides favour both substitution and elimination.

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Alkyl Halides as Precursors

A compound that participates in a chemical reaction and produces another compound is called precursor. Alkyl halides are, therefore, act as precursors and produce many other organic chemicals in the lab such as thiols, Grignard reagents and dialkyl disulphides.

i) Alkyl halides react with an excess of KOH and H_2S to produce thiols.

$$R—X + KOH + H_2S \longrightarrow R—SH + H_2O + KX$$

ii) Alkyl halides react with magnesium metal in the presence of pure diethyl ether in the absence of moisture, CO_2, or O_2 to produce Grignard reagents.

$$R—X + Mg \xrightarrow{\text{Ether}} R—Mg—X$$

Grignard's reagents react with other chemicals to form a variety of valuable compounds.

iii) Alkyl halides react with thiourea in the presence of carbon tetrachloride and triethyl amine (Et_3N) at 50°C in about 12 hours to produce dialkyl disulphides.

$$R—X + NH_2—\overset{\overset{S}{\|}}{C}—NH_2 \xrightarrow[50°C,\ 12\ h]{Et_3N,\ CCl_4} R—S—S—R$$

Dialkyl disulphide is used to make other chemicals.

17.2 Organometallic Compounds

Compound that has a metal-carbon bond are called organometallic compounds. For example, alkyl magnesium halides (RMgX) are organometallic compounds because they have metal carbon bonds. Alkyl magnesium halides are also known as Grignard reagents. They are named after French Chemist Victor Grignard, who discovered them in 1900, and got Noble Prize in 1912. The Grignard reagents are used in the preparations of alkanes, alkenes, alcohols, aldehydes, ketones and carboxylic acids. Their general formula is RMgX. Where '*R*' is an alkyl or aryl group and '*X*' is chlorine, bromine or iodine.

17.2.1 Preparation of Grignard Reagents

Grignard reagents are prepared in the laboratory by the reaction of an alkyl or aryl halides with magnesium metal in the presence of pure diethyl ether in the absence of moisture, CO_2, or O_2.

$$R—X + Mg \xrightarrow{\text{Ether}} RMgX$$

$$CH_3—Cl + Mg \xrightarrow{\text{Ether}} CH_3—MgCl$$

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17.2.2 Reactivity of Grignard Reagents

Grignard reagents are highly reactive compounds due to the presence of high polar carbon-magnesium bond. In alkyl magnesium halide, carbon is more electronegative than magnesium. Hence, carbon has partial negative charge and magnesium has partial positive charge.

$$R^{\delta-}—Mg^{\delta+}—X$$

The partial negative charge of carbon makes the alkyl group highly reactive towards electrophile and acts as a source of nucleophile.

The order of reactivity for various halides with same alkyl group to magnesium is as:

RI > RBr > RCl

Alkyl iodide is more reactive than alkyl bromide which in turn is more reactive than alkyl chloride.

The order of reactivity for the given halogen with various alkyl groups to magnesium is as:

$CH_3X > C_2H_5X > C_3H_7X$

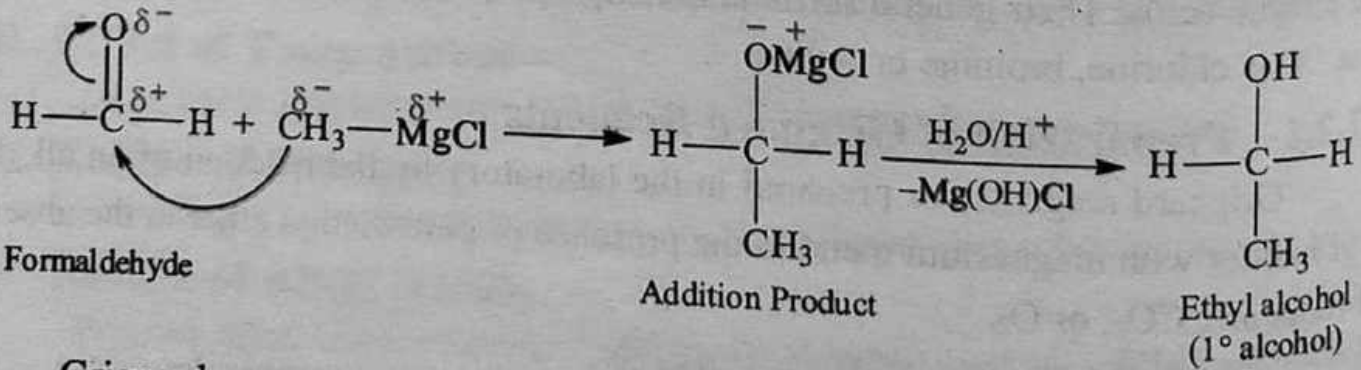
Methyl halide is more reactive than ethyl halide which in turn is more reactive than propyl halide.

17.2.3 Reactions of Grignard Reagents

Grignard reagents react with organic and inorganic compounds to form a variety of valuable compounds.

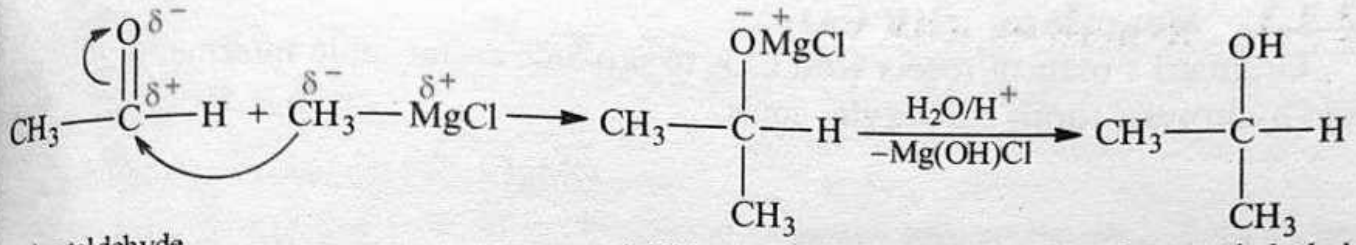
17.2.3.1 Reactions with Aldehydes and Ketones

Grignard reagents react with formaldehyde to produce addition products which on acid hydrolysis form primary alcohols. This reaction can be used to increase the length of carbon chain.



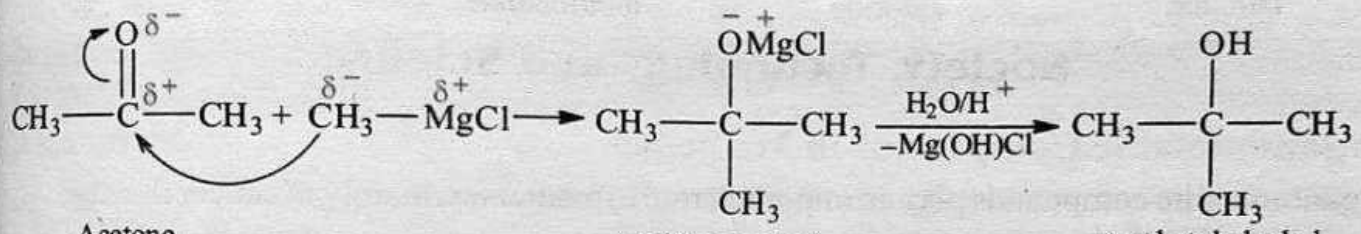
Grignard reagents react with aldehydes other than formaldehyde to produce addition products which on acid hydrolysis form secondary alcohols.

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Acetaldehyde | Addition Product | Isopropyl alcohol (2° alcohol)

Grignard reagents react with ketones to produce addition products which on acid hydrolysis form tertiary alcohols.

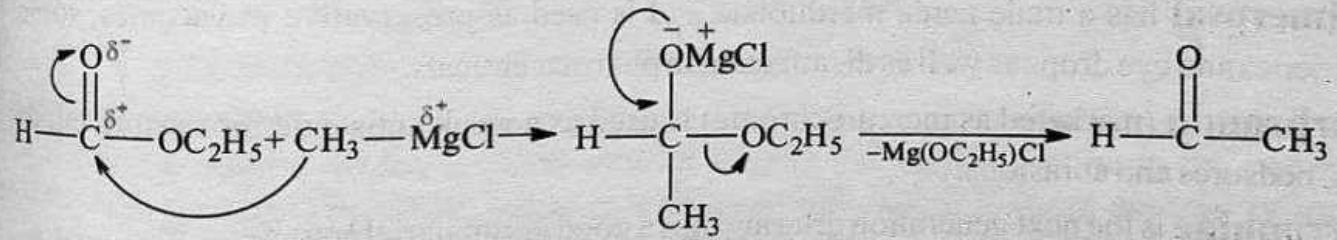


Acetone | Addition Product | *tert.*butyl alcohol (3° alcohol)

17.2.3.2 Reactions with Esters

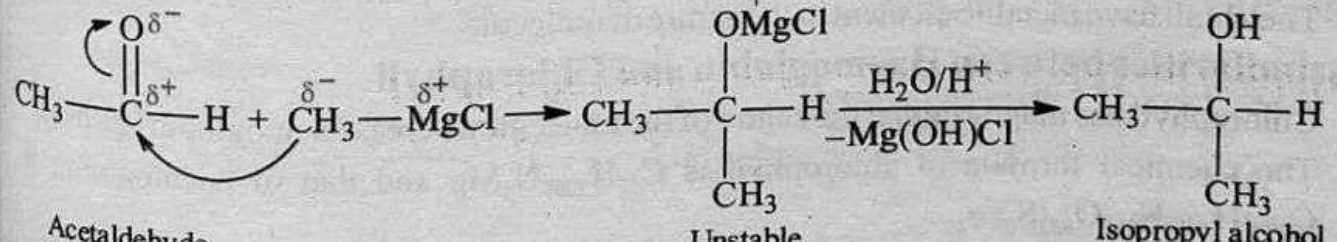
It involves two steps:

Step 1: Ethyl formate reacts with Grignard's reagent to produce an unstable intermediate that expels an alkoxide ion in the ester to produce an aldehyde.



Ethyl formate | Unstable intermediate | Acetaldehyde

Step 2: The acetaldehyde reacts with a second molecule of the Grignard's reagent to produce an unstable intermediate which on acid hydrolysis forms secondary alcohol.



Acetaldehyde | Unstable intermediate | Isopropyl alcohol (2° alcohol)

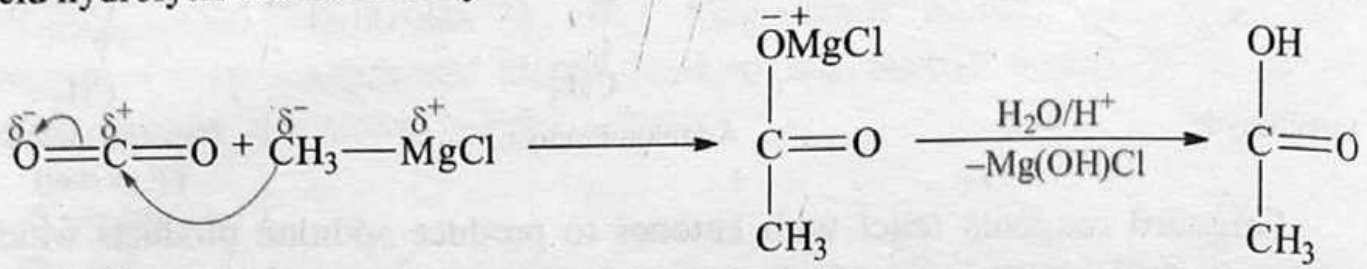
Keep in Mind

The esters, other than ethyl formate, reacts in the same way with an excess of Grignard's reagents to form tertiary alcohols.

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17.2.3.3 Reactions with CO_2

Grignard's reagent reacts with CO_2 to produce an unstable intermediate which on acid hydrolysis forms carboxylic acids.



Carbon Dioxide | Methyl magnesium chloride | Unstable intermediate | Acetic acid

Society, Technology and Science

Organometallic Compounds in Medicines

Organometallic compounds play an important role in medicines, mainly in cancer therapy. Salvarsan, the first important organometallic medicine, was discovered in 1908 and used as an anti-syphilis.

Cisplatin is a chemotherapy drug and is highly effective in treating several cancers such as ovarian and testicular cancers.

Carboplatin is used to treat ovarian cancer.

Thimerosal has a trade name merthiolate and is used as preservative in vaccines, some cosmetics and eye drops as well as disinfectant in pharmaceuticals.

Merbromin (marketed as mercurochrome) is used as a weak antiseptic for treating minor cuts, bedsores and abrasions.

Ferroquine is the next generation drug and has a good antimalarial activity.

Vanadoceneacetylacetonate (VDacac) shows anti-HIV properties.

Comparison between Haemoglobin and Chlorophyll

- Haemoglobin and chlorophyll both are pigments found in the organisms.
- They both have metallic element in the centre of molecule.

Dissimilarities between Haemoglobin and Chlorophyll

- Chlorophyll has magnesiumat the centre of the moleculewhereas haemoglobin has iron.
- The chemical formula of chlorophyll is $C_{55}H_{7205}N_4Mg$ and that of haemoglobin is $C_{2952}H_{4664}N_{812}O_{832}S_8Fe_4$.
- Chlorophyll is found in the chloroplast of plant cells while haemoglobin is found in the blood of all vertebrates and some invertebrates.
- Chlorophyll gives green colour to the leaves, seaweed, algae and vegetables whereas haemoglobin gives red colour to the blood in the form of RBC.

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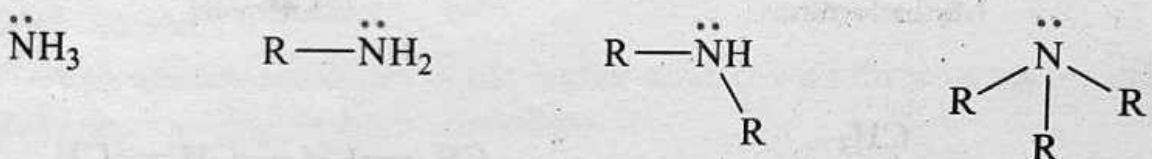
- The main function for haemoglobin is to transport oxygen from the lungs to various parts of the body whereas the main function of chlorophyll is to absorb light energy from the sun and changes it into chemical energy by the process of photosynthesis. Chlorophyll is considered as the factory of oxygen on earth.

It is important to note that no life is possible on our planet without chlorophyll. Because of this chlorophyll is also known as the *blood of plants* just like haemoglobin is the blood of the body.

17.3 Amines

Amines are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. Amines are classified as primary, secondary and tertiary, depending on the number of alkyl groups bonded to the nitrogen atom.

Primary amine has one alkyl group bonded to nitrogen atom. Secondary amine has two alkyl groups bonded to the nitrogen atom. Tertiary amine has three alkyl groups bonded to the nitrogen atom.

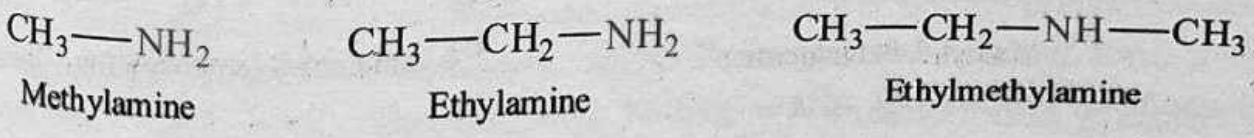


Ammonia | Primary amine | Secondary amine | Tertiary amine

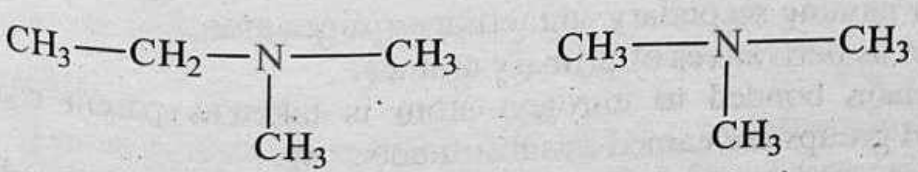
17.3.1 Nomenclature

Common Names

Their common names are obtained by adding the suffix *amine* to the name of alkyl or aryl groups. The entire name is written as one word. If there are two or more alkyl or aryl groups, then the prefix di-, or tri- is used before the name of alkyl or aryl group. If there are two or more different alkyl or aryl groups, then the names of alkyl or aryl groups are arranged in alphabetical order. Examples are:



Methylamine | Ethylamine | Ethylmethylamine



Ethyldimethylamine | Trimethylamine

Keep in Mind

In common system, most of the primary amines are named as ***alkylamines***.

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IUPAC Names

Amines are classified as primary, secondary or tertiary.

Primary Amines

The primary amines having more complex alkyl or aryl groups are generally named as ***alkanamines***. Main points for naming amines are:

i) Select the longest continuous chain of carbon atoms containing amino group and name it.

ii) Their names are obtained by replacing the ending –e of parent alkanes by adding the suffix *amine*.

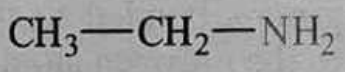
iii) Number the parent chain from that end which is nearer to the functional group that is amino group.

iv) When another functional group is present in the compound, the amino group is generally listed as a substituent.

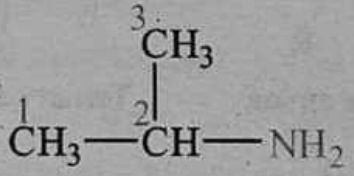
Examples are:



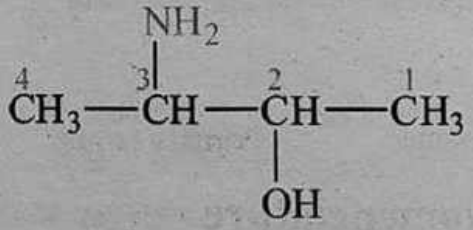
Methanamine



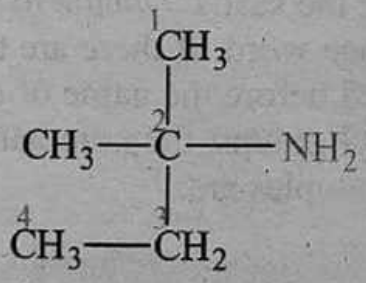
Ethanamine



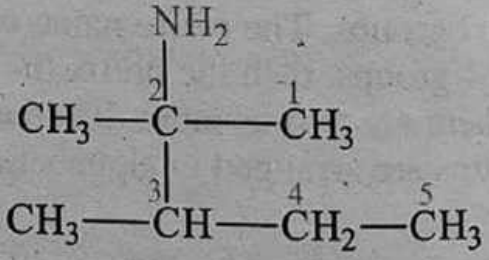
2-Propanamine



3-Amino-2-butanol



2-Methyl-2-butanamine



2,3-Dimethyl-2-pentanamine

Secondary and Tertiary Amines

Main points for naming secondary and tertiary amines are:

i) They are named as derivatives of primary amines.

ii) The longest chain bonded to nitrogen atom is taken as parent chain. The remaining alkyl groups are named as substituents.

iii) The locant *N* is used to designate the location of substituents bonded to a nitrogen atom of amino group.

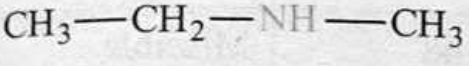
iv) If the same alkyl groups appear more than once, then the prefix di or tri is used. If the amines have two or three different alkyl groups, then designate the groups individually in alphabetical order.

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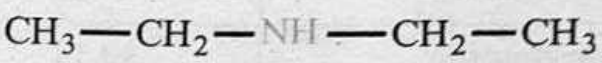
v) The secondary amines are generally named as ***N*-alkylalkanamines**.

vi) The tertiary amines are generally named as ***N,N*-dialkylalkanamines** (when both alkyl groups are the same) or as ***N*-alkyl-*N*-alkylalkanamines** (when both alkyl groups are different).

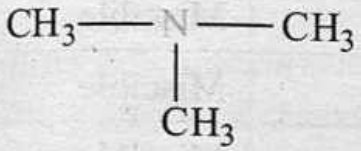
Examples are:



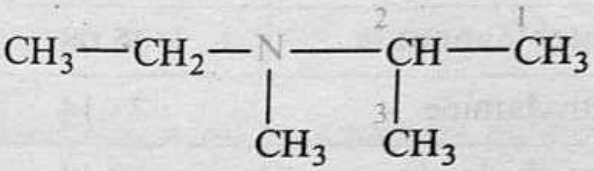
N-methylethanamine



N-ethylethanamine



N,N-dimethylmethanamine



N-ethyl-N-methyl-2-propanamine

17.3.2 Physical Properties of Amines

Physical State

Lower amines are gases while higher amines with three or more carbon atoms are liquids and still higher ones are solids.

Odour

Methyl amine and ethyl amine have ammoniacal smell but higher amines have fishy smell.

Boiling Points

Amines are polar compounds. Polarity of amines is due to the presence of nitrogen atom. Both primary and secondary amines form intermolecular hydrogen bonds. The hydrogen bonds in alcohols are much stronger than amines as the oxygen of alcohols is more electronegative than the nitrogen of amines. Amines have higher boiling points than corresponding hydrocarbons and lower boiling points than those of corresponding alcohols or carboxylic acids. Tertiary amines do not form hydrogen bonds with each other, therefore their boiling points are similar to those of the corresponding alkanes.

Solubility

Lower amines are soluble in water due to formation of hydrogen bonds with water molecules. However, the solubility of amines decreases with increase in the size of alkyl group (hydrophobic part). Higher members of amines are predominantly insoluble in water. Amines are more soluble in water than corresponding alcohols and ethers. This may be due to the increased basicity of the amines.

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Table 17.6: Physical Properties of Some Amines

Name	Molar Mass (g/mol)	Boiling Point (°C)	Solubility at 25°C in water
Methylamine	31.1	6	Miscible
Ethylamine	45.08	17	Miscible
Propylamine	59.11	48	Miscible
Butylamine	73.41	78	Miscible
Dimethylamine	45.08	7	Miscible
Diethylamine	73.14	56	Miscible
Trimethylamine	59.11	3	Miscible
Triethylamine	101.19	89	Slightly soluble

17.3.3 Structure of Amines

The nitrogen atom present in amines is sp^3 hybridized. The nitrogen atom has five electrons in the valence shell. It has three unpaired electrons and one lone pair of electrons. The three unpaired electrons form sigma bonds with hydrogen atoms or carbon atoms of alkyl groups. According to VSEPR theory, molecules having three bond pairs and one lone pair give trigonal pyramidal shapes. Hence, the structure of amines is trigonal pyramidal. The $\widehat{CNC}$ angle in amines is less than 109.5°. The angles in amines is approximately 108°.



17.3.4 Basicity of Amines

Amines are basic in nature due to the presence of lone pair of electrons on the nitrogen atom. Alkanamines are more basic than ammonia due to the presence of electron releasing alkyl groups. Alkyl groups concentrate the electron density of nitrogen and hence, make the lone pair of nitrogen more easily available for sharing with acids. Thus, the expected order of basicity of amines is: > 3° alkylamines > 2° alkylamines > 1° alkylamines.

The observed basicity of methylamine, dimethylamine and trimethylamine have been found to follow the expected order in gas phase. Conversely, they do not follow the expected trend of basicity order in aqueous solution and gets changed as:

$(CH_3)_2NH$ ($pK_b = 3.29$) > CH_3NH_2 ($pK_b = 3.36$) > $(CH_3)_3N$ ($pK_b = 4.28$)

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The larger the value of pK_b, the smaller is the tendency to accept a proton from water.

The basic strength of amines in aqueous solutions not only depends on electron releasing effect of alkyl groups but also depends on steric effect and hydration effect.

Due to high steric effect 3° alkylamine cannot donate electron to proton.

17.3.5 Preparation of Amines

Some of the methods for the preparation of amines are mentioned below:

17.3.5.1 Alkylation of Ammonia by Alkyl Halides

Alkyl halide reacts with aqueous or alcoholic solution of ammonia in a sealed tube on heating to produce primary, secondary and tertiary amines. This is a nucleophilic substitution reaction (S_N2 reaction).

The process of cleavage of the carbon-halogen bond by ammonia molecule is known as ***ammonolysis***.

$$NH_3 + CH_3I \longrightarrow CH_3NH_2 + HI$$
$$CH_3NH_2 + CH_3I \longrightarrow (CH_3)_2NH + HI$$
$$(CH_3)_2NH + CH_3I \longrightarrow (CH_3)_3N + HI$$
$$(CH_3)_3N + CH_3I \longrightarrow [(CH_3)_4\overset{+}{N}]\overset{-}{I}$$

Primary amine is the major product when ammonia is present in excess. Conversely, tertiary amine is the major product when alkyl halide is present in excess.

The resulting salt (methylammonium iodide) on treatment with a base regenerates amines.

$$[(CH_3)_4\overset{+}{N}]\overset{-}{I} + NaOH \longrightarrow (CH_3)_3N + NaI + CH_3OH$$

17.3.5.2 Reduction of Nitrogen containing Functional Groups

Amines are obtained by the reduction of nitrogen containing functional groups such as nitriles, nitro compounds and amides.

17.3.5.2.1 Reduction of Nitriles

Nitriles are reduced to primary amines by $LiAlH_4$ or catalytic hydrogenation.

$$\underset{\text{Methyl cyanide}}{CH_3CN} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

$$\underset{\text{Methyl cyanide}}{CH_3CN} + 2H_2 \xrightarrow{Ni} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

This method is used for increasing the length of carbon chain.

17.3.5.2.2 Reduction of Nitro Compounds

Nitro compounds are reduced to primary amines by $LiAlH_4$ or Zn/HCl or H_2/Ni or H_2/Pt.

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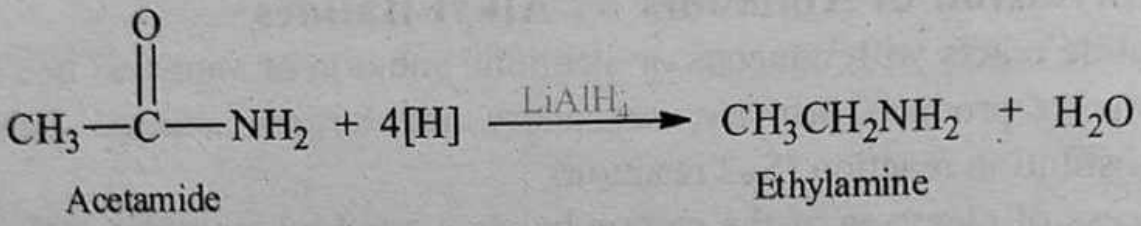
$$CH_3NO_2 + 6[H] \xrightarrow{LiAlH_4} CH_3NH_2 + 2H_2O$$

Nitromethane — Methylamine

$$CH_3NO_2 + 3H_2 \xrightarrow{Pt} CH_3NH_2 + 2H_2O$$

17.3.5.2.3 Reduction of Amides

Amides are reduced to primary amines by $LiAlH_4$.



17.3.6 Reactivity of Amines

Amines can act both as bases and nucleophiles. The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom. These electrons attack the electron deficient centres (positive or slightly positive parts) of other molecules.

17.3.7 Reaction of Amines

17.3.7.1 Overview

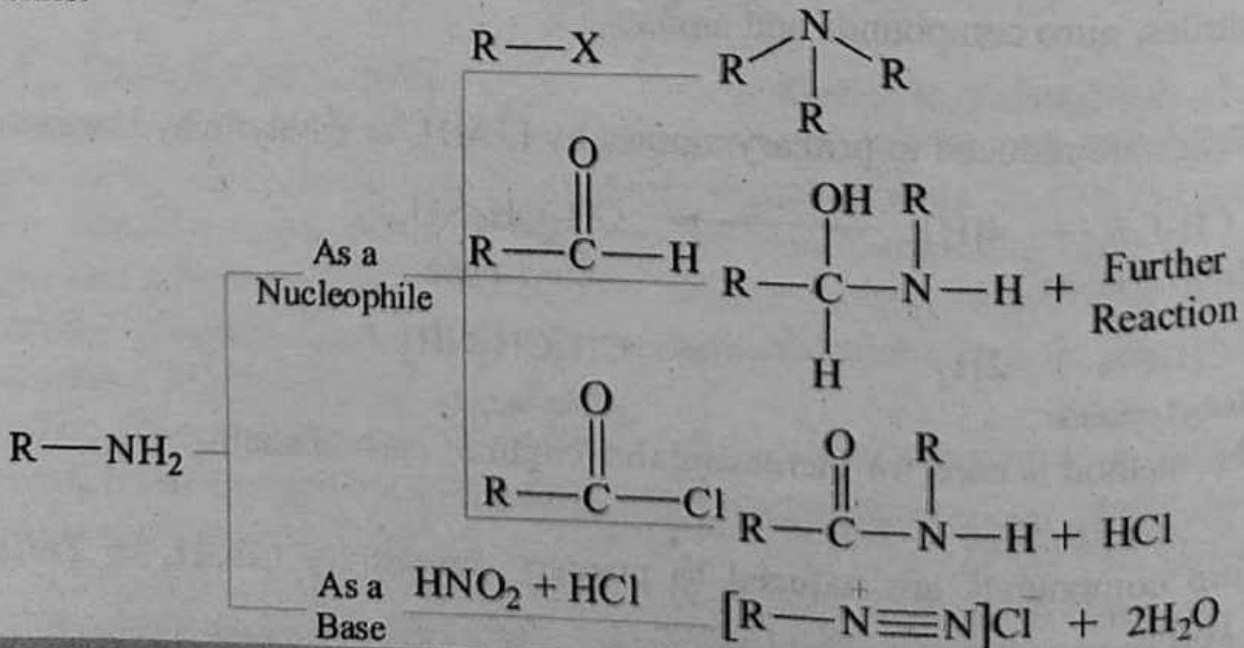
The important organic reactions of amines as nucleophiles are:

i) Amines are alkylated by alkyl halides through nucleophilic substitution.

ii) Amines reacts with alkyl halides through nucleophilic substitution to form a mixture of products.

iii) Amines reacts with acid halides (or acid anhydrides) through nucleophilic acyl substitution to form substituted amides.

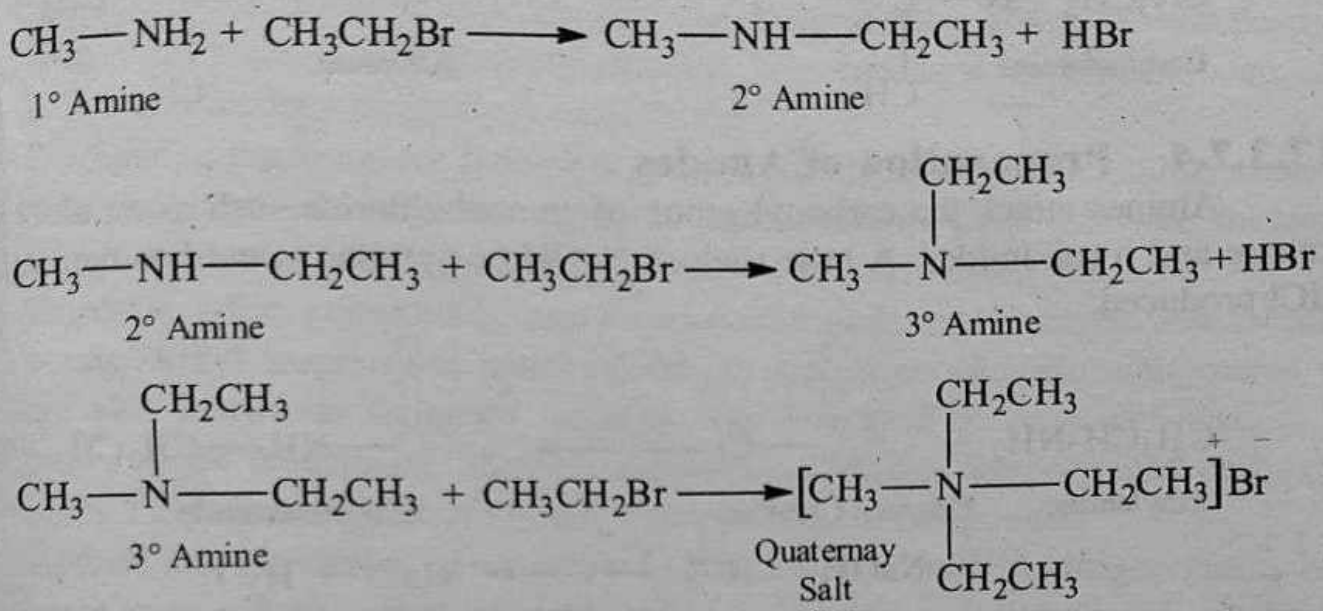
iv) Amines can also act as bases and react with nitrous acid to from diazonium salts.



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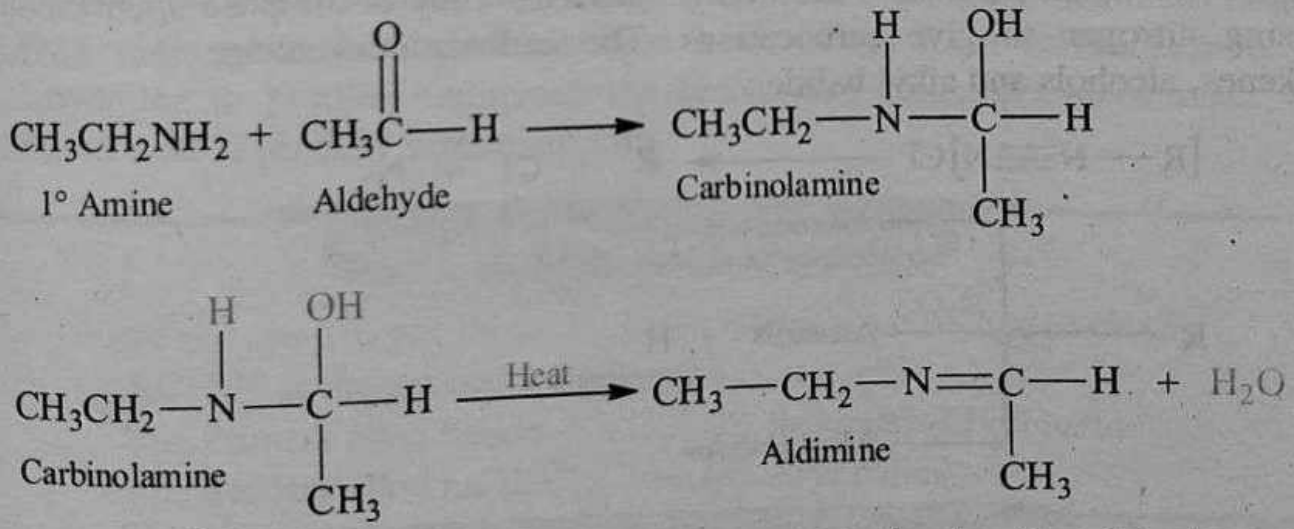
17.3.7.2 Alkylation of Amines by Alkyl Halides

Amines react with primary alkyl halides to form alkylated ammonium halides.

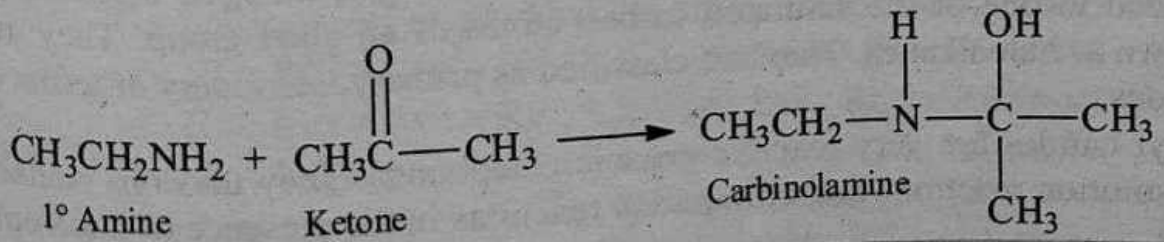


17.3.7.3 Reaction of Amines with Aldehydes and Ketones

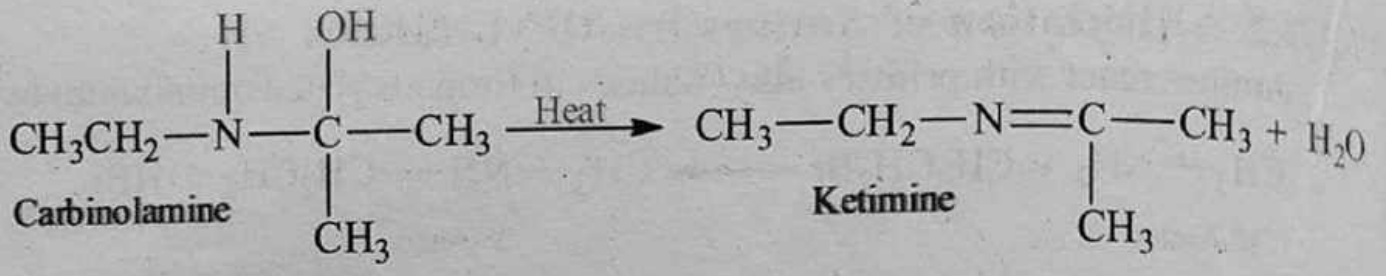
Aldehydes react with primary amines to form carbinolamine that dehydrates to produce aldimines (Schiff's bases).



Ketones react with primary amines to form carbinolamine that dehydrates to produce ketimines (Schiff's bases).

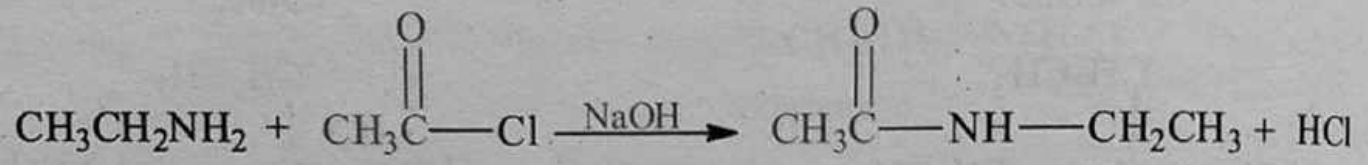


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17.3.7.4 Preparation of Amides

Amines attack the carbonyl group of an acid chloride such as an aldehyde or ketone and form amides. A base such as NaOH or pyridine is used to neutralize the HCl produced.



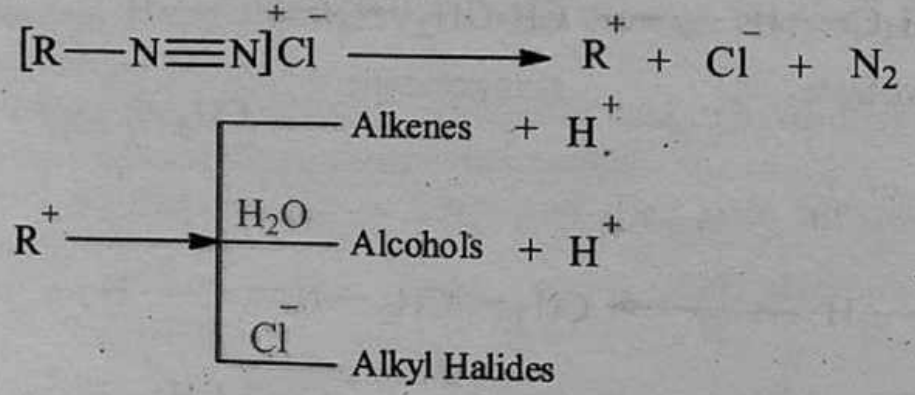
$$NaOH + HCl \longrightarrow NaCl + H_2O$$

17.3.7.5 Preparation of Diazonium Salts

Amines react with nitrous acid to produce diazonium salts.

$$R{-}NH_2 + HNO_2 + HCl \longrightarrow [R{-}N{\equiv}N]^{+}Cl^{-} + 2H_2O$$

The diazonium salts are highly unstable. They decompose spontaneously by losing nitrogen to give carbocations. The carbocations change into mixtures of alkenes, alcohols and alkyl halides.



Summary of Facts and Concepts

- Alkyl halides are organic compounds containing a halogen atom covalently bonded to one of the saturated carbon atoms of an alkyl group. They are also known as haloalkanes. They are classified as primary, secondary or tertiary alkyl halides.
- Alkyl halides are very reactive organic compounds. They undergo nucleophilic substitution reactions and elimination reactions in the presence of nucleophile or base.

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- Nucleophilic substitution reactions or S_N reactions are the reactions in which an electron rich nucleophile replaces another nucleophile to form a new molecule. In nucleophilic substitution reactions, the nucleophile is always Lewis base and it may be neutral or negatively charged. The substrate is frequently an alkyl halide and the leaving group is a halide ion.
- Elimination reactions are type of organic reactions in which two substituents are removed from two adjacent saturated carbon atoms of a substrate molecule. Elimination reactions occur simultaneously with substitution reactions.
- Organometallic compounds are those compounds that contain metal-carbon bonds. Alkyl magnesium halides (RMgX) are organometallic compounds and are also known as Grignard reagents. The Grignard reagents are used in the preparations of alkanes, alkenes, alcohols, aldehydes, ketones and carboxylic acids. Grignard reagents are highly reactive organic compounds.
- Amines are derivatives of ammonia in which one or more hydrogen atoms have been replaced by alkyl or aryl groups. Amines are classified as primary, secondary and tertiary. Amines can act both as bases and nucleophiles. The main reactions of amines are due to the presence of a lone pair of electrons on nitrogen atom.
- Amines react with primary alkyl halides to form alkylated ammonium halides. They also react with aldehydes (or ketones) to form carbinolamine that dehydrates to produce aldimines (or ketimines). Primary amines react with nitrous acid to produce diazonium salts.

Multiple Choice Questions

Select one answer from the given choices for each question:

i) RCH_2X is the general formula of:

(a) Primary alkyl halide (b) Secondary alkyl halide
(c) Tertiary alkyl halide (d) Aryl halide

ii) The formula of chloroform is:

(a) CCl_4 (b) $CHCl_3$
(c) CH_2Cl_2 (d) CH_3Cl

iii) The boiling point of alkyl halides are in the following order:

(a) RI > RCl > RBr > RF (b) RI > RBr > RF > RCl
(c) RI > RBr > RCl > RF (d) RF > RCl > RBr > RI

iv) The alkyl halide on which a nucleophile attacks is known as:

(a) Reagent (b) Substrate
(c) Electrophile (d) Both reagent and substrate

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v) Alkyl halides are considered to be very reactive compounds because they have:
(a) an electrophilic carbon
(b) A nucleophilic carbon
(c) an electrophilic carbon and a good leaving group
(d) a nucleophilic carbon and a good leaving group

vi) Which statement is correct about carbocations?
(a) They are reactive species (b) They are stable species
(c) They are electron rich species (d) They have filled orbitals

vii) Which statement is true about bases?
(a) They are electron pair acceptor species.
(b) They can accept electrons from hydrogen
(c) Their strength is measured by rate constant
(d) Their strength is measured by base dissociation constant

viii) In S_N1 reactions, the rate of reaction depends upon the concentration of:
(a) One reactant molecule (b) Two reactant molecules
(c) Nucleophile (d) Both nucleophile and electrophile

ix) The S_N2 reactions can be best performed with:
(a) Primary alkyl halides (b) Secondary alkyl halides
(c) Tertiary alkyl halides (d) Aryl halide

x) Primary alcohol is obtained by the reaction of Grignard's reagent with:
(a) Aldehydes other than formaldehyde (b) Acetone
(c) Formaldehyde (d) Ethyl formate

Short Answer Questions

Q.1. What is the difference between a base and nucleophile?
Q.2. Can a good nucleophile be a strong base?
Q.3. Is iodine more nucleophilic than chlorine?
Q.4. What is a poor leaving group?
Q.5. The halogens are good leaving groups why?
Q.6 Why alkyl halides undergo nucleophilic substitution reaction?
Q.7. What is the carbocation intermediate?
Q.8 Do S_N2 reactions have carbocation intermediates?
Q.9. Why is a tertiary carbocation more stable than a secondary?
Q.10. Why are organometallic compounds important?
Q.11. What is the general formula of Grignard reagent? Give two examples of Grignard's reagents.

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Q.12. Write the general equation for the preparation of Grignard reagents.
Q.13. What type of solvents can be used in Grignard reactions?
Q.14. Why is ether a good solvent for Grignard reactions?
Q.15. Why is a Grignard reagent so reactive?
Q.16. Is the carbon of Grignard's reagent electrophilic or nucleophilic?
Q.17. Define secondary amine and give two examples.
Q.18. Why do amines act as bases?
Q.19. Why aliphatic amines are more basic while aromatic amines are less basic than ammonia?

Long Answer Questions

Q.1. What are alkyl halides? Explain both the systems of nomenclature of alkyl halides.
Q.2. Draw structures for the following compounds.
i) Bromoethane
ii) Dichlorodibromomethane
iii) 2-bromo-3-chloropentane
iv) 1,1,2,2-tetrachloro-3,4-difluorohexane
v) 3-bromo-1-pentene
Q.3. Give common and IUPAC names to the following compounds:
i) CHI_3
ii) $CHCl_3$
iii) CH_3I
iv) $(CH_3)_2CHCl$
v) $(CH_3)_3CBr$
Q.4. Explain the structure and reactivity of alkyl halides.
Q.5. Write down three different methods for the preparation of alkyl halides. Which one is the best method for the preparation of alkyl halides?
Q.6. Write short note on the following:
i) Carbocations and their stability
ii) Nucleophile and base
iii) Substrate and leaving group
Q.7. What is the difference between S_N1 and S_N2 mechanisms?
Q.8. What are nucleophilic substitution reactions? Explain in detail the mechanism of nucleophilic substitution (S_N) reactions.
Q.9. What are β-elimination reactions? Explain the types and mechanism of elimination reactions.

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Q.10. Discuss the factors that influence nucleophilic substitution and elimination reactions of alkyl halides.

Q.11. What are organometallic compounds? Discuss preparation and reactivity of Grignard's reagents.

Q.12. Explain important reactions of Grignard's reagent.

Q.13. What are amines? Explain nomenclature of amines.

Q.14. Draw structures for the following compounds.

i) 2-Methyl-2-propanamine
ii) 3-Methyl-2-hexanamine
iii) N-Methylethanamine
iv) N-Ethyl-3-hexanamine
v) N-Ethyl-N-methyl-2-butanamine

Q.15. Give common and IUPAC names to the following compounds:

i) CH_3NH_2
ii) $CH_3CH_2NH_2$
iii) $(CH_3)_2NH$
iv) $(CH_3)_3N$
v) $(CH_3)_2NCH_2CH_3$

Q.16. Discuss the structure, basicity and reactivity of amines.

Q.17. Write down methods for the preparation of amines.

Q.18. Describe physical and chemical properties of amines.

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Chapter 18

Alcohols, Phenols and Ethers

Major Concepts

18.1 Alcohols
18.2 Phenols
18.3 Ethers

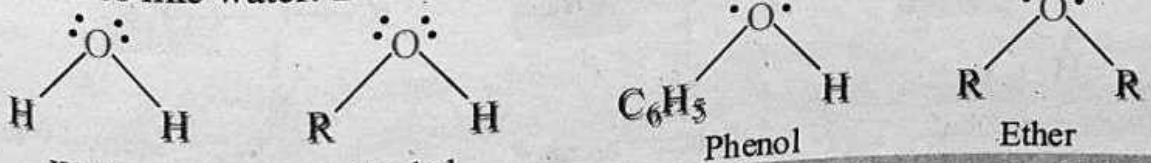
Learning Outcomes:

Students will be able to:

- Explain nomenclature, structure and acidity of alcohols as exemplified by ethanol. **(Understanding)**
- Describe the preparation of alcohols by reduction of aldehydes, ketones, carboxylic acids and esters. **(Applying)**
- Explain reactivity of alcohols. **(Understanding)**
- Describe the chemistry of alcohols by preparation of ethers and esters, oxidative cleavage of 1,2-diols. **(Applying)**
- Discuss thiols (RSH). **(Understanding)**
- Explain the nomenclature, structure and acidity of phenols. **(Applying)**
- Describe the preparation of phenol from benzene sulphonic acid, chlorobenzene, acidic oxidation of cumene and hydrolysis of diazonium salts. **(Applying)**
- Discuss the reactivity of phenol and their chemistry by electrophilic aromatic substitution reaction with Na metal and oxidation. **(Applying)**
- Differentiate between alcohol and phenol. **(Understanding)**
- Describe isomerism in alcohols and phenols. **(Understanding)**
- Identify ethers from their formula. **(Understanding)**

Introduction

In this chapter, we will focus on those hydrocarbon derivatives whose functional groups contain one oxygen atom participating in two single bonds (alcohols, phenols and ethers). Alcohols, phenols and ethers are organic compounds containing hydroxyl groups. They are very close to each other in structures. They have structures like water. Because of this, they are said to be derivatives of water.



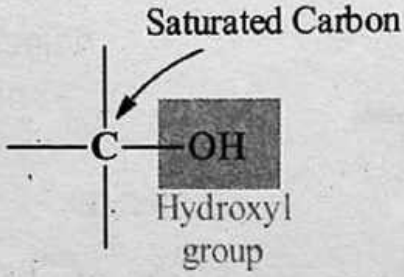
Water Alcohol Phenol Ether

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Alcohols and phenols both have hydroxyl (−OH) groups in their structures. Alcohols are hydroxyl derivatives of alkanes while phenols are hydroxyl derivatives of benzene. They (alcohols, phenols and ethers) occur widely in nature. They have many pharmaceutical, biological and industrial applications.

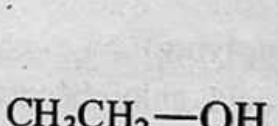
18.1 Alcohols

Alcohols are compounds in which hydroxyl group (−OH) is bonded to saturated carbon atom. A saturated carbon atom is a carbon atom, which is bonded to four other carbon atoms.

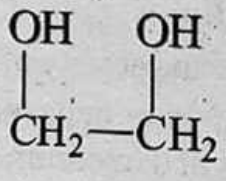


On the basis of number of hydroxyl groups, alcohols are classified into two major types: Monohydric alcohols and polyhydric alcohols.

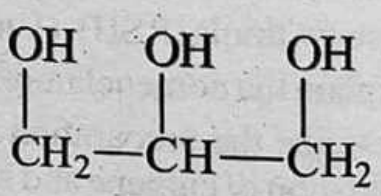
Monohydric alcohols have only one hydroxyl group in their molecules while polyhydric alcohol have two or more hydroxyl groups in their molecules. Ethyl alcohol and tertiary butyl alcohol are examples of monohydric alcohols whereas glycol and glycerol are examples of polyhydric alcohols.



Ethyl alcohol
(Monohydric alcohol)

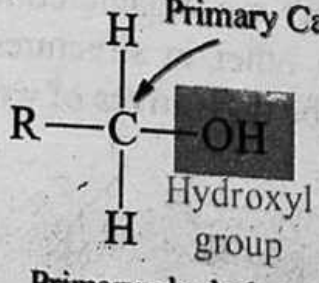


Glycol
(Polyhydric alcohol)

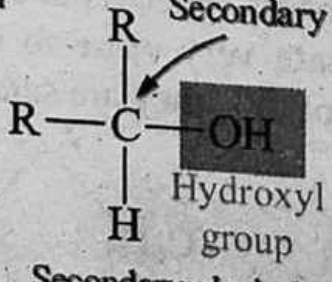


Glycerol
(Polyhydric alcohol)

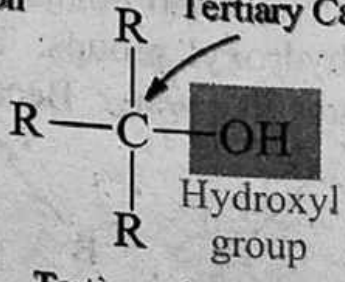
Monohydric Alcohols are further classified as primary (1°) alcohols, secondary (2°) alcohols, or tertiary (3°) alcohols, depending on whether the OH group is bonded to a primary, secondary, or tertiary carbon. In primary alcohols, the hydroxyl group is directly bonded to primary carbon. In secondary alcohols, the hydroxyl group is directly bonded to secondary carbon. In tertiary alcohols, the hydroxyl group is directly bonded to tertiary carbon.



Primary alcohol



Secondary alcohol



Tertiary alcohol

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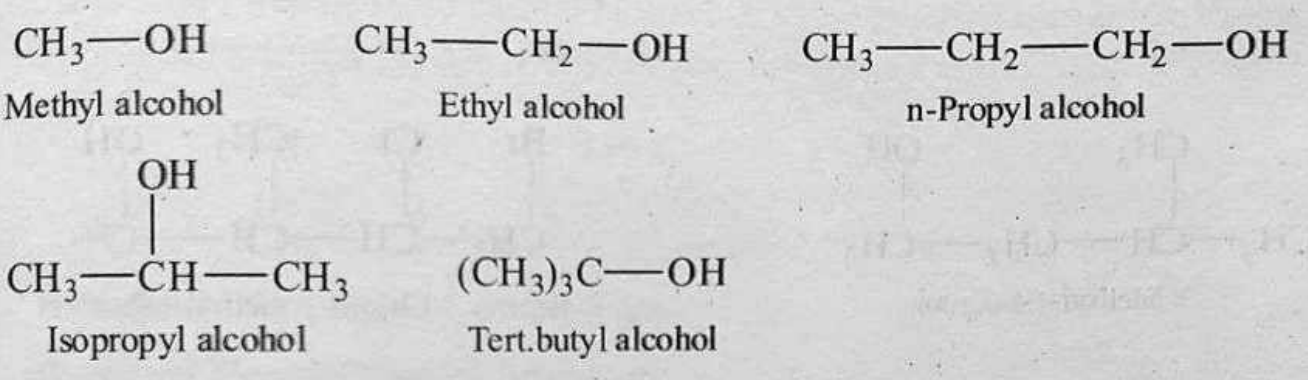
18.1.1 Nomenclature of Alcohols

Alcohols are named by two systems: common system and IUPAC system.

18.1.1.1 Common System

The common names are obtained by adding the word alcohol after the name of alkyl group. All of the carbon atoms are named as a single alkyl group of the molecule. We can say that, in this system, they are named as alkyl alcohols.

Examples are:



Common names exist generally for those alcohols which have simple (C_1 to C_4) alkyl groups.

18.1.1.2 IUPAC System

In this system, alcohols are considered as derivatives of alkanes in which one of the hydrogen atoms has been replaced by hydoxyl group and are named as ***alkanols***. The IUPAC names of alcohols are one-word names. The rules for naming alcohols are:

Step 1: Select the longest continuous chain of carbon atoms containing the hydroxyl group.

Step 2: Drop the final ***–e*** from the alkane name and add the suffix ***–ol*** to give the root name.

Step 3: Number the carbon chain from that end which is nearer to hydroxyl group. The hydroxy group takes precedence over alkyl groups, halogen atoms, double and triple bonds while numbering the parent chain.

Step 4: Indicate the position of hydroxyl group and other substituents by the number of carbon atoms to which they are bonded.

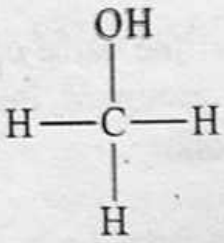
When two or more hydroxyl groups are present in a chain, then alcohols are named as diols (for alcohols containing two hydroxyl groups), triols (for alcohols containing three hydroxyl groups), tetraols (for alcohols containing four hydroxyl groups), etc.

Step 5: When hydroxy group is present in the structures of carbonyl compounds such as aldehydes, ketones, carboxylic acids and their derivatives, the preference in numbering the chain is not given to hydroxyl group. The hydroxyl group is taken as a

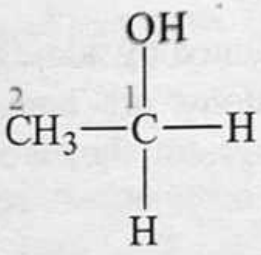
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side group in the carbonyl compounds. Use the word hydroxy for –OH group and indicate the position of this group by the number of carbon to which it is bonded.

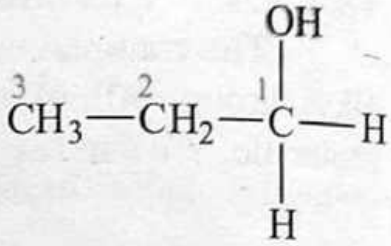
Examples are:



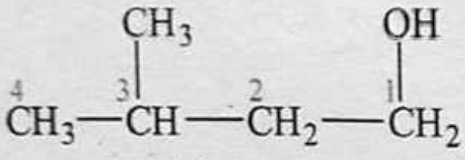
Methanol



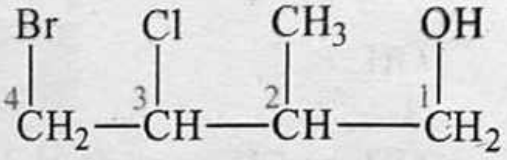
Ethanol



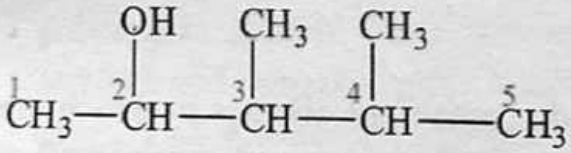
1-Propanol



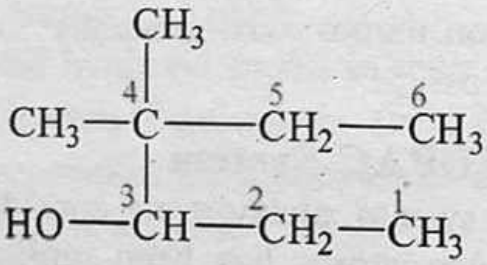
3-Methyl-1-butanol



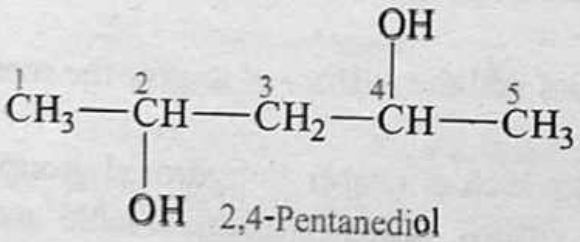
4-Bromo-3-Chloro-2-methyl-1-butanol



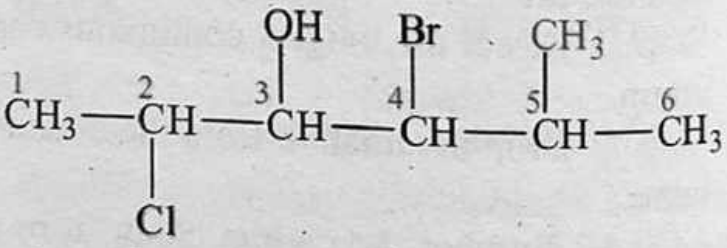
3,4-dimethyl-2-pentanol



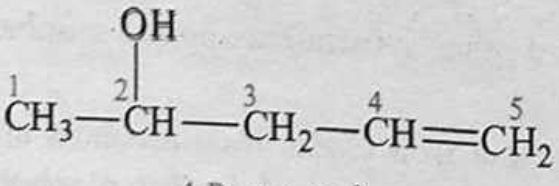
4,4-Dimethyl-3-hexanol



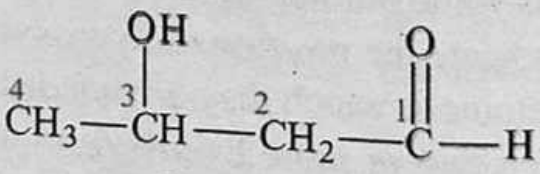
2,4-Pentanediol



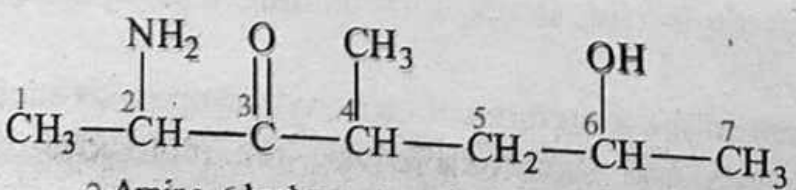
4-Bromo-2-chloro-5-methyl-3-hexanol



4-Penten-2-ol



3-Hydroxybutanal



2-Amino-6-hydroxy-4-methyl-3-heptanone

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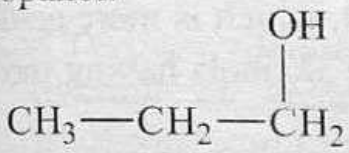
Isomerism in Alcohols

Alcohols with two or more carbon atoms can show functional isomerism with ethers. Thus alcohols and ethers have same molecular formula but have different functional groups. For example, dimethyl ether is the functional isomer of ethyl alcohol.

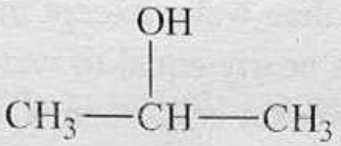
$CH_3—CH_2—OH$ Ethyl alcohol

$CH_3—O—CH_3$ Dimethyl ether

Alcohols with three or more carbon atoms can show position isomerism due to different position of hydroxyl groups. For example, 2-propanol is the position isomer of 1-propanol.



1-Propanol



2-Propanol

18.1.2 Physical Properties of Alcohols

i) Lower alcohols are colourless liquids. The higher members are colourless waxy solids.

ii) They have characteristic alcoholic smell and burning taste.

iii) They are volatile and inflammable.

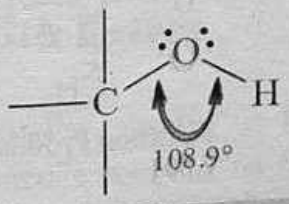
iv) They have higher boiling points than corresponding alkanes, ethers and haloalkanes.

v) They are readily soluble in water up to four carbon atoms. Higher alcohols, from carbon five onwards, are insoluble in water. The solubility is due to the presence of the intermolecular hydrogen bonding in the molecules of alcohol and water. Solubility of alcohols in water decreases with increase in the size of the alkyl groups and increases with increase in the branching of alkyl groups.

vi) They (esp. monohydric alcohols) are lighter than water. The density of methanol is 0.792 g/mL and that of ethanol is 0.789 g/mL at 20°C. The density of water at 20°C is 0.998 g/mL.

18.1.3 Structure of Alcohols

The oxygen atom of an alcohol is sp^3 hybridized and has four sp^3 hybrid orbitals. Two sp^3 hybrid orbitals of oxygen atom form σ-bonds to atoms of carbon and hydrogen, and the remaining two sp^3 hybrid orbitals each contain a lone pair of electrons.



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The $\widehat{CO}H$ bond angle in methanol is 108.9°. The carbon-oxygen bond length is 142 pm and the oxygen-hydrogen bond length is 96 pm.

18.1.4 Acidity of Alcohols

Alcohols are acidic in nature due to presence of polar O—H bond. Greater the polarity of –OH group, greater would be the acidity of alcohols. Primary alcohols are more acidic than secondary alcohols which in turn are more acidic than tertiary alcohols. The polarity of –OH group decreases by increase in the number of electron releasing groups, namely alkyl groups bonded to α-carbon. For example, tert-butyl alcohol is weaker acid than either methyl alcohol or ethyl alcohol.

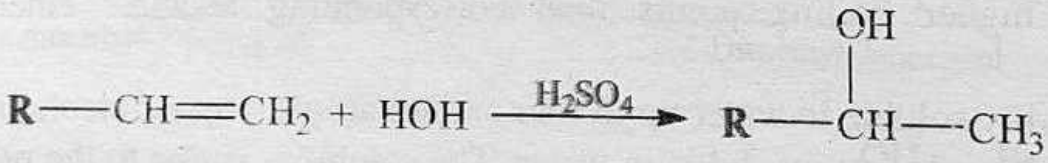
Alcohols are less acidic than water except methanol, which is more acidic than water. The acidity of ethanol is nearly equal to water. The alcohols having more than two carbon atoms are slightly weaker acids than water.

18.1.5 Preparations of Alcohols

The alcohols can be prepared by the methods given below:

18.1.5.1 Hydration of Alkenes

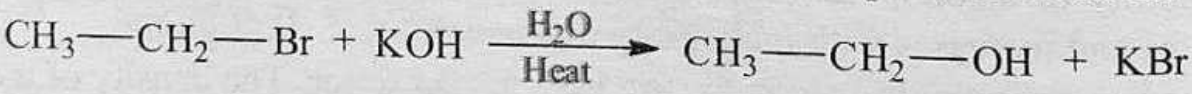
Alkenes react with water in the presence of cold concentrated sulphuric acid to produce an alcohol. The predominant product of alcohol can be obtained by using Markovnikov's rule.



$$R{-}CH{=}CH_2 + HOH \xrightarrow{H_2SO_4} R{-}\underset{\displaystyle OH}{\overset{\displaystyle |}{CH}}{-}CH_3$$

18.1.5.2 Hydrolysis of Alkyl Halides

Alkyl halides react with aqueous NaOH or KOH to produce alcohols.

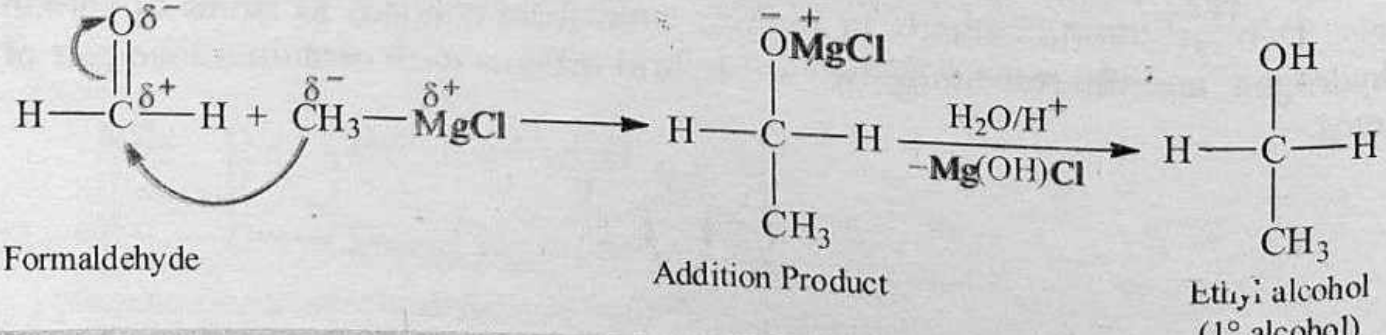


$$CH_3{-}CH_2{-}Br + KOH \xrightarrow[\text{Heat}]{H_2O} CH_3{-}CH_2{-}OH + KBr$$

18.1.5.3 Reaction of RMgX with Aldehydes and Ketones

Formation of Primary Alcohol

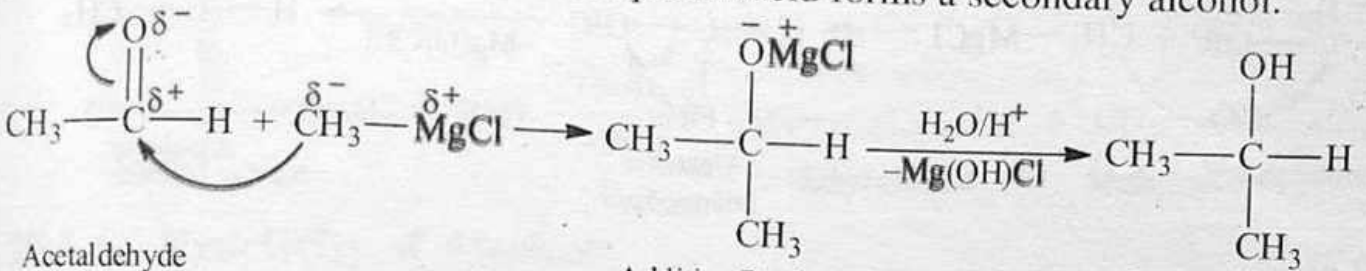
The reaction of formaldehyde with Grignard reagent (RMgX) is followed by protonation in aqueous acid forms a primary alcohol.



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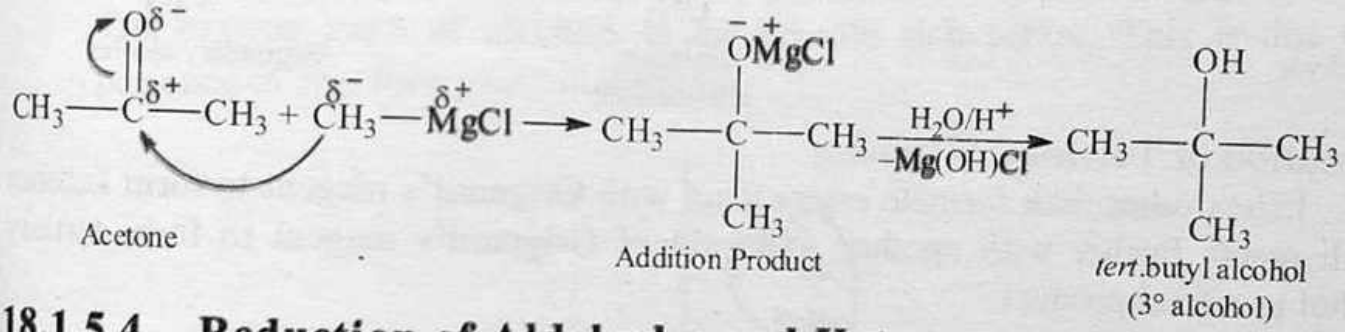
Formation of Secondary Alcohol

The reaction of aldehydes other than formaldehyde with Grignard reagent (RMgX) followed by protonation in aqueous acid forms a secondary alcohol.



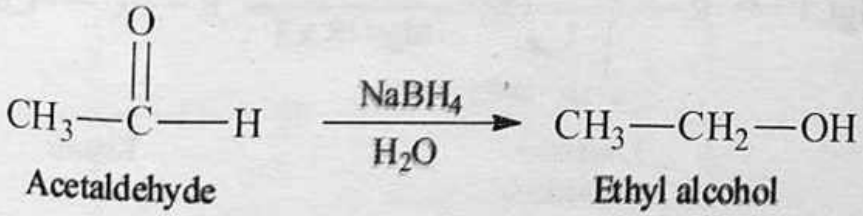
Formation of Tertiary Alcohol

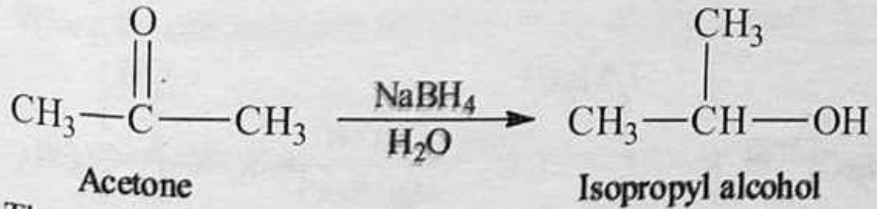
The reaction of ketones with Grignard reagent (RMgX) followed by protonation in aqueous acid forms a tertiary alcohol.



18.1.5.4 Reduction of Aldehydes and Ketones

Metal hydrides such as $NaBH_4$ (sodium borohydride) or $LiAlH_4$ (lithium aluminiumhydride) reduce aldehydes to primary alcohols and ketones to secondary alcohols.





The reduction with $NaBH_4$ needs polar solvents such as water and ethyl alcohol.

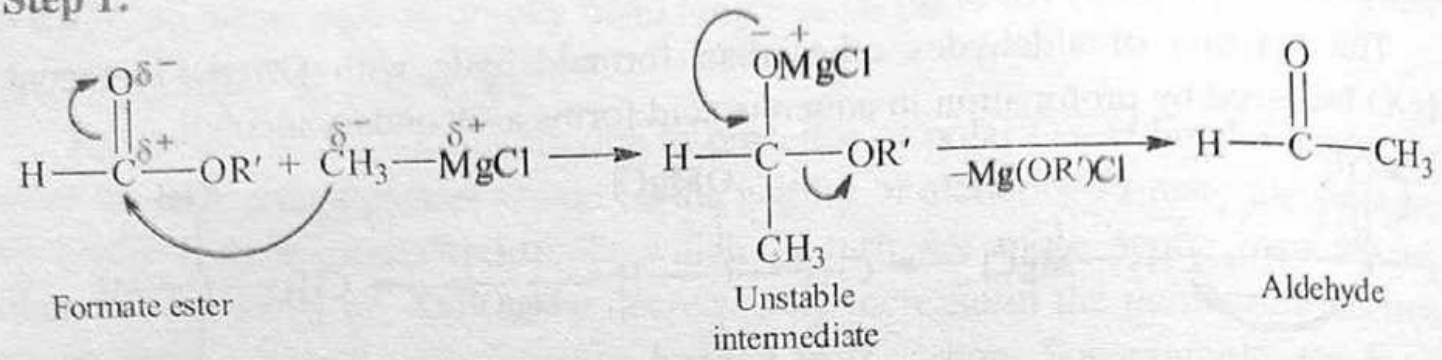
18.1.5.5 Reaction of RMgX with Esters

Formation of Secondary Alcohol

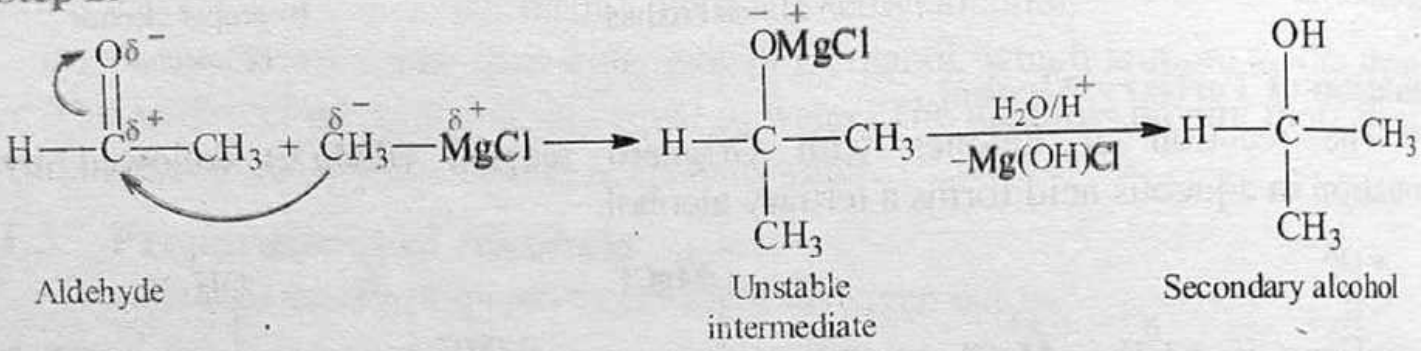
Formate esters react with Grignard's reagent to form aldehydes which reacts further with another molecule of Grignard's reagent to form secondary alcohols as a final product.

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Step 1:



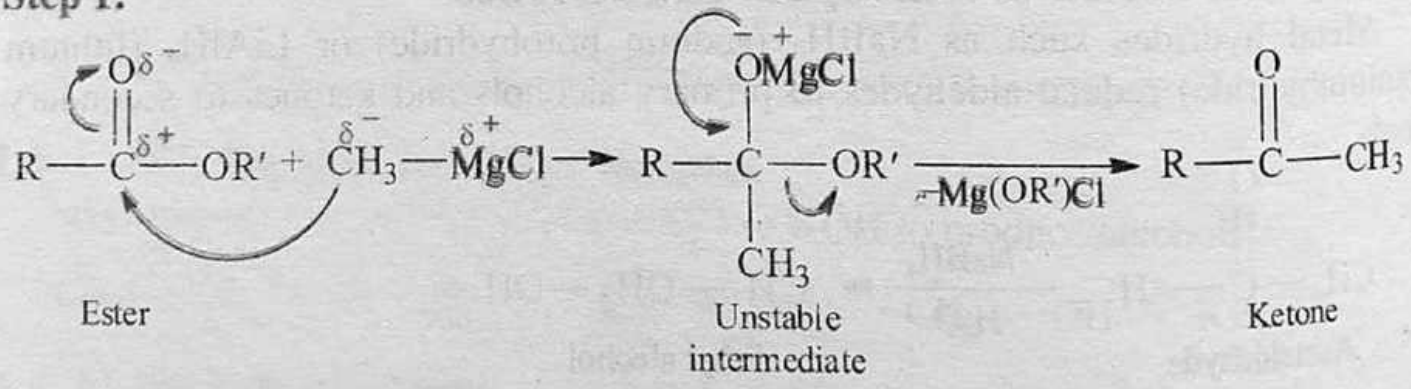
Step 2:



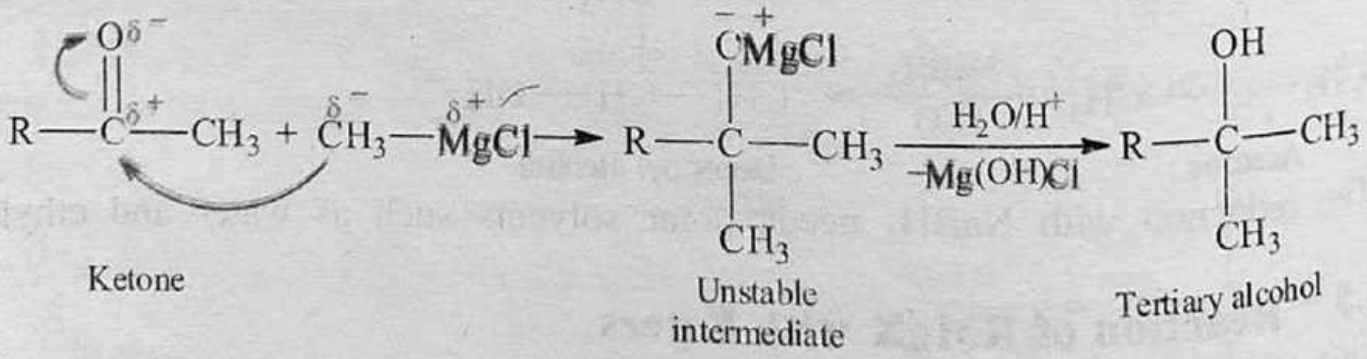
Formation of Tertiary Alcohol

Esters other than formate esters react with Grignard's reagent to form ketones which reacts further with another molecule of Grignard's reagent to form tertiary alcohol as a final product.

Step 1:



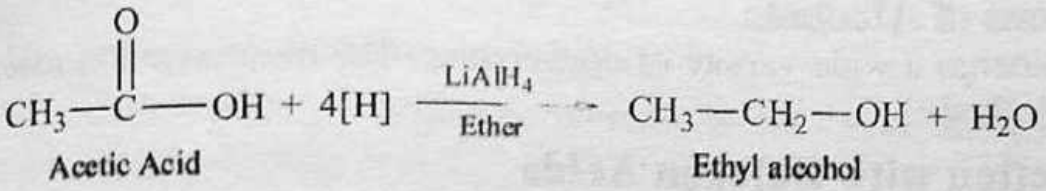
Step 2:



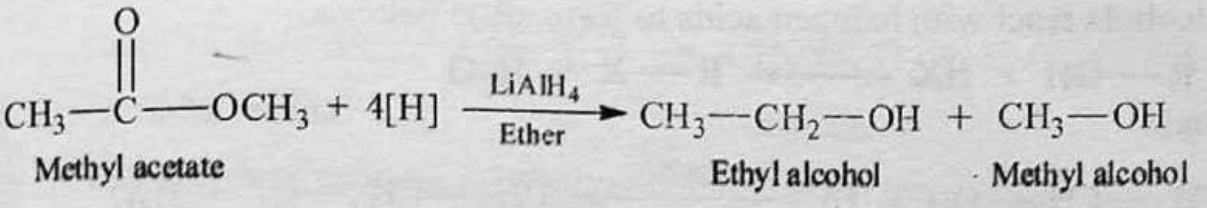
18.1.5.6 Reduction of Carboxylic Acids and Esters

Carboxylic Acids and Esters are easily reduced by strong reducing agents such as $LiAlH_4$. Both carboxylic acids and esters are reduced to alcohols.

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Acetic Acid — Ethyl alcohol



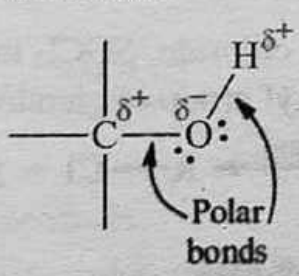
Methyl acetate — Ethyl alcohol — Methyl alcohol

18.1.6 Reactivity of Alcohols

Alcohols are reactive compounds. They act both as electrophiles and nucleophiles. They are attacked by polar or ionic reagents. This is for the reason that:

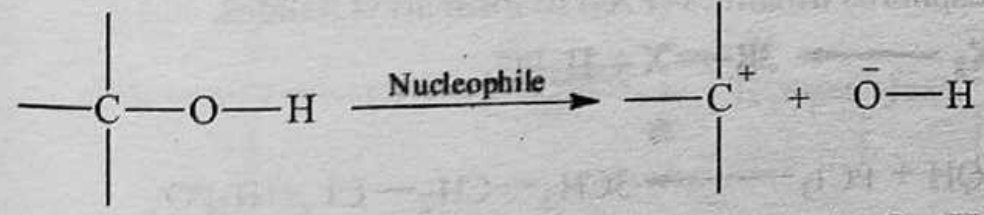
i) The carbon-oxygen (C—O) and hydrogen-oxygen (O—H) bonds are polar due to presence of highly electronegative oxygen atom.

ii) The oxygen atom of alcohols is an electron rich centre. This is due to the presence of two lone pairs of electrons.

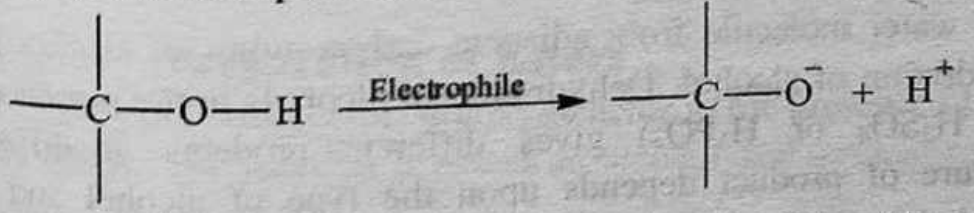


Alcohols react with other reagents in two ways:

i) When nucleophile attacks on an alcohol, then its C—O bond breaks.



ii) When an electrophile attacks on an alcohol, then its O—H bond breaks.



The order of reactivity of alcohols when C—O bond breaks:

Tertiary alcohols > Secondary alcohols > Primary alcohols > CH_3OH

The order of reactivity of alcohols when O—H bond breaks:

CH_3OH > Primary alcohols > Secondary alcohols > Tertiary alcohols

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18.1.7 Reactions of Alcohols

Alcohols undergo a wide variety of conversions. The most common reactions of alcohols are as follows:

18.1.7.1 Reaction with Halogen Acids

Alcohols react with halogen acids to form alkyl halides.

$$R—OH + HX \longrightarrow R—X + H_2O$$

For example:

$$CH_3—CH_2—OH + HCl \xrightarrow{ZnCl_2} CH_3—CH_2—Cl + H_2O$$

HBr and HI react in the same way but in the absence of catalyst. The reaction of alcohols with HCl in the presence of $ZnCl_2$ is called Lucas test. This test is used to differentiate between primary, secondary and tertiary alcohols due to different speed of reactions. The order of reactivity for halogen acids is:

$$HI > HBr > HCl$$

18.1.7.2 Reaction with $SOCl_2$ and PX_3

Reaction with $SOCl_2$

Alcohols react with thionyl chloride, $SOCl_2$ in the presence of pyridine catalyst to form alkyl chloride. The hydroxyl group of alcohol is replaced by chlorine atom.

$$R—OH + SOCl_2 \xrightarrow{Pyridine} R—Cl + SO_2 + HCl$$

For example:

$$CH_3—CH_2—OH + SOCl_2 \xrightarrow{Pyridine} CH_3—CH_2—Cl + SO_2 + HCl$$

Reaction with PX_3

Alcohols react with phosphorus trihalides (PX_3) to form alkyl halides.

$$3R—OH + PX_3 \longrightarrow 3R—X + H_3PO_3$$

For example:

$$3CH_3—CH_2—OH + PCl_3 \longrightarrow 3CH_3—CH_2—Cl + H_3PO_3$$

18.1.7.3 Dehydration of Alcohols

The removal of water molecule from adjacent carbon atoms of alcohol in a reaction is called dehydration of alcohol. Dehydration of alcohols in the presence of acid catalyst (conc. H_2SO_4 or H_3PO_4) gives different products at different temperatures. The nature of product depends upon the type of alcohol and the conditions of reaction that is temperature and concentration of an acid. The hydroxyl group is removed from α-carbon and hydrogen is removed from β-carbon. The ease of dehydration of alcohols follows the order: $3° > 2° > 1°$. This is also the order of the ease of stability of carbocations.

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Dehydration of Primary Alcohols

Dehydration of primary alcohols is the most difficult. It requires high temperature and strong acid.

$$\underset{\text{Ethyl alcohol}}{CH_3—CH_2—OH} \xrightarrow[170\text{–}180°C]{\text{Conc. } H_2SO_4} \underset{\text{Ethylene}}{CH_2=CH_2} + H_2O$$

The excess of primary alcohol (ethyl alcohol) at low temperature gives ether.

$$\underset{\text{Ethyl alcohol}}{2\,CH_3—CH_2—OH} \xrightarrow[140°C]{\text{Conc. } H_2SO_4} \underset{\text{Diethyl ether}}{CH_3—CH_2—O—CH_2—CH_3} + H_2O$$

Dehydration of Secondary Alcohols

The secondary alcohols undergo dehydration at somewhat lower temperatures (100-140°C).

$$\underset{\text{2-Butanol}}{CH_3—CH_2—\underset{\displaystyle CH_3}{\underset{|}{CH}}—OH} \xrightarrow[100°C]{75\%\ H_2SO_4} \underset{\text{2-Butene}}{CH_3—CH=CH—CH_3} + H_2O$$

Dehydration of Tertiary Alcohols

Tertiary alcohols generally undergo dehydration at temperatures only slightly above room temperature (25-80°C).

$$\underset{\text{2-Methyl-2-Propanol}}{CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}}—CH_3} \xrightarrow[50°C]{5\%\ H_2SO_4} \underset{\text{2-Methyl-1-propene}}{CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=CH—CH_3} + H_2O$$

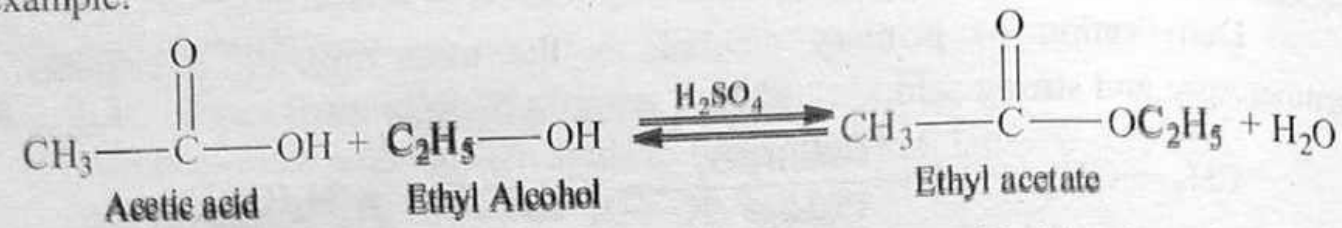
18.1.7.4 Preparation of Esters

Alcohols react with carboxylic acids in the presence of conc. H_2SO_4 catalyst to form esters. The reaction between an alcohol and an acid to form an ester is called esterification.

$$\underset{\text{Carboxylic acid}}{R—\overset{\displaystyle O}{\overset{\|}{C}}—OH} + \underset{\text{Alcohol}}{R—OH} \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} \underset{\text{An ester}}{R—\overset{\displaystyle O}{\overset{\|}{C}}—OR} + H_2O$$

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For example:



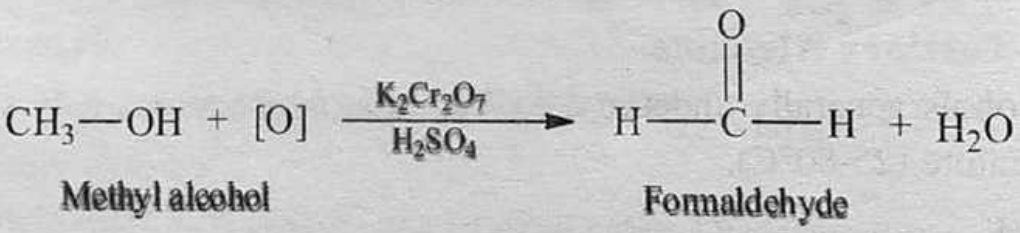
This reaction is reversible. Its reversibility can be controlled by the addition of conc. H_2SO_4 to remove water from the product. In this way, nearly all of the mass of the reactants is converted to products.

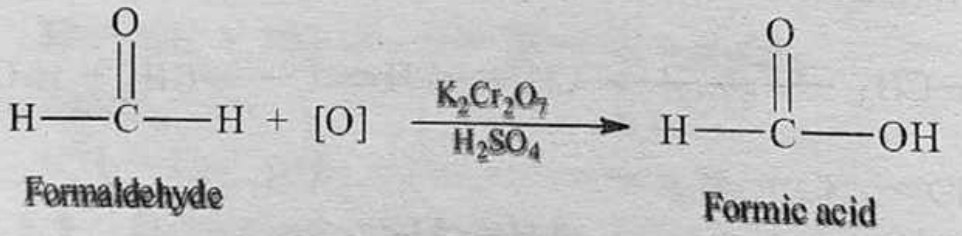
18.1.7.5 Oxidation of Alcohols

The addition of oxygen to alcohol molecule in a reaction is called oxidation of alcohol.The oxidation of alcohols in the presence of oxidizing agents gives different products. The reagent most commonly used for the oxidation of alcohols to acids is potassium dichromate dissolved in aqueous sulphuric acid. The nature of product depends upon the type of alcohol and the conditions of reaction. Oxidation of alcohols is used to differentiate between 1°, 2° and 3° alcohols.

Oxidation of Methyl Alcohol

Methyl alcohol is first oxidized to formaldehyde and then to formic acid.

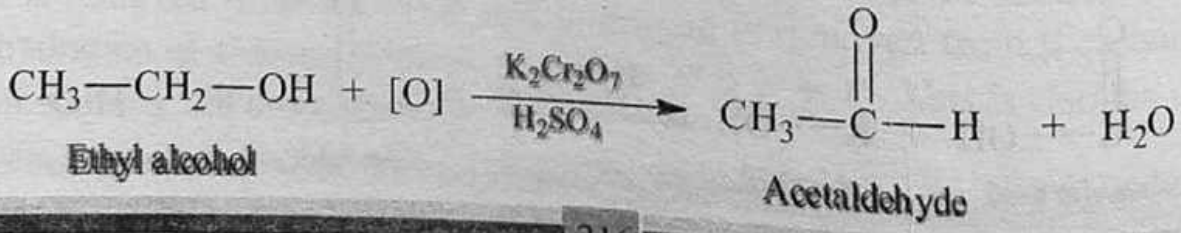




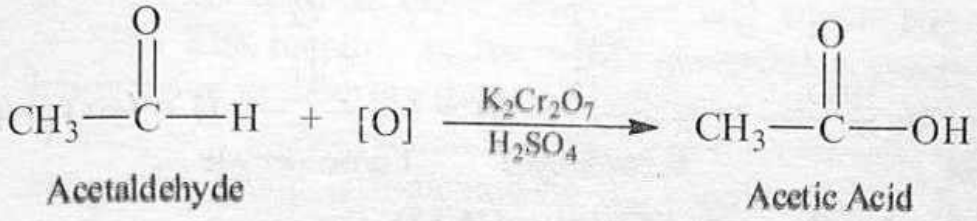
The reaction can be stopped at aldehyde stage by removing it from the oxidizing medium.

Oxidation of Primary Alcohols

Primary alcohols are first oxidized to aldehydes other than formaldehyde and then to carboxylic acids other than formic acid.



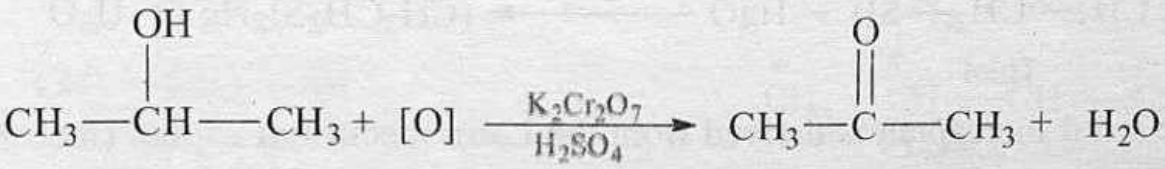
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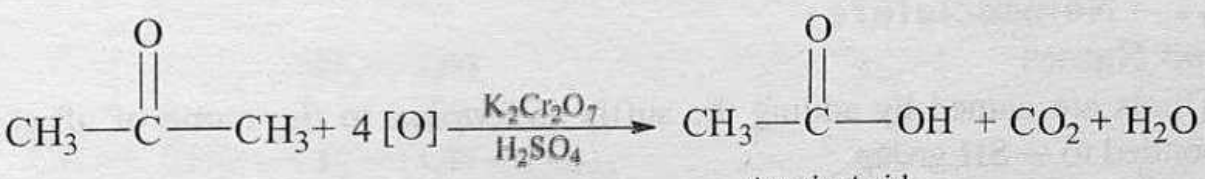
Acetaldehyde — Acetic Acid

Oxidation of Secondary Alcohols

Secondary alcohols are oxidized to ketones, which are not oxidized further easily. Because they require breaking of carbon-carbon bond. They can be oxidized to acids at drastic conditions.



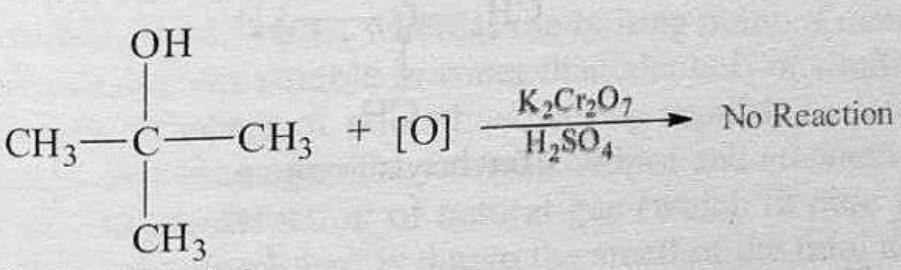
Sec. propyl alcohol — Acetone



Acetone — Acetic Acid

Oxidation of Tertiary Alcohols

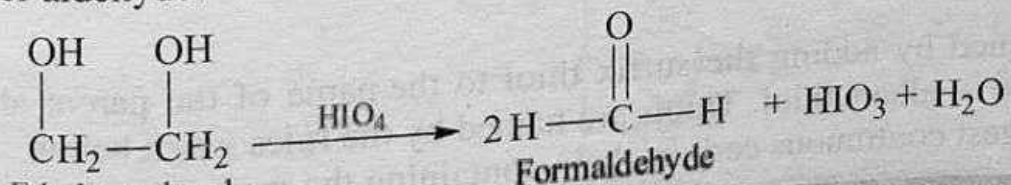
Tertiary alcohols are not oxidized under acidic conditions because the carbon bearing the —OH group is attached to three carbon atoms and, hence cannot form a carbon-oxygen double bond.



Tert-butyl alcohol

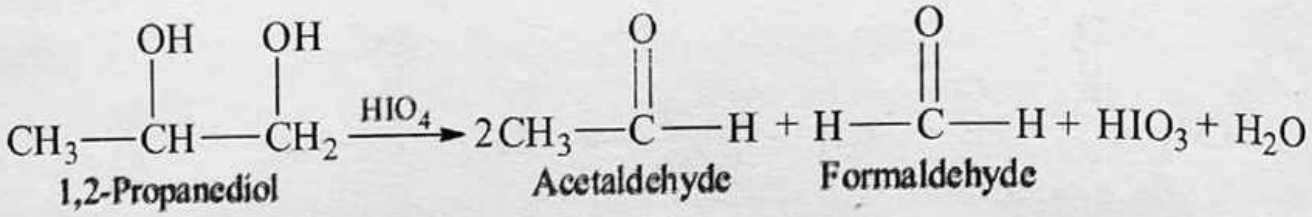
18.1.7.6 Cleavage of 1,2-diols (Glycols)

The vicinal diols are cleaved into two carbonyl compounds by the action of periodic acid, HIO_4 or lead tetraacetate, $(CH_3COO)_4Pb$. The carbonyl compounds can be either aldehydes or ketones.



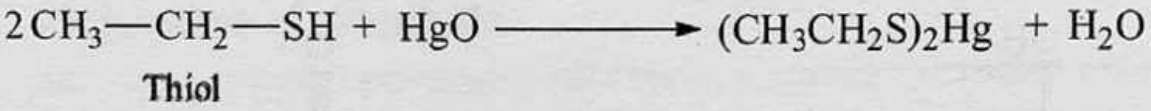
Ethylene glycol — Formaldehyde

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18.1.8 The Sulphur Analogous (Thiols, RSH)

Thiols are sulphur analogues of alcohols and are known as thioalcohols. They have mercapto group (—SH) instead of hydroxyl group (—OH). Since they form strong complexes with mercuric oxide that is they capture mercury hence, they are also called mercaptans.

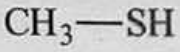


The word mercaptan is derived from the Latin mecurium captan (mecurium = mercury; captans = capturing).

18.1.8.1 Nomenclature

Common Names

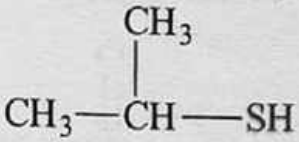
Thiols are named by adding the suffix *mercaptan* to the name of alkyl group that is bonded to —SH group.



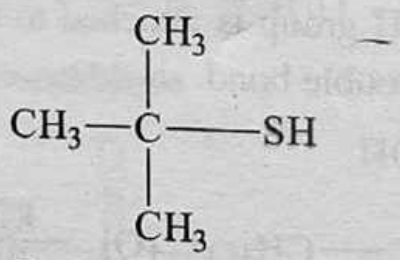
Methyl mercaptan



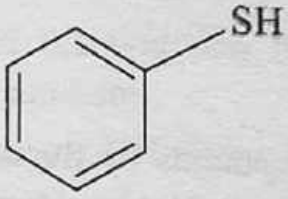
Ethyl mercaptan



Isopropyl mercaptan



Tert-butyl mercaptan



Phenyl mercaptan

IUPAC Names

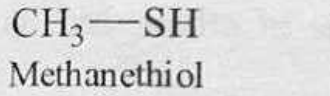
Thiols are named by adding the suffix thiol to the name of the parent alkane. Thus they are named as alkanethiol. Thiols are named by the rules given below:

i) Select the longest continuous carbon chain containing the mercapto group.

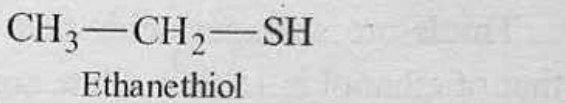
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ii) Number the carbon chain from that end which is nearer to mercapto group (—SH). The location of the —SH group takes priority over alkyl groups and halogens in numbering the parent chain.

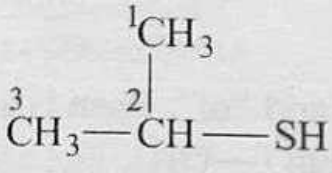
iii) If there is a second functional group in the molecule with a higher priority, then the —SH group is indicated by the prefix *sulfanyl*. It may be indicated by the prefix mercapto-. For exampl , the —OH (higher priority group) takes priority over —SH (lower priority grc ip) in both numbering and naming. Examples are:



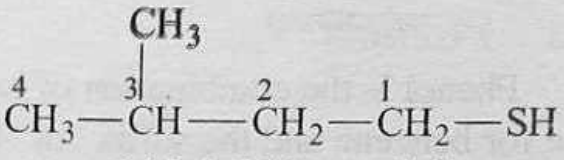
Methanethiol



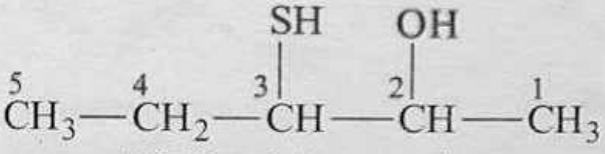
Ethanethiol



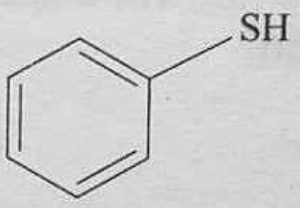
2-Propanethiol
(Propane-2-thiol)



3-**Methyl**-1-butanethiol
(3-**Methyl**butane-1-thiol)



3-Sulfanyl-2-pentanol
(β-Mercapto-2-Pentanol)



Benzenethiol

18.1.8.2 Physical Properties

i) Methanethiol is a gas whereas higher members are colourless volatile liquids.

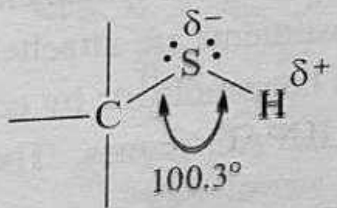
ii) They have considerably lower boiling points than alcohols because they have much weaker intermolecular attractive forces. For example, the boiling point of methanethiol is 6°C, whereas the boiling point of methyl alcohol is 65°C.

iii) Thiols are less soluble in water than alcohols of similar molecular masses.

iv) Lower members of thiols have strong repulsive odours. They smell like that of garlic or rotten egg. They (methanethiol and ethanethiol) are used as odorants to assist in the detection of natural gas (which in pure form is odourless), and the "smell of natural gas" is due to the smell of the thiol used as the odorant.

18.1.8.3 Structure

The functional group of thiol is —SH (mercapto) group bonded to sp^3 hybridized carbon. Their structures are similar to alcohols. The $C\widehat{S}H$ bond angle in methanethiol is 100.3°.



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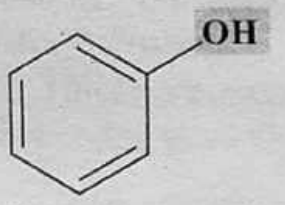
The electronegativity of sulphur and carbon are nearly equal while sulphur is slightly more electronegative than hydrogen. Hence, hydrogen attain partial positive charge and sulphur attains slight negative charge. The sulphur-hydrogen bond is less polar than oxygen-hydrogen bond because sulphur is less electronegative than oxygen.

18.1.8.4 Acidity

Thiols are stronger acids than alcohols. The pK_a value of ethanethiol is 10.5 and that of ethanol is 15.9 in dilute aqueous solution.

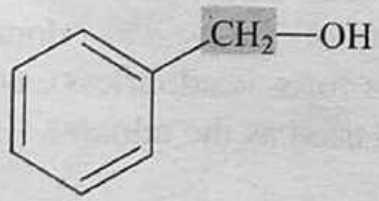
18.2 Phenols

Phenol is the combination of two words that is "phen" and "ol". Phen is an old name for benzene and the suffix "ol" is used for hydroxyl group (—OH). Phenols are those organic compounds in which one or more —OH groups are directly bonded to the carbon of benzene ring. The simplest member of this family is phenol.

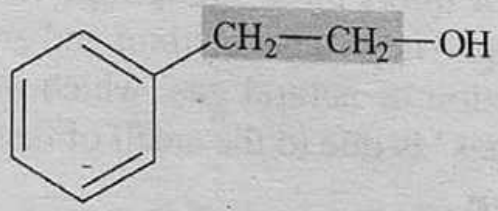


Phenols may be monohydric or polyhydric. It depends on the number of hydroxyl groups attached to the carbon of benzene ring. The phenols containing one —OH are known as monohydric phenols and the phenols containing two or more —OH groups are known as polyhydric phenols.

The aromatic compounds in which hydroxyl (—OH) group is not directly bonded to the benzene ring are not phenols but are called aromatic alcohols. These may be regarded as derivatives of aliphatic alcohols. For example:



Phenylmethanol



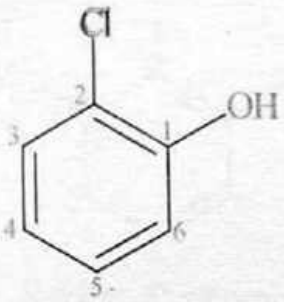
2-Phenylethanol

18.2.1 Nomenclature of Phenols

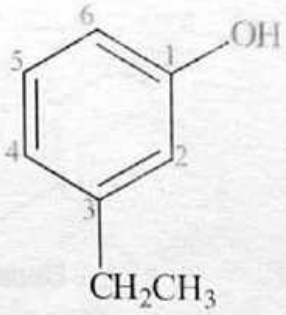
Phenol is the specific name for hydroxybenzene, but the word phenol is also used as the parent name when substituents are attached. We name substituted phenols either as derivatives of phenol, as benzenols, or by common names. Common names are given in parenthesis below IUPAC names. The IUPAC rules for substituted phenols are as:

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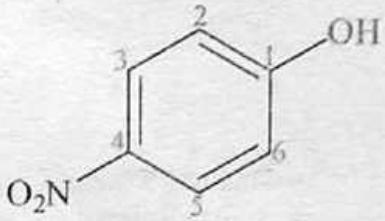
i) In substituted phenols, the position 1 is given to that carbon which has hydroxyl group. For example:



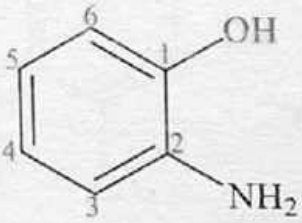
2-Chlorophenol
(*o*-Chlorophenol)



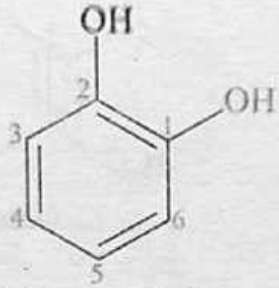
3-Ethylphenol
(*m*-Ethylphenol)



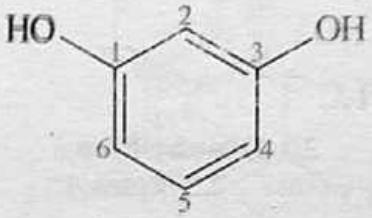
4-Nitrophenol
(*p*-Nitrophenol)



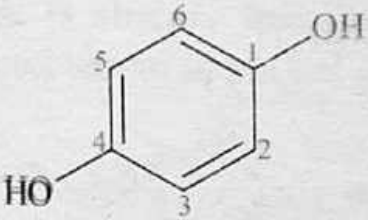
2-Aminophenol
(*o*-Aminophenol)



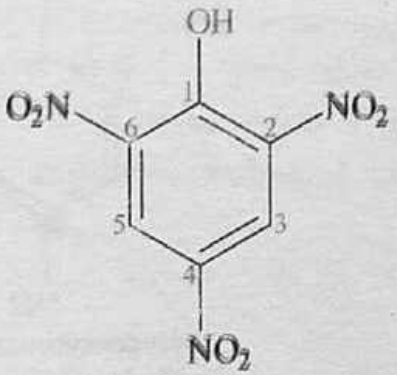
1,2-Benzenediol
(Catechol)



1,3-Benzenediol
(Resorcinol)

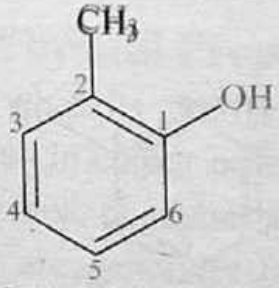


1,4-Benzenediol
(Hydroquinone)

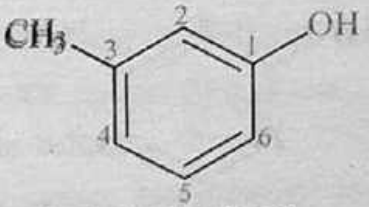


2,4,6-Trinitrophenol
(Picric acid)

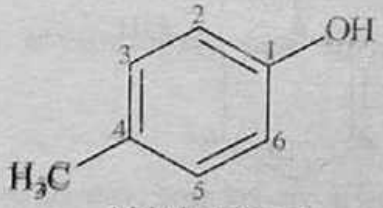
The methylphenols are called cresols.



2-Methylphenol
(*o*-Cresol)



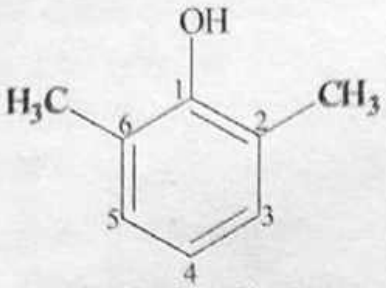
3-Methylphenol
(*m*-Cresol)



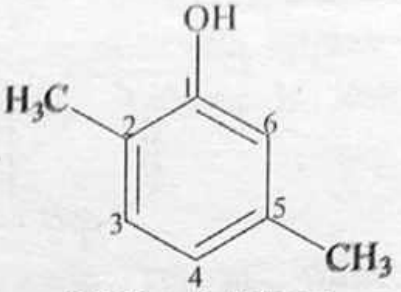
4-Methylphenol
(*p*-Cresol)

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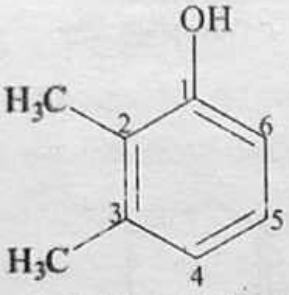
Derivatives of phenols with two methyl groups are called xylenols.



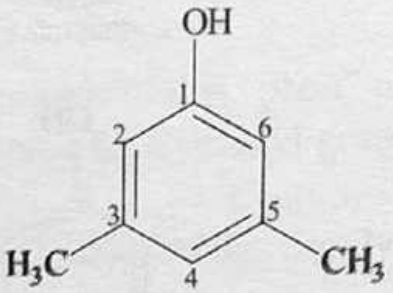
2,6-**Dimethylphenol**
or 2,6-**Xylenol**



2,5-**Dimethylphenol**
or 2,5-**Xylenol**

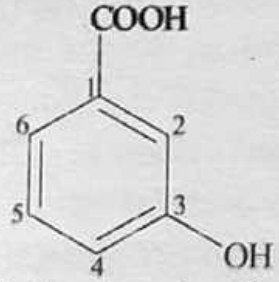


2,3-**Dimethylphenol**
or 2,3-**Xylenol**

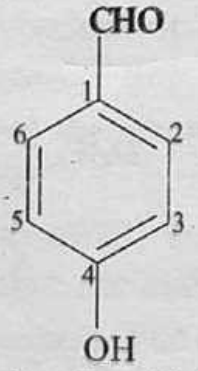


3,5-**Dimethylphenol**
or 3,5-**Xylenol**

ii) If phenol has another functional group which is superior in priority order, then phenols are named as hydroxyl derivatives.



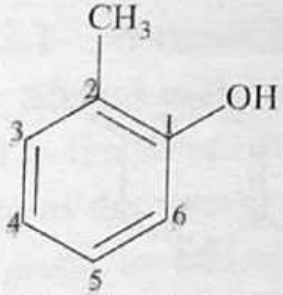
3-**Hydroxy**benzoic acid
(*m*-**Hydroxy**benzoic acid)



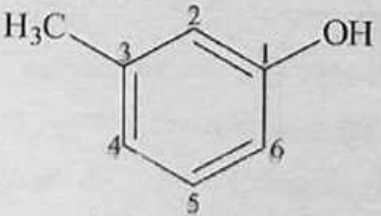
4-**Hydroxy**benzaldehyde
(*p*-**Hydroxy**benzaldehyde)

Isomerism in Phenols

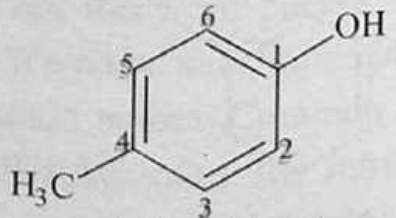
Phenols with two or more substituents can show position isomerism due to different position of substituents. For example, the methylphenol also called cresol has three isomers i.e. *o*-cresol, *m*-cresol and *p*-cresol.



2-Methylphenol
(*o*-Cresol)



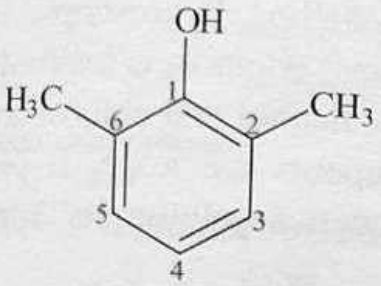
3-Methylphenol
(*m*-Cresol)



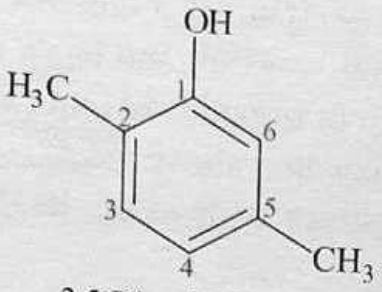
4-Methylphenol
(*p*-Cresol)

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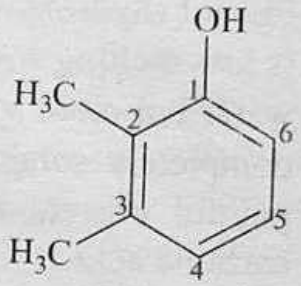
Xylenol has one hydroxyl group and two methyl groups and contains six isomers.



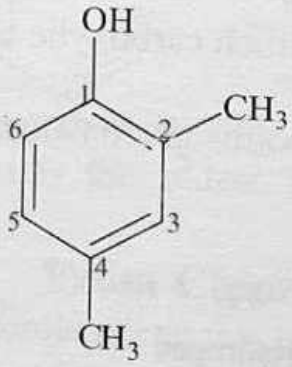
2,6-DimethylPhenol



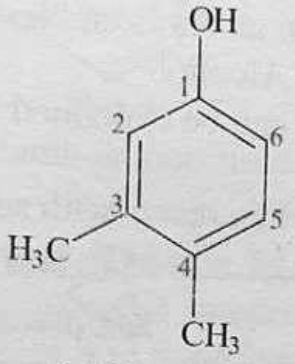
2,5-DimethylPhenol



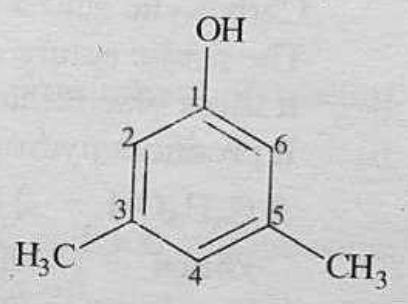
2,3-DimethylPhenol



2,4-DimethylPhenol



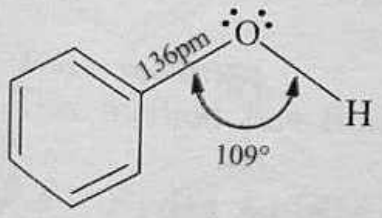
3,4-DimethylPhenol



3,5-DimethylPhenol

18.2.2 Structure of Phenol

In phenols, the hydroxyl group is bonded to aromatic ring. The oxygen atom of the hydroxyl group has two bond pairs and two lone pairs of electrons, hence, it has bent shape as water molecules. The $C\hat{O}H$ bond angle in phenol is 109°. C—O—H bond angle is slightly less than the regular tetrahedral angle (109.5°). the carbon-oxygen bond length in phenol is 136 pm.



Phenol

Phenol is a polar compound and has a dipole moment of 1.54 D.

18.2.3 Physical Properties of Phenols

i) Pure phenols are generally colourless solids at room temperature but turn reddish in colour on exposure to air due to oxidation.

ii) They have characteristic phenolic odour.

iii) They are generally insoluble in water but phenol itself and di- and tri-hydric phenols are fairly soluble.

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iv) They usually have higher boiling points than aliphatic alcohols due to presence of strong intermolecular hydrogen bonding and high molecular mass.

v) Phenol (hydroxybenzene) itself is a colourless, crystalline, hygroscopic solid. It is low melting solid (mp. = 43°C) and has a medicinal odour. It is less soluble in water but more soluble in organic solvents such as alcohol and chloroform. It is completely soluble in water above 68.5°. Its vapours are toxic. It produces painful blisters in contact with skin. Its 5% aqueous solution is known as carbolic acid.

18.2.4 Acidity of Phenol

Phenols are more acidic than alcohols and less acidic than carboxylic acids.

Carboxylic acid > Phenol > Alcohol

The acidic nature of phenol can be explained by the points given below:

i) It turns blue litmus red.

ii) It produces hydrogen gas when reacts with sodium.

$$2\,C_6H_5OH + 2\,Na \longrightarrow 2\,C_6H_5ONa + H_2$$

Phenol **Sodium** **Sod. phenoxide** **Hydrogen**

iii) It has ability to produce hydrogen ions in water.

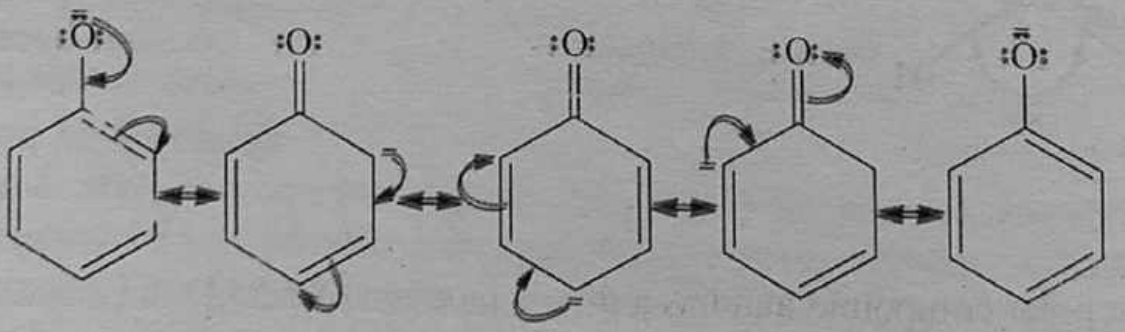
iv) It reacts with a strong base to produce salt and water.

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

Phenol **Sodium hydroxide** **Sod. phenoxide**

(Acid) (Base) (Salt) Water

v) It forms a stable phenoxide ion (phenolate ion) after loss of hydrogen ion. The stability of phenoxide ion as compared to alkoxide ion is due to delocalization of negative charge in the benzene ring. It is shown by the following resonating structures.



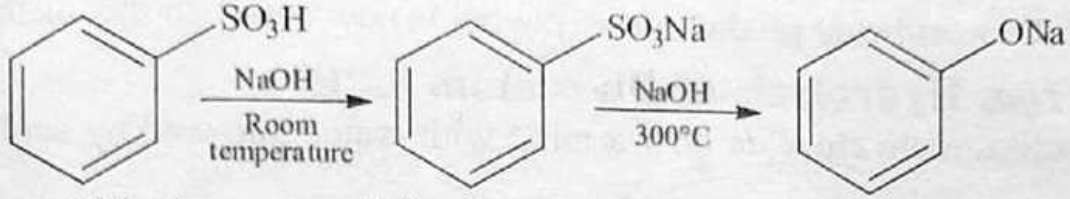
18.2.5 Preparation of Phenol

Phenol can be prepared by the following methods:

18.2.5.1 From Benzene Sulphonic Acid

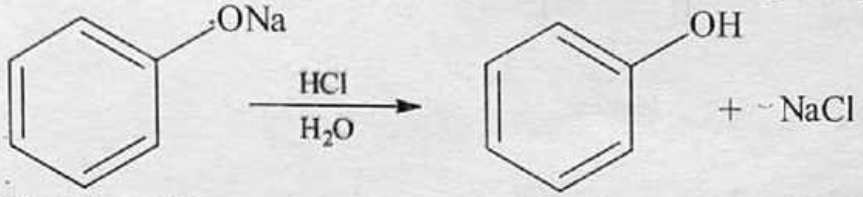
Benzene sulphonic acid reacts with sodium hydroxide to produce sodium benzene sulphonate which on further reaction with NaOH at about 300°C produces sodium phenoxide.

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Benzene sulphonic acid — Sodium benzene sulphonate — Sodium phenoxide

The sodium phenoxide on hydrolysis with HCl gives phenol.

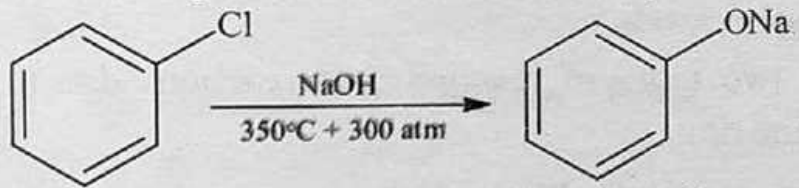


Sodium phenoxide — Phenol

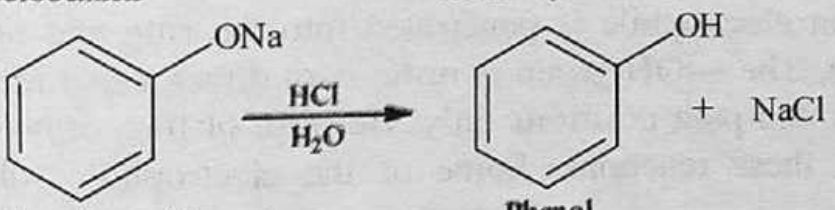
This is the oldest method and is not used for the preparation of phenol nowadays.

18.2.5.2 From Chlorobenzene (Dow's Method)

Chlorobenzene reacts with 10% NaOH solution at 350°C and 300 atm pressure to produce sodium phenoxide which on acid hydrolysis gives phenol.



Chlorobenzen — Sodium phenoxide

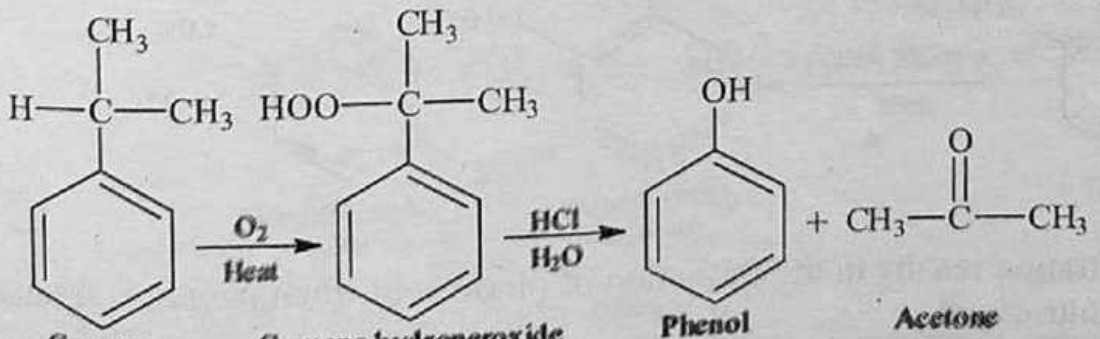


Sodium phenoxide — Phenol

This method has limited application in the laboratory synthesis of simple phenols.

18.2.5.3 From Acidic Oxidation of Cumene

Cumene is readily oxidized by air to produce cumene hydroperoxide on hydrolysis with HCl gives phenol.



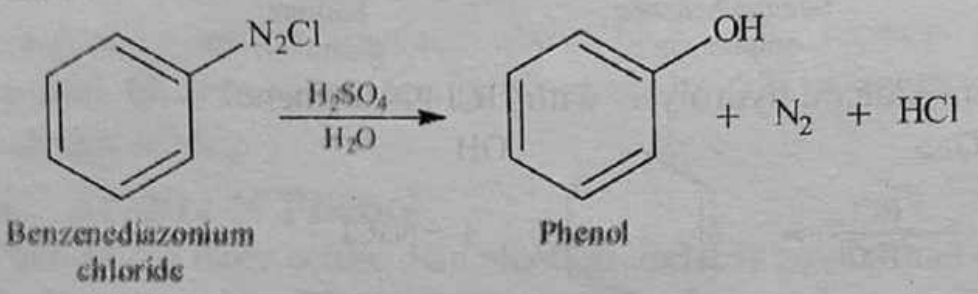
Cumene — Cumene hydroperoxide — Phenol — Acetone

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Most of the worldwide production of phenol is now based on this method.

18.2.5.4 From Hydrolysis of Diazonium Salts

Benzenediazonium chloride on warming with water followed by acidification, gives phenol.



Benzenediazonium chloride — Phenol

18.2.6 Reactivity of Phenol

The phenolic (—OH) group is electron donating group and increases the electron density at ortho and para positions by donating its electron pair to the benzene ring. This makes the benzene ring of phenol more reactive towards electrophilic substitution reactions. Because of this reason, phenols behave as nucleophiles in most of their reactions.

18.2.7 Reactions of Phenols

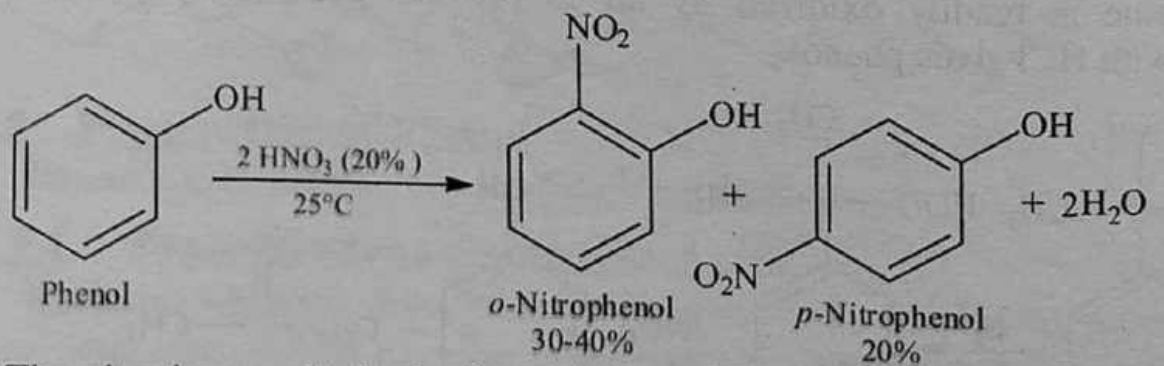
Phenols generally show two types of reactions: (i) reactions due to —OH group (ii) reactions due to benzene ring.

18.2.7.1 Electrophilic Aromatic Substitutions

In these reactions, an electrophile is penetrated into the ring and breaks the electronic cloud of benzene. The —OH group is ortho-para director and most of the substitutions occur at ortho and para positions only. Because of this, ortho and para derivative are obtained in these reactions. Some of the electrophilic substitution reactions of phenols are:

Nitration

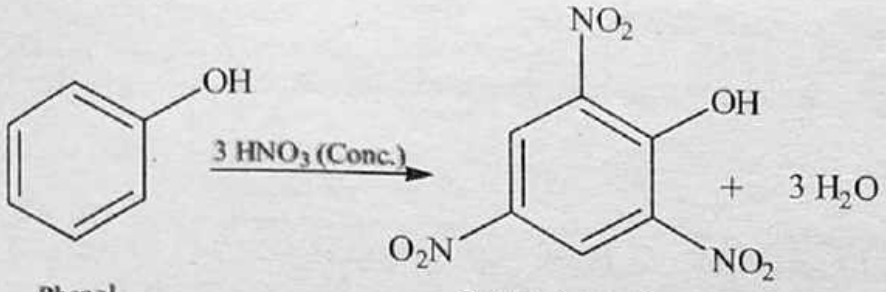
Phenol reacts with dilute nitric acid at room temperature to give a mixture of ortho and para nitrophenols.



Phenol — *o*-Nitrophenol 30-40% — *p*-Nitrophenol 20%

The nitration results in the formation of picric acid when phenol is treated with concentrated nitric acid.

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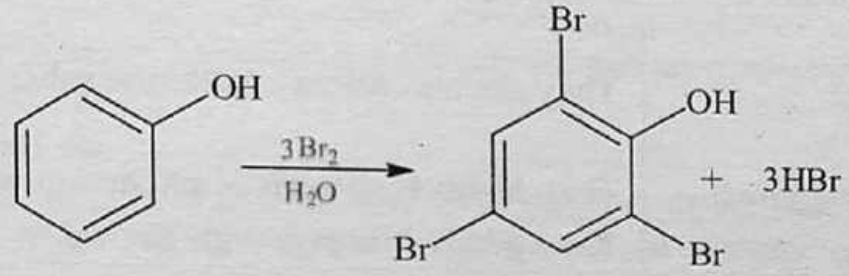


Phenol

2,4,6-trinitrophenol
(Picric acid)

Halogenation

Phenols react with bromine water to produce white precipitate of 2,4,6-tribromophenol.

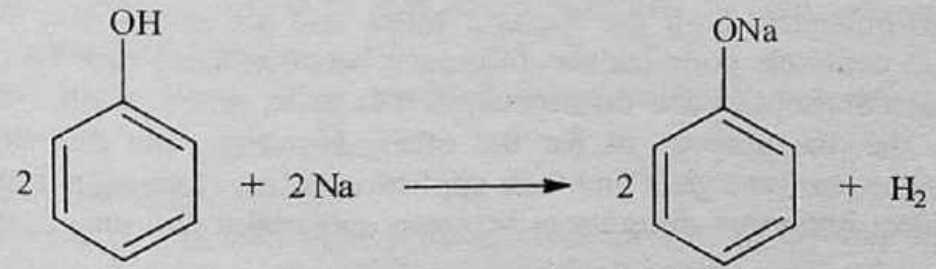


Phenol

2,4,6-Tribromophenol

18.2.7.2 Reaction with Sodium Metal

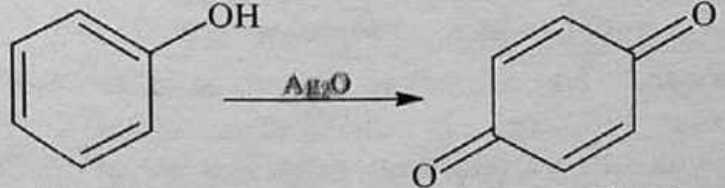
Phenol reacts with sodium metal on warming to form water soluble salt (sodium phenoxide) with release of hydrogen gas.



Phenol Sodium metal Sod. phenoxide

18.2.7.3 Oxidation

Phenol is oxidized to *p*-benzoquinone in the presence of stronger oxidizing agents. The oxidizing agents used are silver oxide, lead tetraacetate, dichromate, and atmospheric oxygen. Phenols are more easily oxidized than simple alcohols.



Phenol

p-Benzoquinone

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18.2.8 Difference between Alcohols and Phenols

The main difference between alcohols and phenols are given in the table:

Alcohol	Phenol
Hydroxyl group is bonded to an alkyl group.	Hydroxyl group is bonded to an aryl group.
Hydroxyl derivatives of alkanes.	Hydroxyl derivatives of benzene.
General formula is R—OH.	General formula is Ar—OH.
They are less acidic.	They are more acidic.
The pK_a value is nearly equal to 16-20.	The pK_a value is nearly equal to 10.
Lower alcohols are generally colourless liquids.	They are colourless crystalline solids.
They have characteristic sweet smell.	They have characteristic phenolic smell.
They have no action with Br_2 water.	They give white ppt. with Br_2 water.
They do not react with NaOH.	They react with NaOH to form phenoxides.

Society, Technology and Science

Antiseptics and Disinfectants

Antiseptic and disinfectants both are bacteria killer and are considered to be antimicrobial. It is hard to definitely point out the difference between these two. There is no real difference between antiseptics and disinfectants. It is to be noted that the same chemicals are used for the one purpose as for the other. However, the differences between these two chemicals are very great and their applications (uses) are significantly different. Some of the most important differences between antiseptics and disinfectants are given in the table.

Antiseptics	Disinfectants
They are mild chemicals that are applied to the skin or body to kill germs.	They are strong chemicals that are applied to the non-living surfaces, spots and places to kill germs.
They are safe and do not harmful to the body of humans and animals. They are used locally outside the body.	They are harmful to the body of humans and animals. They are not applied on the body due to their corrosive nature.
They are used on or in living tissue including skin, oral cavities and open wounds to remove, inhibit the growth of, or inactivate microorganisms.	They are often used to sterilize operation theatres, to disinfectant utensils, doors, floors, etc. and to decontaminate reusable instruments.

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Antiseptics	Disinfectants
They are commonly used at healthcare centres or hospitals.	They are commonly found at homes or public places.
Examples are surgical spirit (ethyl alcohol as 60-70% or isopropyl alcohol at least 70%), iodine, dettol, boric acid, listrine, lime, hydrogen peroxide, etc.	Examples are phenol, dettol, formalin, sodium hypochlorite, DDT, etc.

The Role of Disinfectants in Hygiene

Hygiene is a practice or an activity of keeping yourself and your surrounding clean and healthy. Hygiene refers to conditions and practices that prevent illness or the spread of diseases. A good hygiene means to keep your body clean and healthy. Disinfectants are used to kill or inactive germs and other harmful substances.

There are many different chemicals that are used as disinfectants and play key roles in hygiene.

Alcohols

Alcohols such as ethyl alcohol and isopropyl alcohol are widely used as antiseptics and disinfectants. They are used to kill bacteria and viruses.

Phenols

Phenols are widely used as disinfectants in household products.

Sodium Hypochlorite

The 5% solution of sodium hypochlorite is an effective disinfectant for sinks, toilets, etc.

Calcium Hypochlorite

Calcium hypochlorite is used in hospitals as disinfectants for clothing and bedding.

Chlorine and Ozone

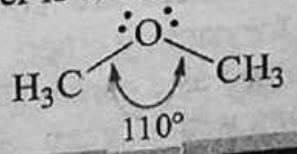
Chorine and ozone gases are used as disinfectants in water treatment to kill harmful bacteria.

Iodine Tincture

It contains 2–7% elemental **iodine** in addition to KI or NaI, dissolved in a mixture of ethanol and water. Iodine tincture is typically used as an antiseptic. It is usually used in hospitals as a disinfectant because it can destroy both bacteria and viruses.

18.3 Ethers

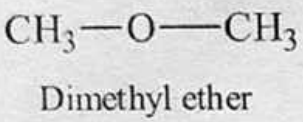
Ethers are compounds in which an oxygen atom is bonded to two alkyl (or aryl) groups. They may be regarded as derivatives of water in which both the hydrogen atoms have been replaced by alkyl (or aryl) groups. They have general formula R—O—R′, where R and R′ may be alkyl or aryl or vinyl groups. The bond angle at the oxygen atom of an ether is to some extent greater than that of water:



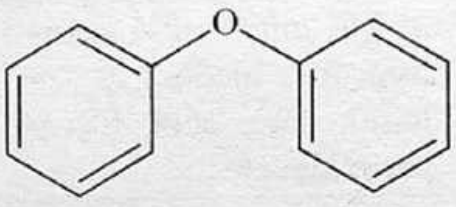
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There are two types of ethers: (i) symmetrical ethers (ii) unsymmetrical ethers.

In symmetrical ethers, the two alkyl (or aryl) groups are the same. They are also known as simple ethers. Examples are:

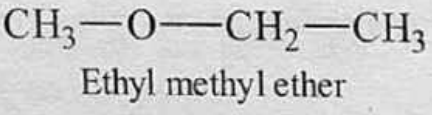


Dimethyl ether

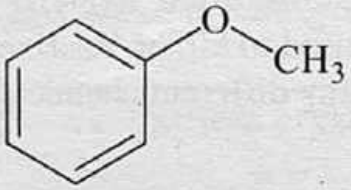


Diphenyl ether

In unsymmetrical ethers, the two alkyl (or aryl) groups are different. They are also known as mixed ethers. Examples are:



Ethyl methyl ether



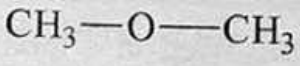
Methyl phenyl ether

18.3.1 Nomenclature of Ethers

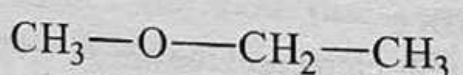
There are two systems for naming ethers: (i) common system and (ii) IUPAC system. Ethers are usually named by common system. IUPAC system is used for those compounds which have more than one ether linkages.

18.3.1.1 Common System

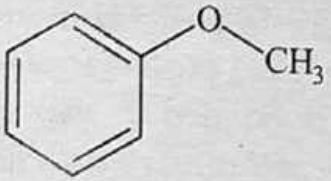
Chemists almost use common names for simple ethers that is, low molecular mass ethers. In common system, the two alkyl (or aryl) groups bonded to oxygen atom are named in alphabetical order and the word ether is added. If the two alkyl (or aryl) groups are similar, then the prefix di- is used. Examples are:



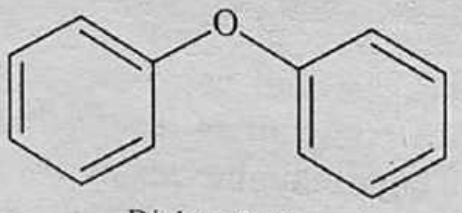
Dimethyl ether



Ethyl methyl ether



Methyl phenyl ether



Diphenyl ether

18.3.1.2 IUPAC System

According to this system, ethers are considered as alkoxy derivatives of hydrocarbons. The IUPAC rules for naming ethers are:

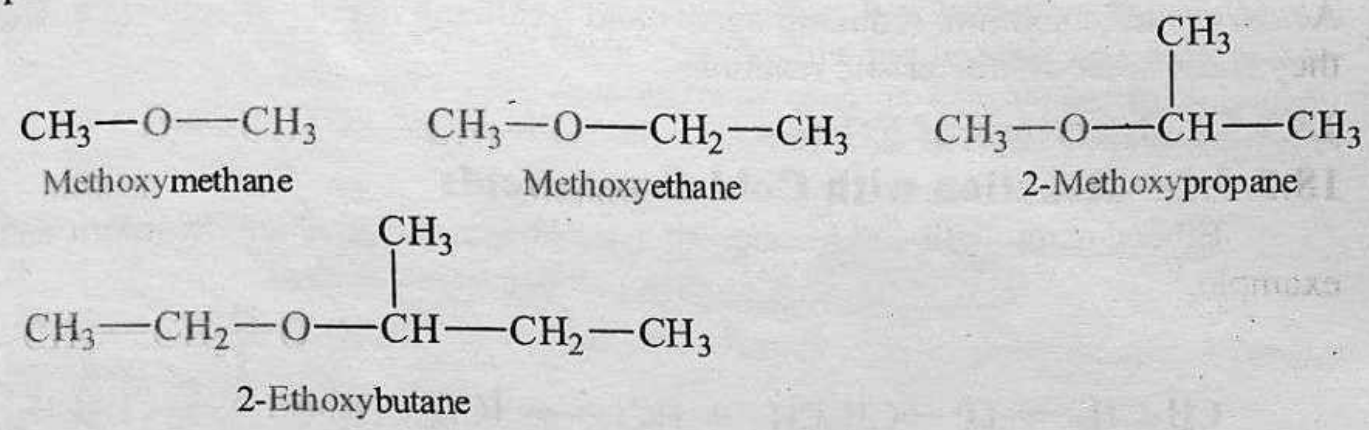
i) The larger alkyl group is named as a parent alkane.

ii) The smaller alkyl group along with oxygen atom is taken as alkoxy group.

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iii) Number the carbon chain from that end which is nearer to alkoxy group.

Examples are:



18.3.2 Physical Properties of Ethers

i) Lower ethers such as dimethyl ether and ethyl methyl ether are gases while higher ethers are colourless, volatile liquids.

ii) They have pleasant odour.

iii) They are highly inflammable.

iv) They have low boiling points due to absence of hydrogen bonding.

v) They are slightly soluble in water because they form hydrogen bonds with water. Their solubility decreases with increase in the size of alkyl groups. They are readily soluble in organic solvents such as benzene, chloroform etc.

vi) They are lighter than water.

vii) Ethers are used as a solvent.

18.3.3 Preparation of Ethers

They are prepared by the following methods:

18.3.3.1 Williamson's Synthesis

Alcohols react with sodium metal to give sodium alkoxide which on further reaction with alkyl halide gives ether.

$$2\,R{-}OH \xrightarrow[-H_2]{2\,Na} 2\,R{-}ONa \xrightarrow[-NaX]{RX} R{-}O{-}R$$

This is the most important and widely used method for the preparation of ethers.

18.3.3.2 Reaction of Alkyl Halides with Dry Silver Oxide

Alkyl halides react with silver oxide on heating to produce ether.

$$2R{-}X + Ag_2O \longrightarrow R{-}O{-}R + 2AgX$$

18.3.5 Reactivity of Ethers

Ethers are stable compounds. They are less reactive than alcohols but are considerably reactive than alkanes. They are less reactive because of the absence of

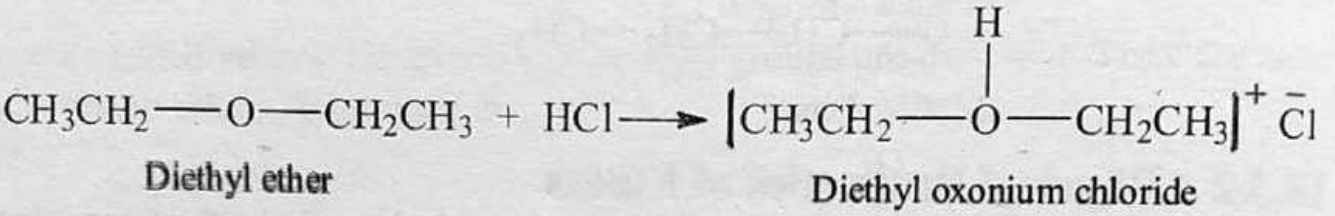
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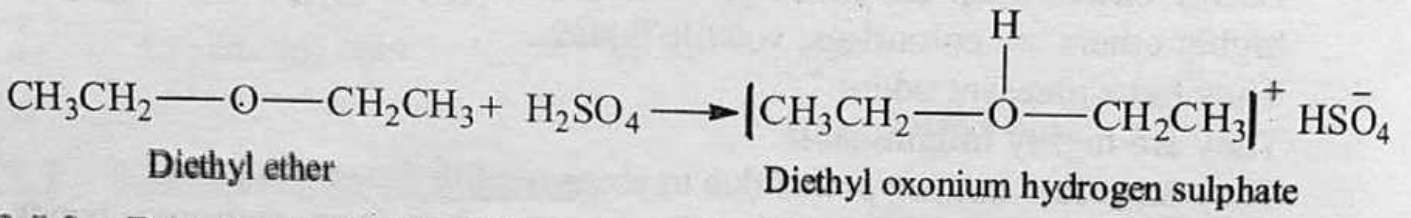
active hydrogen bonded to oxygen as present in alcohols. They are reactive only when the oxygen is protonated in an acidic medium. They do not react with bases, dil. Acids, metallic sodium, reducing agents and oxidizing agents in cold state. However, they show some characteristic reactions.

18.3.5 Reactions of Ethers

18.3.5.1 Reaction with Cold Conc. Acids

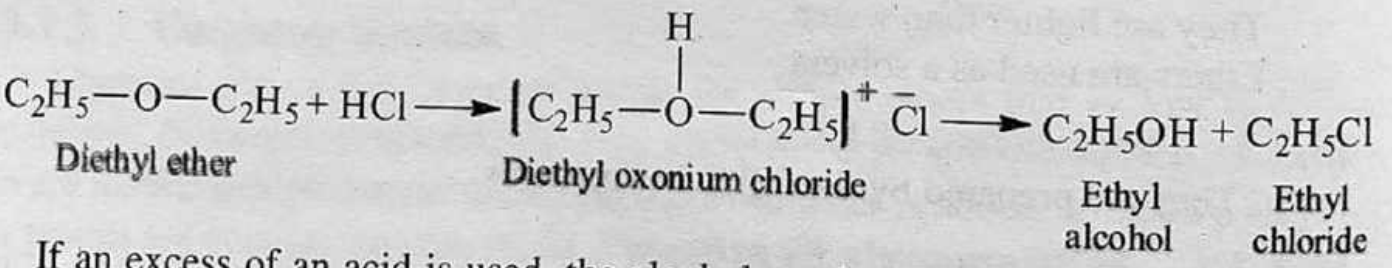
Ethers react with cold conc. HCl or H_2SO_4 to produce oxonium salts. For example:



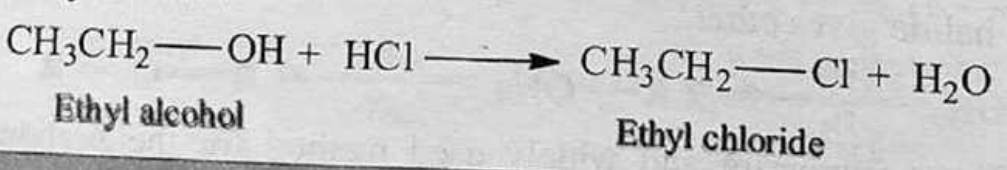


18.3.5.2 Reaction with Hot Concentrated Acids

Ethers react with hot concentrated HCl or HI to produce an alcohol and alkyl halide.



If an excess of an acid is used, the alcohol so obtained reacts further with HX to give alkyl halides.



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Use of Ether as Anesthesia

Ether is colourless, volatile and highly flammable liquid with a characteristic smell. Diethyl ether was one of the first chemicals used as an anesthetic in hospitals. **Anesthetic** is a substance that is used to cause loss of sensation or consciousness in order to undergo surgery without pain. The three important early anesthetics were diethyl ether, chloroform and nitrous oxide. Diethyl ether is safer anesthetic than chloroform and more effective than nitrous oxide. Ether was safe, easy to use, and remained the standard

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general anesthetic until the 1960s. Since then, ether is no longer used in advanced countries (Europe and America) as an anesthetic because it is extremely flammable and has prolonged anesthesia recovery. In these countries, the use of ether was displaced by less flammable and safer fluorinated hydrocarbons such as haloethane. Ether is still used as an anaesthetic these days in some un-developed countries (third world countries) because of its cheapness.

Summary of Facts and Concepts

- Alcohols are hydroxyl derivatives of alkanes while phenols are hydroxyl derivatives of benzene.
- Alcohols are compounds in which hydroxyl group (—OH) is bonded to saturated carbon atom while phenols are those organic compounds in which one or more —OH groups are directly bonded to the carbon of benzene ring. General formula of alcohol is ROH and that of phenol is PhOH.
- Alcohols are categorised into two major groups: (i) Monohydric alcohols (ii) polyhydric alcohols. Monohydric alcohols have only one hydroxyl group while polyhydric alcohol have two or more hydroxyl groups in their structures. Ethyl alcohol is the example of monohydric while glycerine is the example of polyhydric alcohols.
- 95% pure ethyl alcohol is called rectified alcohol and 100% pure ethyl alcohol is called absolute alcohol.
- Alcohols are polar compounds with oxygen carrying a partial negative charge and both the carbon and hydrogen bonded to it carrying partial positive charges.
- The boiling points of alcohols are higher than those of hydrocarbons with similar molecular mass. This is due to presence of hydrogen bonding in alcohols.
- Alcohols are acidic in nature due to presence of polar O—H bond. Greater the polarity of —OH group, greater would be the acidity of alcohols. Primary alcohols are more acidic than secondary alcohols which in turn are more acidic than tertiary alcohols.
- Alcohols are reactive organic compounds. They act both as electrophiles and nucleophiles. They undergo a wide variety of conversions—the majority of which are either oxidation or reduction type reactions.
- An alcohol undergoes dehydration when it is heated with an acid. The major product of alcohol dehydration is the more stable alkene. Tertiary alcohols are the easiest to dehydrate, and primary alcohols are the hardest.
- Thiols are sulphur analogues of alcohols and are known as thioalcohols. They have mercapto group (—SH) instead of hydroxyl group (—OH). Thiols are stronger acids and have lower boiling points than alcohols. Because the S—H

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bond is almost nonpolar, the physical properties of thiols are more like those of hydrocarbons of similar molecular mass.

- In an ether, an oxygen atom (—O—) is connected by single bonds to two alkyl or aromatic groups. Ethers are formed by a condensation reaction of two molecules of alcohol. Ethers of low molecular mass have low boiling points, while ethers with larger alkyl groups have higher boiling points due to London dispersion forces between the alkyl groups. Ethers are often used as solvents for organic reactions.

Multiple Choice Questions

Select one answer from the given choices for each question:

i) The hydrogen bonding is present in:
   (a) C_6H_6 (b) C_2H_5OH
   (c) C_2H_5Br (d) $CH_3—O—CH_3$

ii) Which compound is more soluble in water?
   (a) Phenol (b) Ethyl alcohol
   (c) Dimethyl ether (d) 1-Hexanol

iii) Oxidation of ethyl alcohol gives:
   (a) Formaldehyde (b) Acetaldehyde
   (c) Acetone (d) Ether

iv) Methanol is also known as
   (a) Absolute alcohol (b) Rectified alcohol
   (c) Wood spirit (d) Methylated alcohol

v) Rectified spirit contains about:
   (a) 85% ethyl alcohol (b) 90% ethyl alcohol
   (c) 95% ethyl alcohol (d) 100% ethyl alcohol

vi) Alcohols are prepared by the:
   (a) Hydration of alkenes. (b) Hydrogenation of alkenes.
   (c) Halogenation of alkenes. (d) Oxidation of alkenes.

vii) The protonated ether is called:
   (a) Oxide ion (b) Carbon ion
   (c) Hydronium ion (d) Oxonium ion

viii) Which statement is true about phenol?
   (a) It is more acidic than acetic acid
   (b) It is more acidic than ethyl alcohol.
   (c) It turns red litmus blue.
   (d) It does not react with sodium.

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ix) Which one of the following is the isomer of dimethyl ether?

(a) CH_3CH_2OH (b) CH_3CHO

(c) CH_3COOH (d) $HCOOCH_3$

x) Which statement is correct about ether?

(a) Lower ethers are liquids at room temperature.

(b) They are crystalline solids at room temperature.

(c) They are highly inflammable.

(d) They are denser than water.

Short Answer Questions

Q.1. Why phenols are more acidic than alcohols?

Q.2. Why the boiling point of alcohol is higher than ether?

Q.3. Can ether form a hydrogen bond with water?

Q.4. Why ethers are considered to be good solvents?

Q.5. Ethers are less dense than liquid water, how?

Q.6. Phenols are more reactive than benzene, why?

Q.7. Explain why the boiling points of alcohols and phenols are much higher than those of alkanes and ethers?

Q.8. Why phenols have higher boiling points than alcohols?

Q.9. Which are more soluble in water, alcohols or phenols?

Q.10. What is the difference between primary and secondary alcohols?

Q.11. What do you know about rectified and absolute alcohols?

Long Answer Questions

Q.1. What are alcohols? How are they classified?

Q.2. How will you distinguish between primary, secondary and tertiary alcohols?

Q.3. Describe the nomenclature of alcohols.

Q.4. Draw structures for the following alcohols:

i) 1-propanol

ii) 2-butanol

iii) 1,3-butanediol

iv) 5-methyl-2-hexanol

v) 4-ethyl-3-heptanol

vi) 2,2,4,4-tetramethyl-3-pentanol

vii) 3-chloro-1,2-propanediol

viii) 2,3,4-pentanetriol

Q.5. Draw structures for the following ethers:

i) Methoxymethane

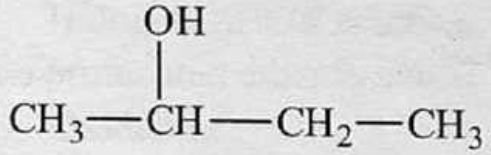
ii) Phenoxybenzene

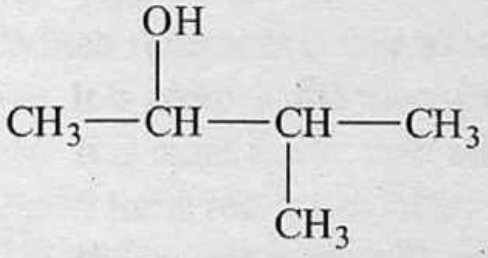
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iii) 2-methoxypropane
iv) 1,2-diphenoxypropane
v) 1-ethoxy-4-methylbenzene

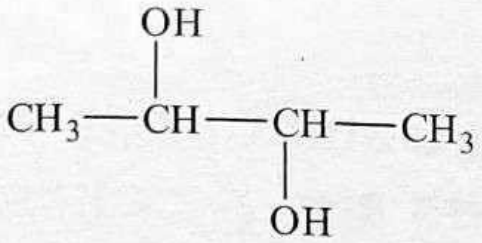
Q.6. Draw structures and then give IUPAC names to the following compounds.
i) Dimethyl ether
ii) Ethylmethyl ether
iii) Methylphenyl ether
iv) Ethyl alcohol
v) Sec. propyl alcohol
vi) Propylene glycol

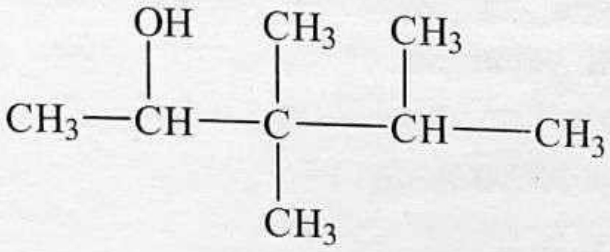
Q.7. Explain the structure and acidity of alcohols.
Q.8. Describe the methods for the preparation of alcohols.
Q.9. What do you know about reactivity of alcohols?
Q.10. Give physical and chemical properties of alcohols.
Q.11. What are thiols? Describe the nomenclature of thiols.
Q.12. Give physical properties and explain structure and acidity of thiols.
Q.13. What are phenols? Explain nomenclature of phenols.
Q.14. Describe structure and acidity of phenol.
Q.15. Write down four different methods for the preparation of phenols.
Q.16. Explain reactivity of phenols.
Q.17. Give physical and chemical properties of phenols.
Q.18. What is the difference between alcohols and phenols?
Q.19. What are ethers? What do you know about simple and mixed ethers?
Q.20. Describe nomenclature of ethers.
Q.21. Describe the preparation of ethers by (i) Williamson's Synthesis (ii) the reaction of alkyl halides with dry silver oxide.
Q.22. Explain reactivity of ethers.
Q.23. What are the physical and chemical properties of ethers?
Q.24. Give IUPAC names to the structures given below:

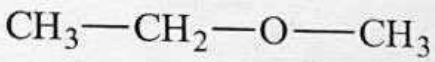
i) 

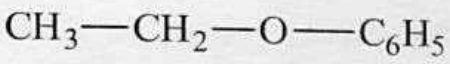
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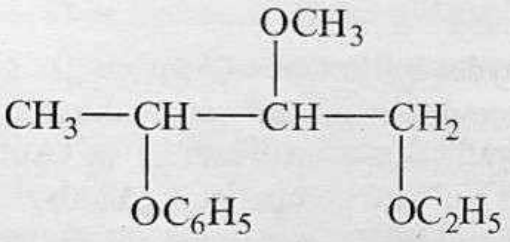
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iii) 

iv) 

v) 

vi) 

vii) 

Q.25. What are locants, prefixes, parent compound and suffixes in 3-methyl-2-pentanol?

Q.26. Describe isomerism in alcohols and phenols.

Q.27. How many isomers are possible for $C_4H_{10}O$? Draw their structures.

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Chapter 19

Carbonyl Compounds 1: Aldehydes and Ketones

Major Concepts

19.1 Nomenclature
19.2 Physical Properties
19.3 Structure
19.4 Preparations of Aldehydes and Ketones
19.5 Reactivity
19.6 Reactions of Aldehydes and Ketones

Learning Outcomes:

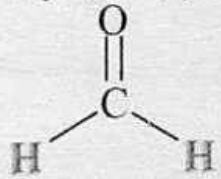
Students will be able to:

- Explain nomenclature and structure of aldehydes and ketones. **(Applying)**
- Discuss the preparation of aldehydes and ketones by ozonolysis of alkenes, hydration of alkynes, oxidation of alcohols and Friedal Craft's acylation of aromatics. **(Applying)**
- Describe reactivity of aldehydes and ketones and their comparison. **(Analyzing)**
- Describe acid and base catalysed nucleophilic addition reactions of aldehydes and ketones. **(Applying)**
- Discuss the chemistry of aldehydes and ketones by their reduction to hydrocarbons, alcohols, by using carbon nucleophiles, nitrogen nucleophiles and oxygen nucleophiles. **(Applying)**
- Describe oxidation reactions of aldehydes and ketones. **(Applying)**
- Describe isomerism in aldehydes and ketones. **(Understanding)**

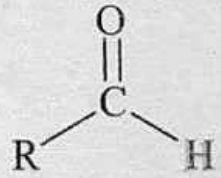
Introduction

Aldehydes and ketones are carbonyl compounds. They play an important role in chemistry, biology and biochemistry. They are responsible for many flavours and odours. Vanillin, an aldehyde, gives vanilla flavour. Benzaldehyde, an aldehyde, gives almond flavour. R-Carvone, a ketone, gives spearmint flavour. The male and female sex hormones (testosterone and progesterone) also contain carbonyl groups.

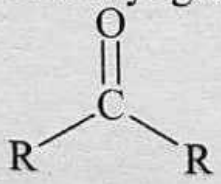
An aldehyde has one alkyl (or aryl) group and one hydrogen atom bonded to the carbon of carbonyl group. Formaldehyde is the exception because it has two hydrogen atoms that are bonded to the carbon of carbonyl group. On the other hand, a ketone has two alkyl (or aryl) groups bonded to carbon of carbonyl group.



Formaldehyde



An aldehyde



A ketone

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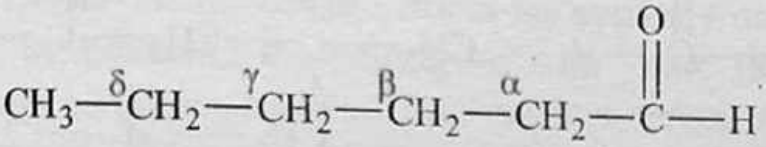
19.1 Nomenclature

Both common and IUPAC names are used for aldehydes and ketones.

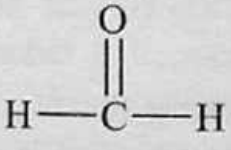
19.1.1 Nomenclature of Aldehydes

19.1.1.1 Common System

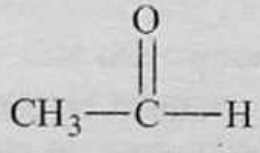
The common names of aldehydes are derived from the names of the corresponding carboxylic acids by replacing the ending ***–ic acid*** with the word ***-aldehyde***. The position of substituents on the chain, if any, is indicated by Greek letters $\alpha, \beta, \gamma, \delta$, etc. The α-carbon atom is one which is directly bonded to the carbon of carbonyl group.



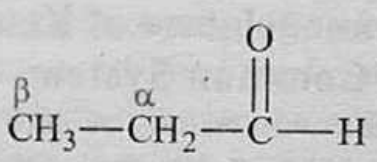
The common names of some aldehydes are given below:



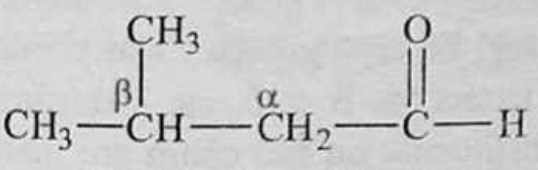
Formaldehyde



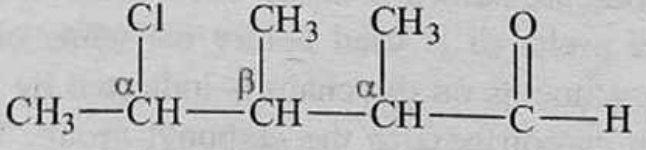
Acetaldehyde



Propionaldehyde



β-Methylbutyraldehyde



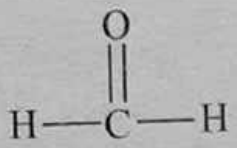
γ-Chloro-α,β-dimethylvaleraldehyde

19.1.1.2 IUPAC System

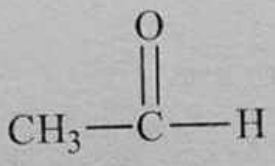
The IUPAC names of aldehydes are derived from the names of the corresponding alkanes by replacing the ending ***–e*** with ***–al***. Hence, the aldehydes are named as '***Alkanals***.' For example, if there are three carbon atoms in the chain of aldehyde, it is derivative of propane and its name is propanal. If there are four carbon atoms in the chain, then it is derivative of butane and its name is butanal and so on.

In case of higher aldehydes when substituents are present, find the longest chain containing aldehyde group and number it in such a way that the aldehyde group is assigned position number one. There is no need to indicate the position of aldehyde group because it must always lie at the end of the carbon chain and it is given position number one. The IUPAC names of some aldehydes are given below:

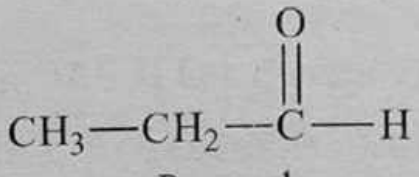
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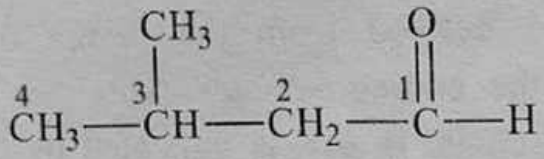
Methanal



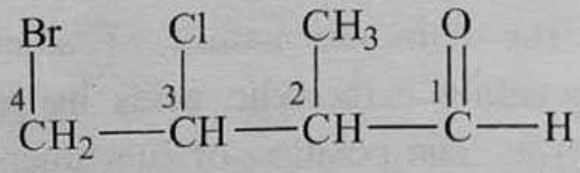
Ethanal



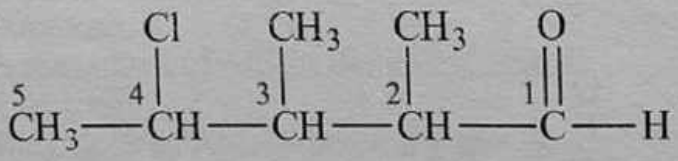
Propanal



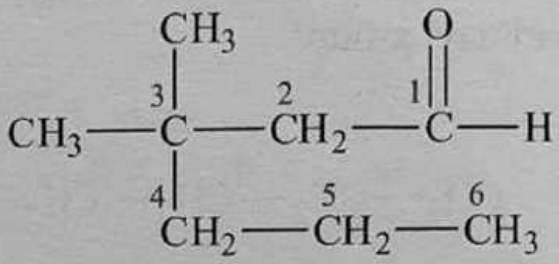
3-Methylbutanal



4-Bromo-3-Chloro-2-methylbutanal



4-Chloro-2,3-dimethylpentanal

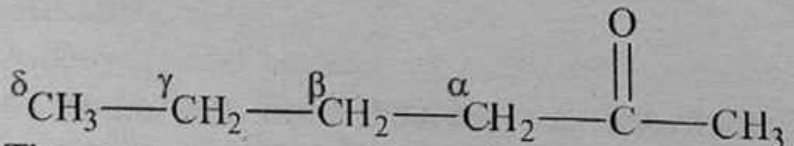


3,3-Dimethylhexanal

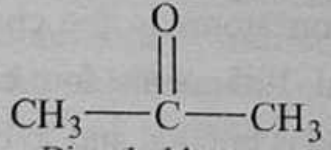
19.1.2 Nomenclature of Ketones

19.1.2.1 Common System

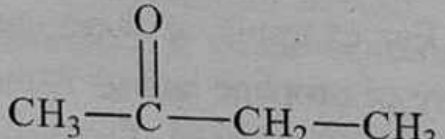
The common names of ketones are obtained by simply naming the two alkyl (or aryl) groups bonded to the carbon of carbonyl group and the word ketone is added as a separate word. The two alkyl (or aryl) groups bonded to the carbon of carbonyl group are named in alphabetical order. If the two alkyl or aryl groups are similar, than the prefix di is used before the name of the alkyl or aryl groups. The position of substituents on the chain is indicated by Greek letters (α, β, γ, δ, etc.), starting with the carbon next to the carbonyl group. The substituents on the chain are named in alphabetical order.



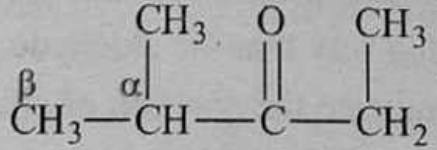
The common names of some ketones are given below:



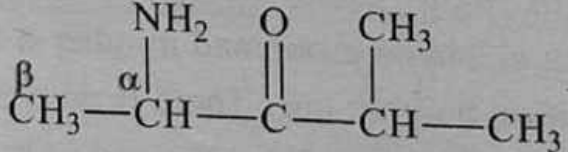
Dimethyl **ketone**



Ethyl methyl **ketone**

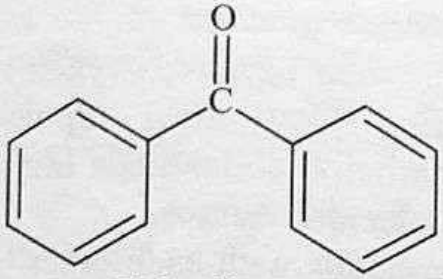


Ethyl isoporpyl **ketone**
(Ethyl-α-methylethyl **ketone**)

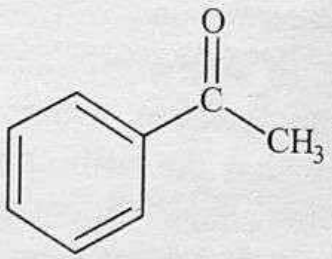


α-Aminoethyl isoporpyl **ketone**

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Dipheyl **ketone**



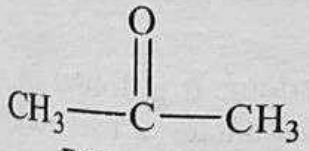
Methyl phenyl **ketone**

Some ketones are also known by their historical names. Dimethyl ketone is always named acetone, diphenyl ketone is called as benzophenone and methyl phenyl ketone is known as acetophenone.

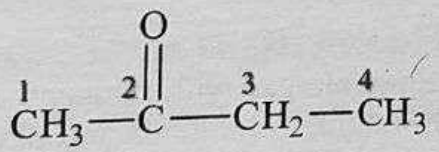
19.1.2.2 IUPAC System

The IUPAC names of ketones are derived from the names of the corresponding alkanes by replacing the ending **–e** with ***–one***. Hence, the ketones are named as *'**Alkanones**.'* For example, if there are four carbon atoms in the chain of ketone, it is derivative of butane and its name is butanone. If there are five carbon atoms in the chain, then it is derivative of pentane and its name is pentanone and so on.

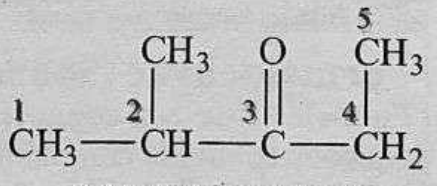
In case of open chain ketones, find the longest chain containing carbonyl group and number it in such a way that the carbonyl group is assigned the lowest possible number. The position of carbonyl carbon is indicated before the stem name of ketone. If two or more ketonic groups are present in the chain, then the prefixes di, tri, tetra are used for two, three, four ketonic groups respectively as dione, trione, tetraone. The position of substituents are indicated by the number of that carbon atom to which they are attached. The IUPAC names of some ketones are given as:



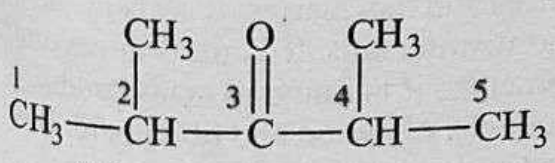
Propanone



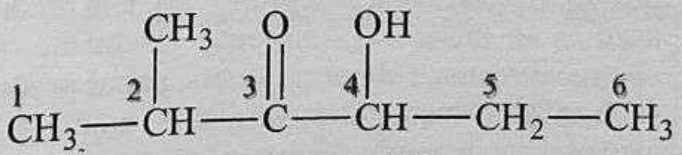
2-Butanone
(Butan-2-one)



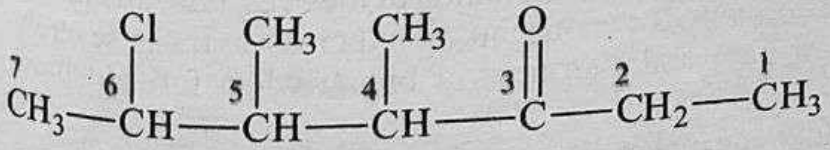
2-Methyl-3-**pentanone**
(2-Methyl**pentan**-3-**one**)



2,4-Dimethyl-3-**pentanone**
(2,4-Dimethyl**pentan**-3-**one**)



4-Hydroxy-2-methyl-3-**hexanone**
(4-Hydroxy-2-methyl**hexan**-3-**one**)



6-Chloro-4,5-dimethyl-3-**heptanone**
(6-Chloro-4,5-dimethyl**heptan**-3-**one**)

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19.2 Physical Properties of Aldehydes and Ketones

i) The carbonyl group of aldehydes and ketones is polar because oxygen is more electronegative than carbon. Due to polarity, they show dipole-dipole interactions which makes the boiling point of carbonyl compounds higher than those of corresponding alkanes of comparable molecular masses.

ii) The carbonyl compounds cannot form hydrogen bonds with each other because they have no O—H bond which makes them less polar than alcohols and carboxylic acids. They, therefore, have low boiling points than alcohols and carboxylic acids.

iii) Aldehydes and ketones having five or less than five carbon atoms are soluble in water because they can form hydrogen bond with water molecules.

iv) Aldehydes and ketones having more than five carbon atoms are insoluble in water because the non-polar hydrocarbon portion is too large to dissolve in the polar water.

v) Methanal and ethanal are gases; the other lower aldehydes and ketones are colourless liquids at room temperature. The higher aldehydes having more than twenty carbon atoms and ketones having more than thirty carbon atoms are solids at room temperature.

vi) Lower aldehydes have pungent smells and higher aldehydes have pleasant smell. Vanillin, an aldehyde, has pungent smell while the camphor, a ketone, has sweet smell.

vii) Density of aldehydes and ketones is less than that of water.

Society, Technology and Science

Formaldehyde (Sources, Health Risks and Recommendations)

Formaldehyde is a colourless, flammable gas with pungent, irritating odour. It is found in aqueous solutions (formalin). All organisms (animals and plants) such as bacteria, fish and humans naturally produce formaldehyde as part of cell metabolism.

Sources

It is commonly used as a preservative in medical laboratories and mortuaries. It is also widely used as an industrial fungicide, germicide, fumigant and disinfectant. It is used in making chemical resins, rubber products, paper products and cosmetics. It is found in many products such as adhesives, glues, varnishes, paints, household products, plywood and fibreboard. It is also present in combustion products such as vehicle exhaust and tobacco smoke.

Health Risks

- **Short term exposure** of formaldehyde can cause irritation of the eyes, nose and throat. It can also cause coughing and sore throat as concentration increases. It can severely irritate the lungs, causing chest pain and shortness of breath when formaldehyde concentration is high.
- **Long term exposure** of formaldehyde makes all symptoms worse. It can cause allergic reactions of the skin (dermatitis), the eyes and the lungs (asthma). Prolonged and

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repeated contact can also cause numbness and a hardening of skin. It can cause cancer in the nose, throat, or lungs when formaldehyde concentration is high.

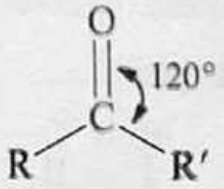
- **Formaldehyde solution (formalin)** is skin irritant. It can cause smarting, drying, cracking, and scaling.
- **Formaldehyde** can decrease fertility and increase the risk of spontaneous miscarriage in humans.

Recommendations

Students, teachers and workers who may be exposed to formaldehyde can inhale it as a gas or vapour or absorb it through the skin as a liquid. Wear safety googles, gloves, face shield and apron of appropriate materials to prevent the formaldehyde contacting the eyes, nose, mouth, hands, arms and trunk of the body before entering the workplace.

19.3 Structure of Aldehydes and Ketones

The carbonyl group of aldehydes and ketones is composed of one sigma bond and one pi bond. Both carbon and oxygen of the carbonyl group are sp^2 hybridized. The fourth p orbital of carbon remains unhybridized. The three sp^2 hybrid orbitals of carbon form three sigma bonds, one with oxygen and two with the other groups bonded to it.

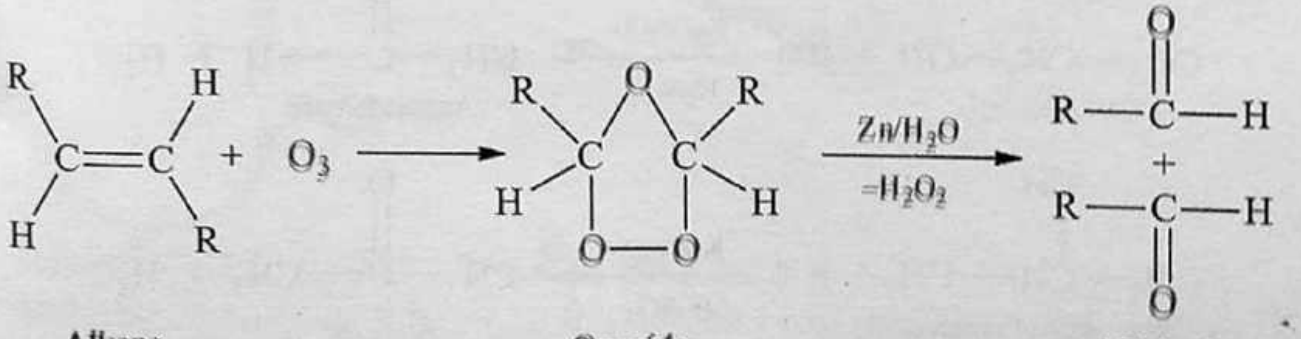


The fourth unhybridized p orbital of carbon forms pi bond with oxygen. The three atoms or groups attached to carbon of carbonyl group lie in the same plane. The bond angles between the bonded atoms or groups are around 120°.

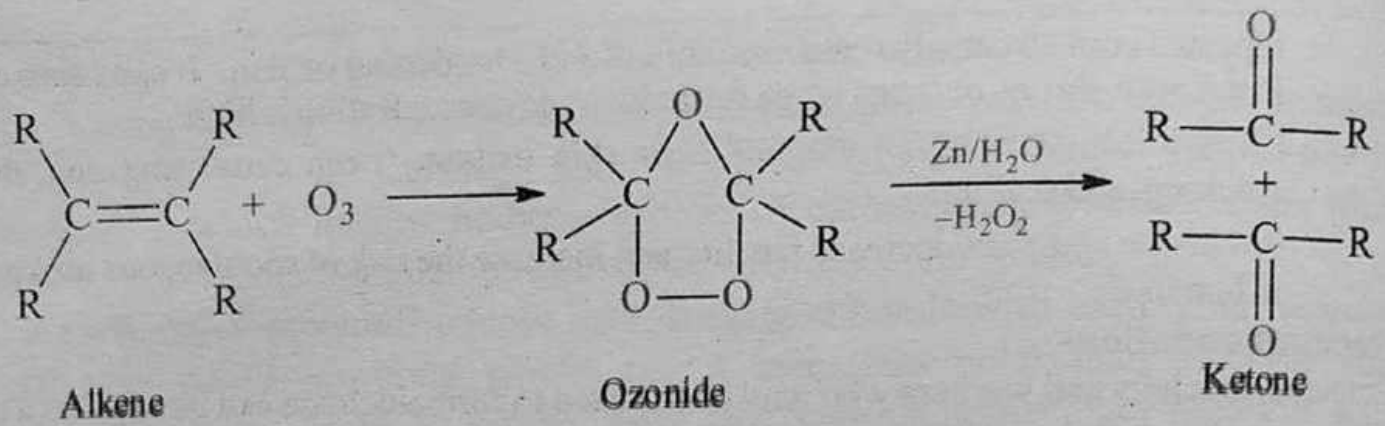
19.4 Preparations of Aldehydes and Ketones

19.4.1 Ozonolysis of Alkenes

Alkenes reacts with ozone to from an explosive compound ozonide, which on subsequent reductive cleavage with zinc dust and water produce aldehydes or ketones or both depending on the structure of alkene.

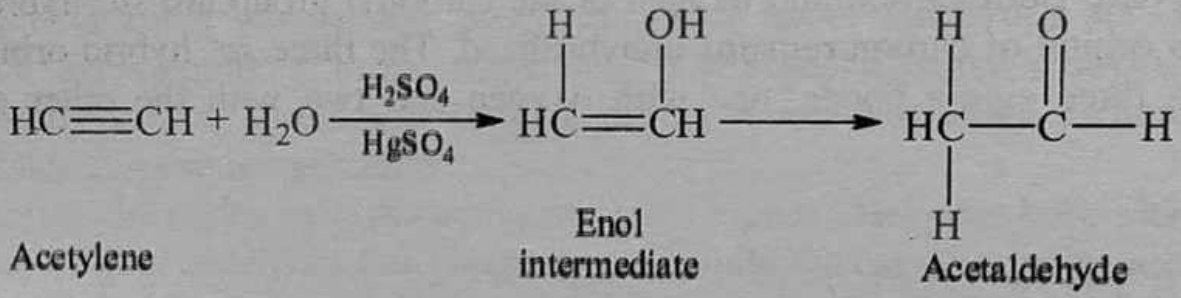


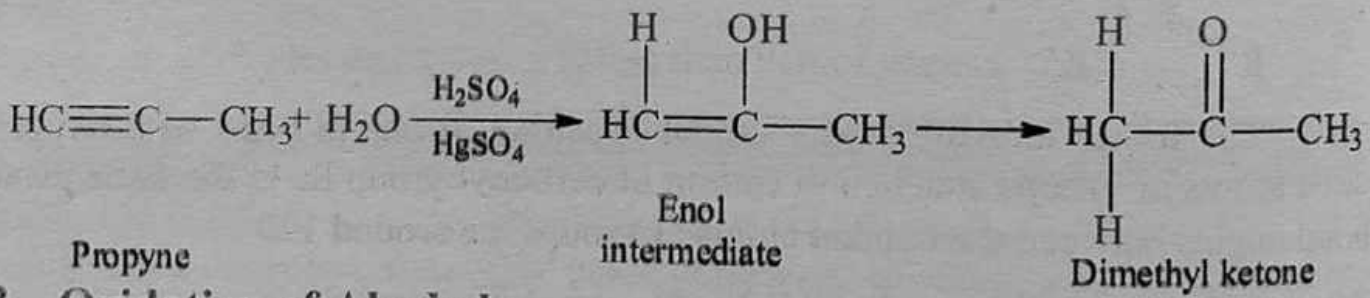
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19.4.2 Hydration of Alkynes

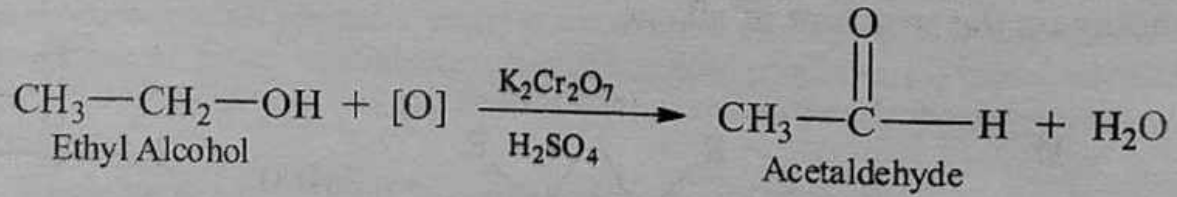
Alkyne undergo hydration according to Markovnikov's rule in the mercuric sulphate and sulphuric acid to form an unstable enol, which on rearrangement gives aldehydes or ketones or both depending on the structure of alkyne. The acetylene produces aldehyde and all other alkynes under same conditions produce corresponding ketones.

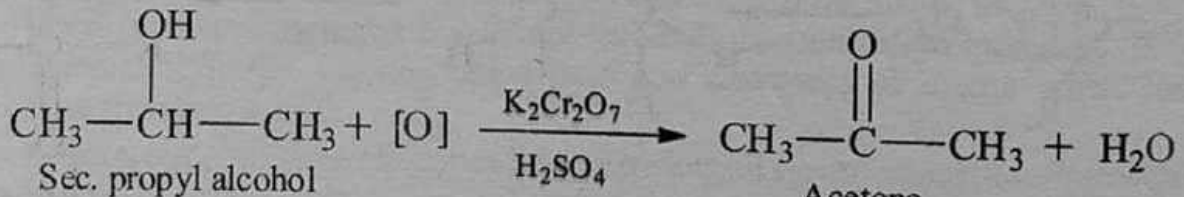




19.4.3 Oxidation of Alcohols

Controlled oxidation of primary alcohols in the presence of acidified solution of potassium dichromate or potassium permanganate produce aldehydes whereas secondary alcohols result in the formation of ketones.

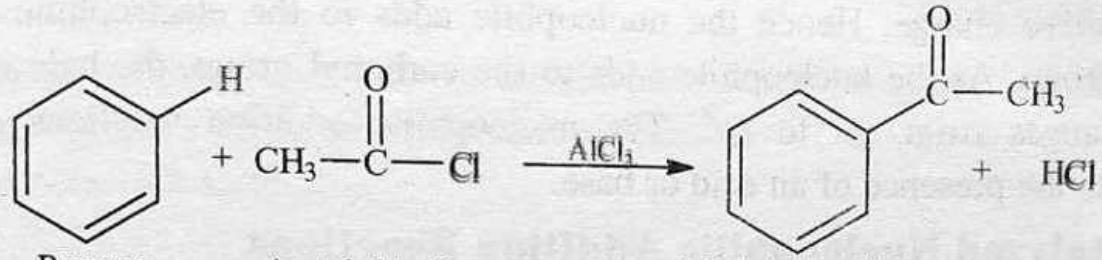




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19.4.4 Friedel-Crafts Acylation of Aromatic Compounds

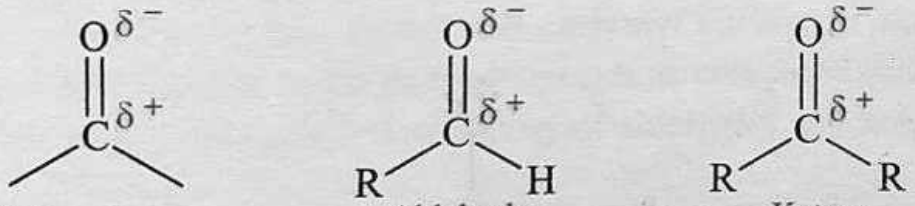
An aromatic compound (benzene) reacts with acyl halide in the presence of Lewis acid ($AlCl_3$) to produce an aryl ketone (methyl phenyl ketone).



Benzene Acetyl chloride Methyl phenyl ketone

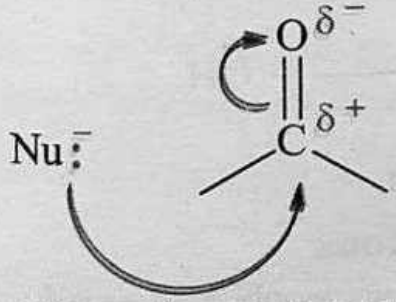
19.5 Reactivity of Carbonyl Compounds

Aldehydes and ketones both contain a carbon-oxygen double bond. Ketone has alkyl or aryl group on each side of the carbonyl and an aldehyde has a hydrogen on one side and an alkyl or aryl group on the other side of the carbonyl. Oxygen of the carbonyl is more electronegative than carbon. Therefore, the less tightly held pi (π) electrons are strongly attracted by oxygen atom. This attraction makes the carbonyl group highly polar in nature. So partial negative charge develops on oxygen and partial positive charge develops on carbon of carbonyl group.



Carbonyl group Aldehyde Ketone

Thus negatively charged oxygen atom acts as a nucleophile and positively charged carbon atom acts as an electrophile. The most characteristic reaction of aldehydes and ketones is nucleophilic addition to the carbon–oxygen double bond. During addition of a reagent to the carbonyl, the negative part of reagent adds to the carbon of carbonyl group and the positive part of the reagent adds to the oxygen of carbonyl group.



19.6 Reactions of Aldehydes and Ketones

Aldehydes and ketones react with nucleophiles and produce a wide variety of useful derivatives. Their most common reaction is the nucleophilic addition reaction, in which a nucleophile adds to the carbon of the carbonyl group.

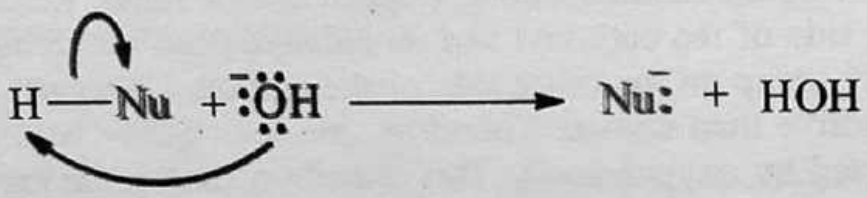
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19.6.1 Nucleophilic Addition Reactions

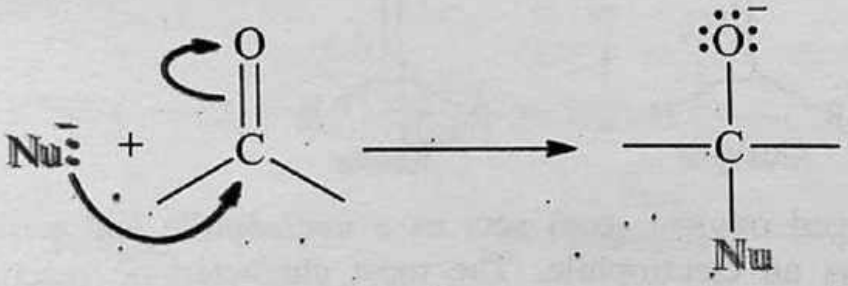
Aldehydes and ketones undergo addition of hydrogen, carbon, nitrogen and oxygen nucleophiles. The carbon of carbonyl group is highly electrophilic due to a partial positive charge. Hence the nucleophile adds to the electrophilic carbon of carbonyl group. As the nucleophile adds to the carbonyl group, the hybridization of carbon changes from sp^2 to sp^3. The nucleophilic addition reactions can either catalyzed in the presence of an acid or base.

Base Catalyzed Nucleophilic Addition Reactions

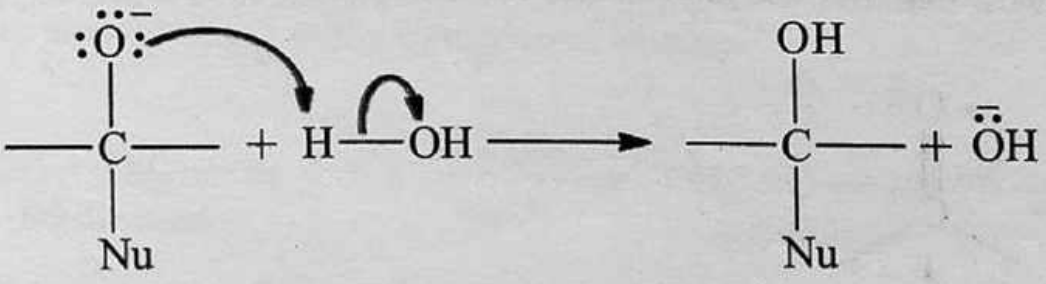
These reactions occur in the presence of a strong nucleophile. A strong nucleophile is produced by the reaction of the base with the reagent.



The nucleophile uses its pair of electrons to make a bond to the carbonyl carbon, the electrons of the π-bond are forced out to the oxygen atom to produce an alkoxide anion.



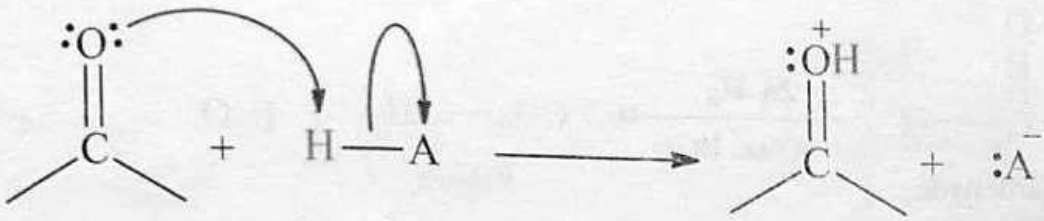
The alkoxide intermediate is protonated upon treatment with water. Here the base is regenerated.



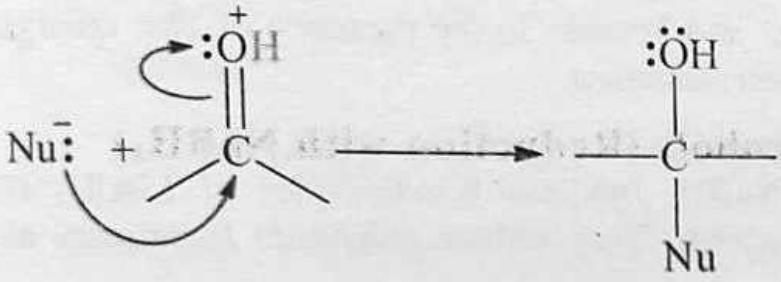
Acid Catalyzed Nucleophilic Addition Reactions

These reactions occur in the presence of a weak nucleophile. A small amount of acid is used to initiate the reaction. The proton of acid attacks the carbonyl oxygen atom to produce protonated carbonyl group. Protonation increases the electrophilic character of the carbonyl carbon and makes it more reactive towards nucleophile.

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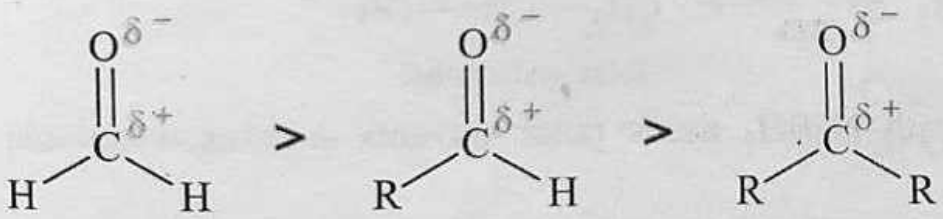


The nucleophile uses pair of its electrons to make a bond to the carbonyl carbon, the electrons of the pi (π) bond is forced out to the oxygen atom to form the addition product (an alcohol).



19.6.2 Relative Reactivity of Aldehydes and Ketones

The aldehydes are more reactive than ketones toward nucleophilic addition reactions because an alkyl group is electron donating group so it makes the carbonyl carbon less electrophilic. Hence the carbonyl carbon of ketones that has two alkyl groups is less reactive towards nucleophiles as compared to aldehydes which has only one alkyl group. The order of reactivity of aldehydes and ketones is as:



Steric effects are also important in the transition state. The aldehyde has only one alkyl (or aryl) group, so the transition state is less crowded while ketone has two alkyl (or aryl) groups, so the transition state is more crowded. As a result of the greater steric crowding in the transition states, ketones are less reactive toward nucleophilic attack as compared to aldehydes.

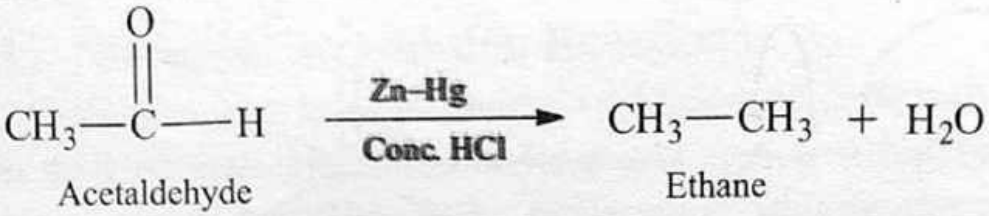
19.6.3 Reduction of Aldehydes and Ketones

Aldehydes and ketones undergo reduction in the presence of different reducing agents to produce hydrocarbons, alcohols or glycols.

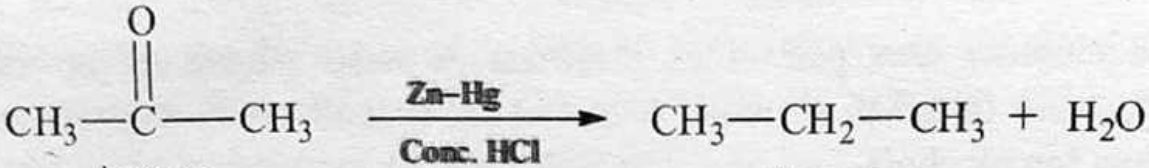
19.6.3.1 Reduction to Hydrocarbon (Clemmensen Reduction)

Aldehydes and ketones produce hydrocarbons on reduction with zinc amalgam and conc. HCl.

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Acetaldehyde Ethane

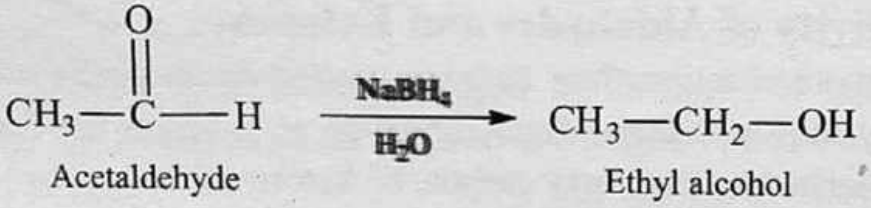


Acetone Propane

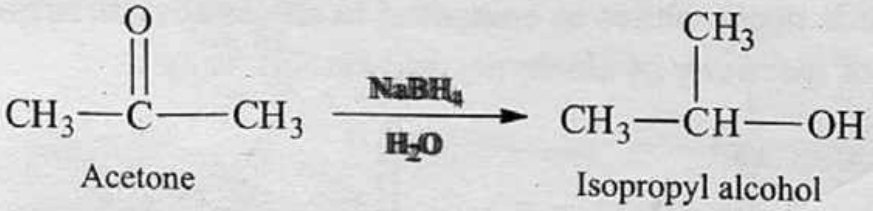
The reduction of aldehydes and ketones in the presence of zinc amalgam and conc. HCl is known as Clemmensen reduction.

19.6.3.2 Reduction to Alcohols (Reduction with $NaBH_4$)

Metal hydrides such as $NaBH_4$ (sodium borohydride) or $LiAlH_4$ (lithium aluminiumhydride) are reducing agents. They reduce aldehydes to primary alcohols and ketones to secondary alcohols.



Acetaldehyde Ethyl alcohol



Acetone Isopropyl alcohol

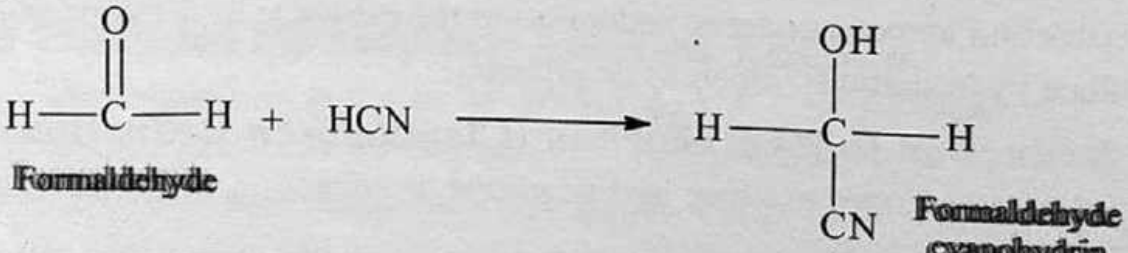
The reduction with $NaBH_4$ needs polar solvents such as water and ethyl alcohol.

19.6.3.3 Reduction with Carbon Nucleophiles

The carbon in HCN, organometallic compounds such as RLi, terminal alkynes and Grignard's reagent acts as a nucleophile and can reduce aldehydes and ketones into various compounds.

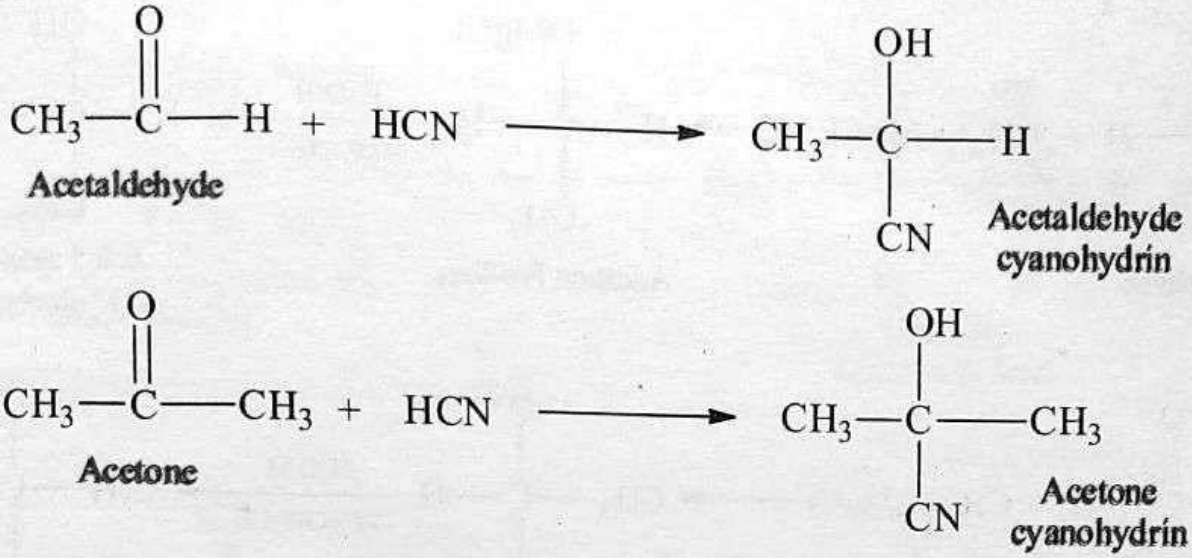
Reduction with HCN

Hydrogen cyanide is a weak acid that adds to aldehydes and ketones to form cyanohydrin.



Formaldehyde Formaldehyde cyanohydrin

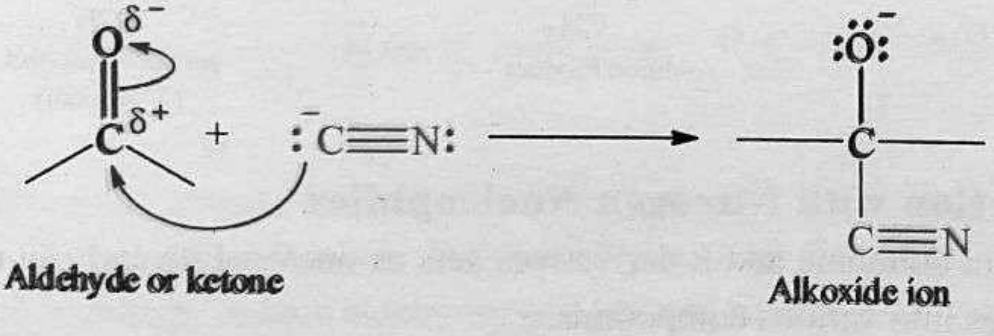
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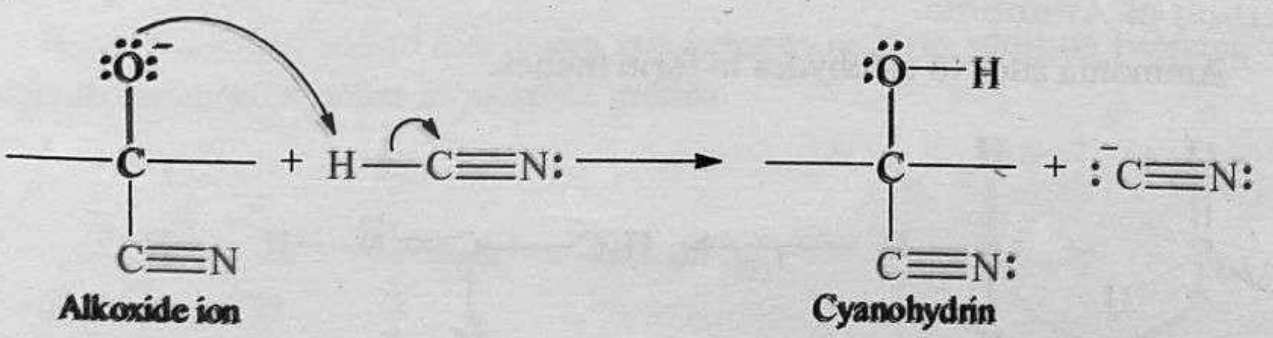
Mechanism

The conjugate base of HCN is the cyanide ion ($:\bar{C}\equiv N:$) which acts as strong nucleophile and strong base. Cyanide ion adds to the carbonyl carbon, giving an alkoxide ion that protonates to produce the cyanohydrin.

Step 1:



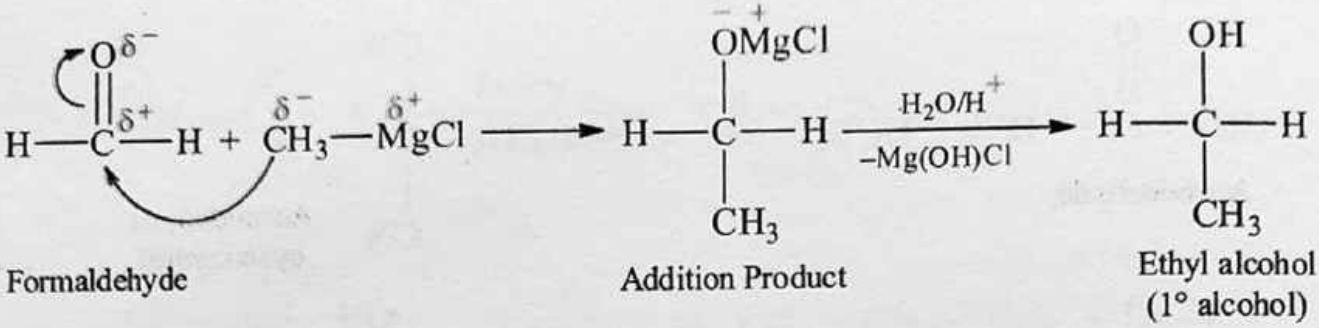
Step 2:

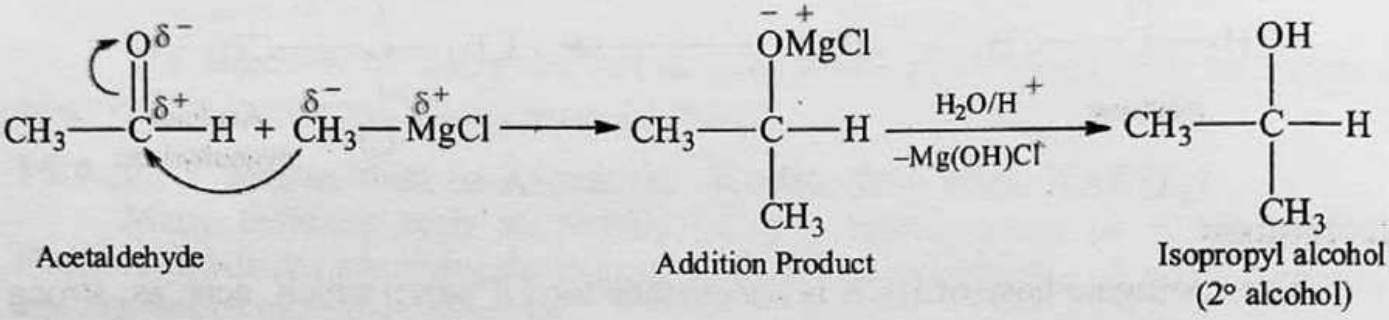


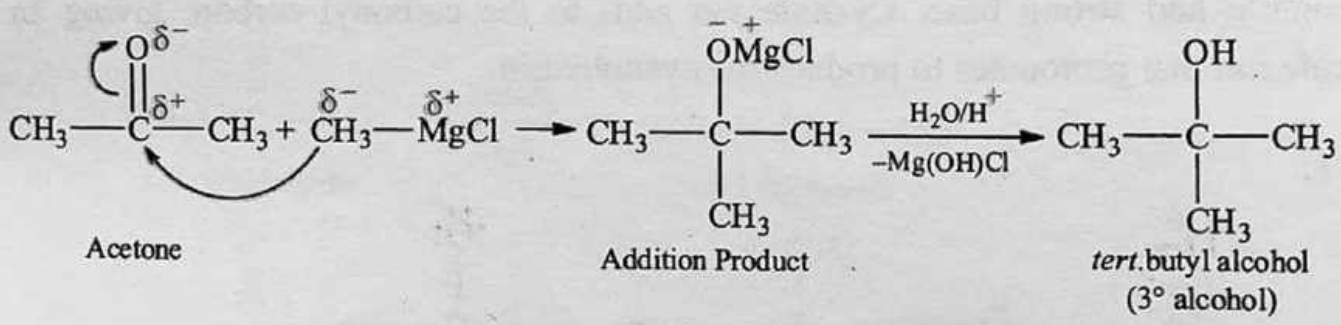
Reduction with RMgX

The reaction of aldehyde or ketone with Grignard's reagent (RMgX) followed by protonation in aqueous acid forms a primary, secondary or tertiary alcohol containing a new carbon-carbon bond.

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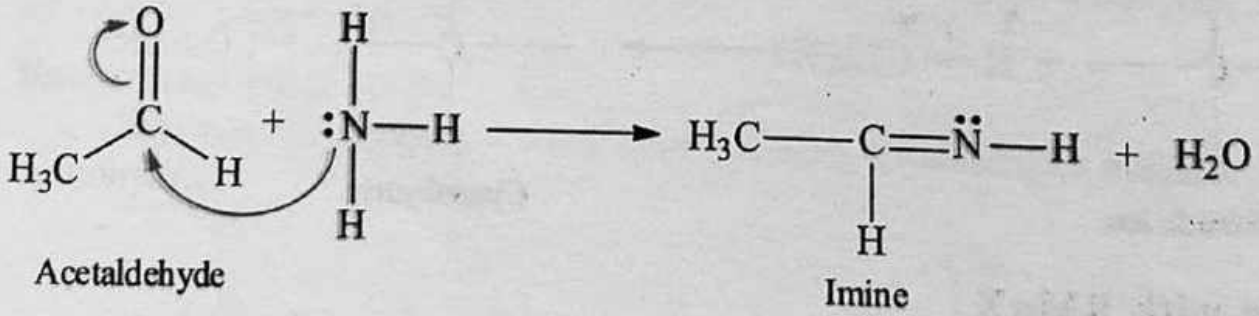


19.6.3.4 Reduction with Nitrogen Nucleophiles

The nitrogen in ammonia and it derivatives acts as nucleophile and can reduce aldehydes and ketones into various compounds.

Addition of Ammonia

Ammonia adds to aldehydes to form imines.

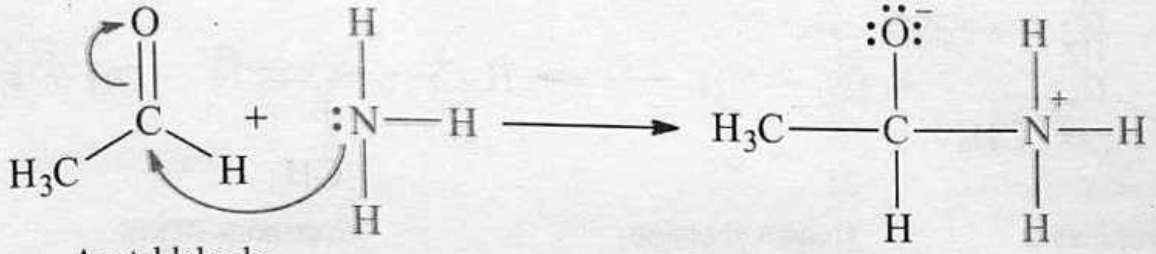


Mechanism

Ammonia adds to aldehydes to form addition product, which go through elimination of water to produce imines.

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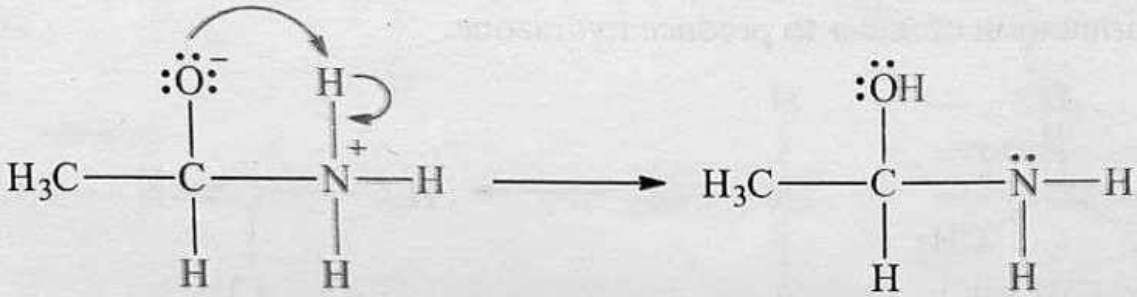
Step 1:



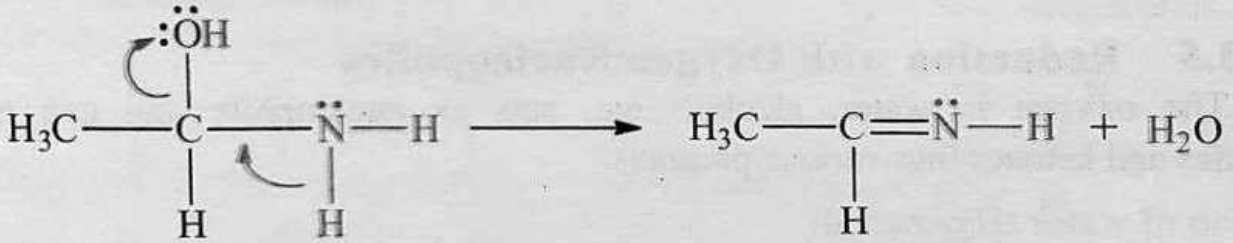
Acetaldehyde

Unstable addition protuct

Step 2:



Step 3

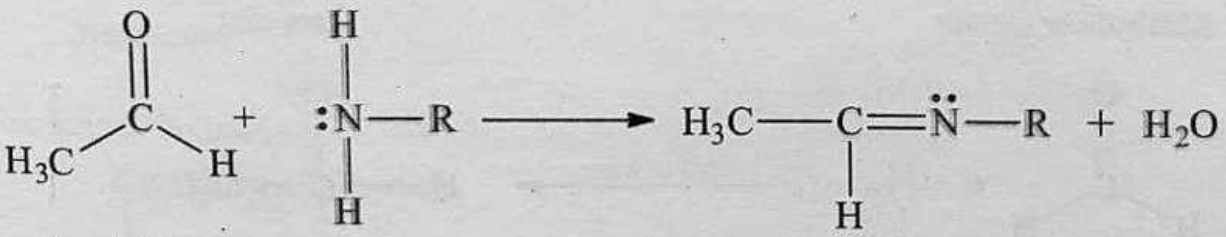


Addition of Ammonia Derivatives

Ammonia derivatives such as alkyl amines, hydroxyl amine, hydrazine and phenyl hydrazine reduce aldehydes and ketones to produce a variety of products.

Addition of Alkyl Amines

Primary amines add to aldehydes and ketones to form addition product, which undergo elimination of water to produce imines.



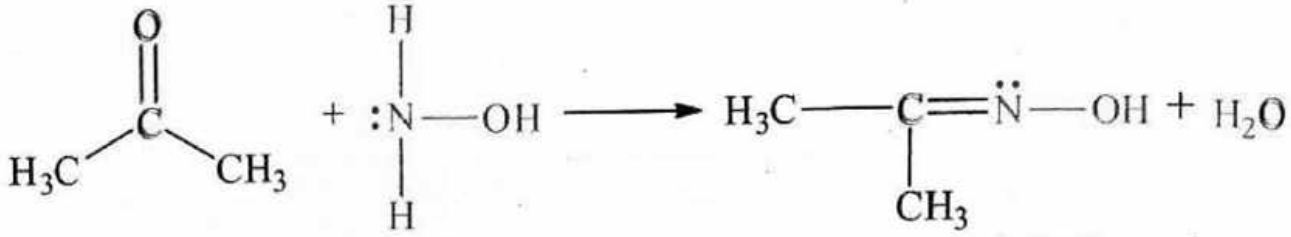
Acetaldehyde

Imine

Addition of Hydroxyl Amine

Hydroxyl amine adds to aldehydes and ketones to form addition product, which undergo elimination of water to produce oxime.

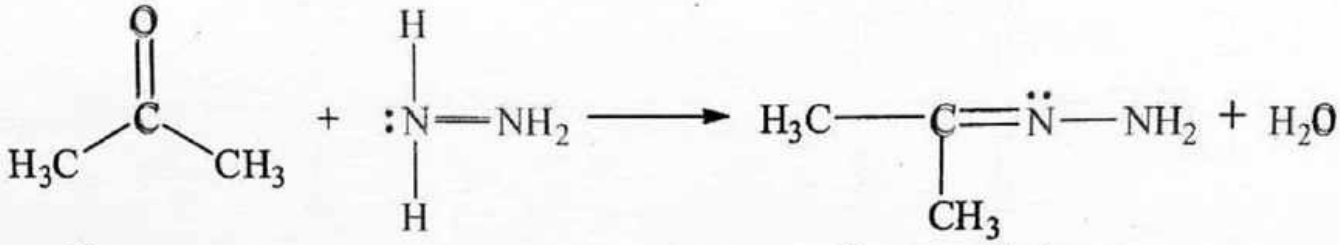
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Propanone | Hydroxyl amine | Propanone oxime

Addition of Hydrazine

Hydrazine adds to aldehydes and ketones to form addition product, which undergo elimination of water to produce hydrazone.



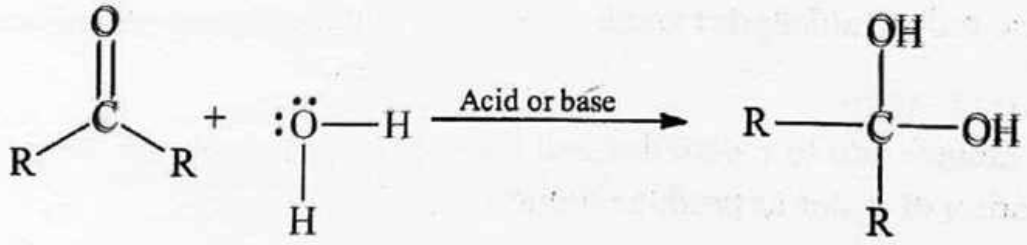
Propanone | Propanone hydrazone (Acetone hydrazone)

19.6.3.5 Reduction with Oxygen Nucleophiles

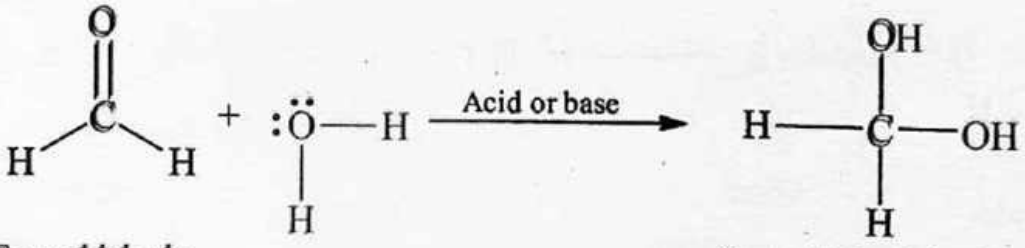
The oxygen in water, alcohols etc. acts as nucleophile and can reduce aldehydes and ketones into various products.

Addition of water (Hydration)

Water adds to aldehydes or ketones to produce germinal diol. The reaction is catalyzed by an acid or a base.



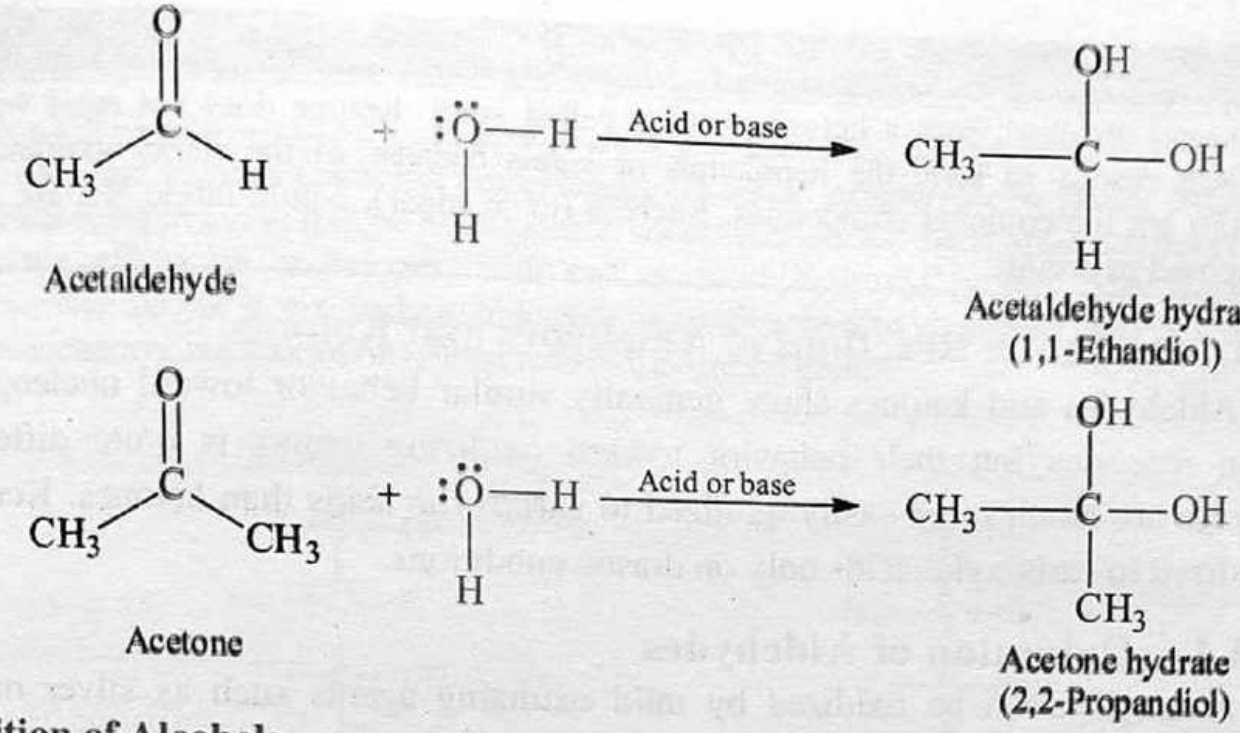
Aldehyde or ketone | gem-diol



Formaldehyde | Formaldehyde hydrate

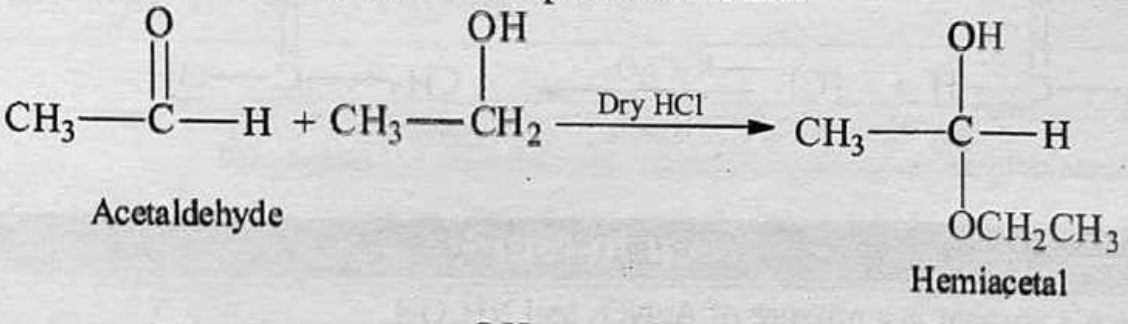
A 37% solution of formaldehyde in water is known as formalin and is used to preserve biological specimens.

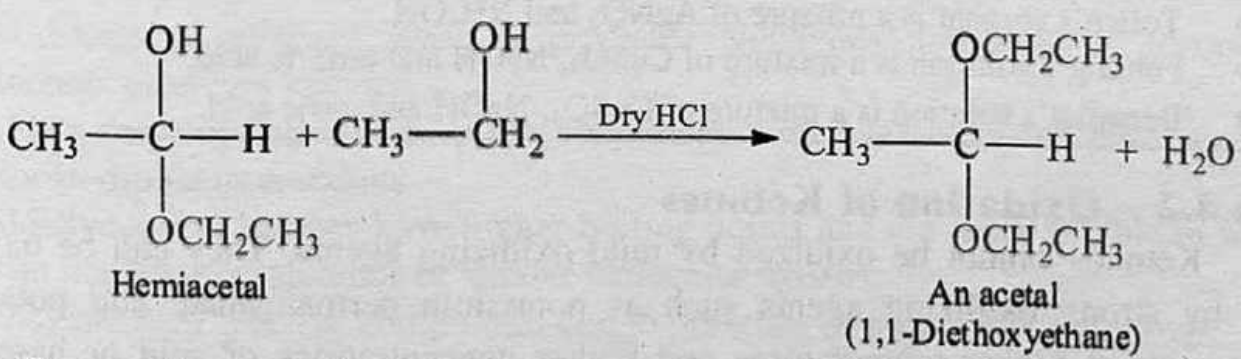
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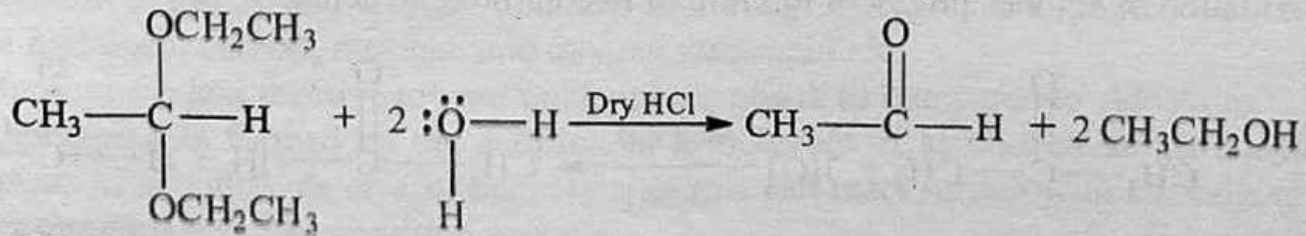
Addition of Alcohols

Alcohols adds to aldehydes (or ketones) in the presence of dry HCl to produce acetals. This reaction occurs in two steps. Addition of alcohols to aldehydes (or ketones) first produce hemiacetals, which are unstable. Therefore, hemiacetals react with the second molecule of alcohol to produce acetals.





The acetal on hydrolysis converts back to original aldehyde.



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Keep in Mind

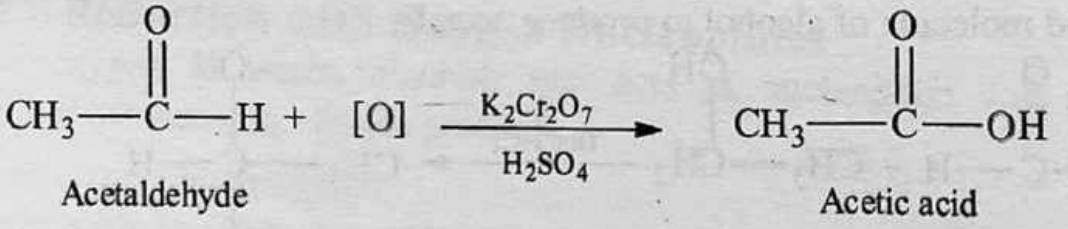
An acetal obtained from a ketone is often called ketal. Ketone does not react with alcohols readily to form the hemiketals or ketals because of the steric hindrance. Acetals are the common compounds. Sucrose (table sugar), cotton fabric etc. are all composed of acetals.

9.6.4 Oxidation Reactions of Aldehydes and Ketones

Aldehydes and ketones show generally similar behavior toward nucleophilic ddition reactions but their behavior toward oxidizing agents is quite different. Aldehydes are much more easily oxidized to carboxylic acids than ketones. Ketones re oxidized to carboxylic acids only on drastic conditions.

19.6.4.1 Oxidation of Aldehydes

Aldehydes can be oxidized by mild oxidizing agents such as silver oxide, Ag_2O (Tollen's reagent), and cupric oxide, CuO (Fehling' solution or Benedict's solution). Aldehydes can also be oxidized by strong oxidizing agents such as potassium permanganate or potassium dichromate in acidic medium.



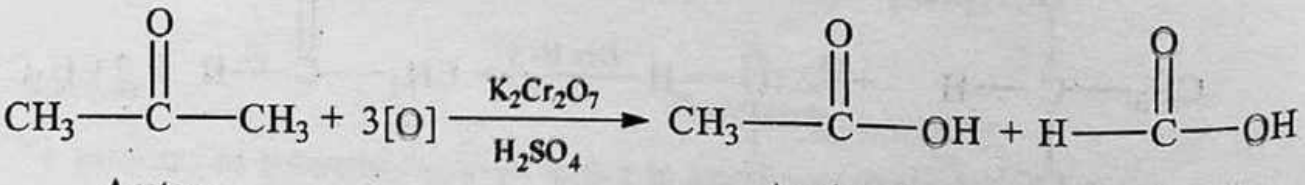
Acetaldehyde — Acetic acid

Keep in Mind

- Tollen's reagent is a mixture of $AgNO_3$ and NH_4OH.
- Fehling's solution is a mixture of $CuSO_4$, NaOH and tartaric acid.
- Benedict's solution is a mixture of $CuSO_4$, NaOH and citric acid.

19.6.4.2 Oxidation of Ketones

Ketones cannot be oxidized by mild oxidizing agents. They can be oxidized only by strong oxidizing agents such as potassium permanganate and potassium dichromate at higher temperatures and higher concentrations of acid or base. The oxidation of ketones produces mixture of two carboxylic acids.

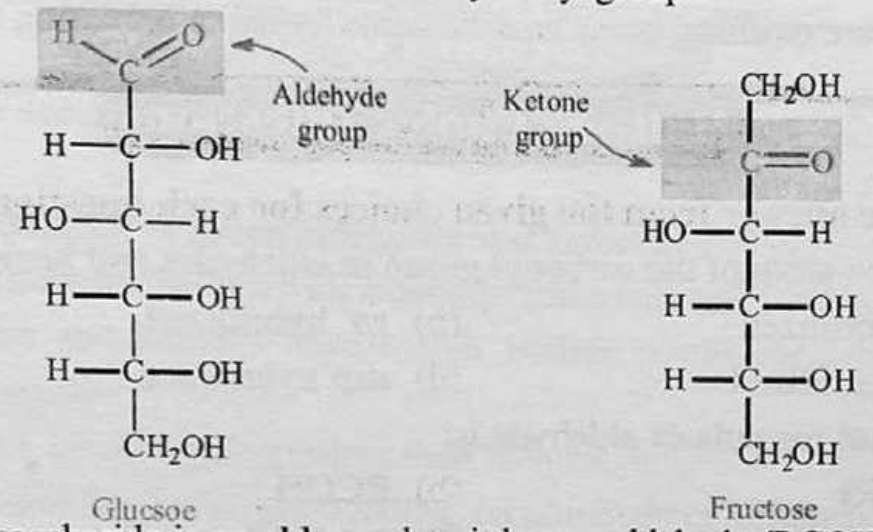


Acetone — Acetic acid — Formic acid

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Glucose and Fructose as Examples of Aldehydes and Ketones

Aldehydes and ketones (carbonyl compounds) are found extensively in nature. They play important roles in living things. For example, monosaccharides, the simplest carbohydrates, are either aldehydes or ketones, with one or more hydroxyl groups. The glucose, a monosaccharide, is a six carbon aldehyde with five hydroxyl groups and fructose, a monosaccharide, is a six carbon ketone with five hydroxyl groups.



The monosaccharide is an **aldose** when it has an aldehyde (RCOH) group, but is **a ketose** when it has a ketone (RCO) group.

Summary of Facts and Concepts

- Aldehydes and ketones are organic compounds containing carbonyl group as a functional group.
- Oxidation of primary alcohols produces aldehydes and that of secondary alcohols produces ketones.
- Aldehydes and ketones are polar compounds and interact in the pure state by dipole–dipole interactions.
- Aldehydes and ketones have higher boiling points and are more soluble in water than nonpolar compounds of similar molecular masses.
- They are very reactive compounds due to presence of polar carbonyl group.
- The most characteristic reaction of aldehydes and ketones is nucleophilic addition to the carbon–oxygen double bond. They undergo nucleophilic addition of hydrogen, carbon, nitrogen and oxygen nucleophiles.
- Ketones are less reactive toward nucleophilic attack as compared to aldehydes.
- Hemiacetal is formed by the addition of a molecule of alcohol to the carbonyl group of an aldehyde or a ketone. Hemiacetals can react further with alcohols to give acetals and a molecule of water.

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- Ammonia and amines (primary aliphatic and aromatic amines) react with the carbonyl group of aldehydes and ketones in the presence of an acid catalyst to produce imines. Imines have carbon-nitrogen double bonds.
- Aldehydes and ketones are reduced to alcohols with reducing agents such as sodium borohydride or lithium aluminium hydride.
- Aldehydes and ketones undergo acid-catalyzed addition of water to give a hydrate.
- Aldehydes are oxidized to carboxylic acids by using oxidizing agents.

Multiple Choice Questions

Q. Select one answer from the given choices for each question:

i) The carbon atom of the carbonyl group in aldehydes and ketones is:

(a) *sp* hybridized (b) sp^2 hybridized

(c) sp^3 hybridized (d) dsp^2hybridized

ii) The general formula of aldehyde is:

(a) RCHO (b) RCOH

(c) RCOR (d) RCOOH

iii) Which one of the following is the example of mild oxidizing agents?

(a) Potassium permanganate (b) Potassium dichromate

(c) Silver oxide (d) Nitric acid

iv) Which one of the following has an aldehyde group?

(a) Vanillin (b) R-carvone

(c) Testosterone (d) Progesterone

v) Which one of the following compounds show acidic properties?

(a) Aldehyde (b) Ketone

(c) Alcohol (d) Alkene

vi) Aldehydes are reduced to:

(a) Primary alcohols (b) Secondary alcohols

(c) Tertiary alcohols (d) Dihydric alcohols

vii) Ketones are reduced to:

(a) Primary alcohols (b) Secondary alcohols

(c) Tertiary alcohols (d) Dihydric alcohols

viii) Aldehydes are obtained by the oxidation of:

(a) Primary alcohols (b) Secondary alcohols

(c) Tertiary alcohols (d) Dihydric alcohols

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ix) Indentify that reagent which reacts with both aldehydes and ketones.

(a) Water (b) Grignard's reagent

(c) Hydrogen cyanide (d) Tollen's reagent

x) Which one of the following reagents can oxidize ketones?

(a) Tollen's reagent (b) Potassium dichromate

(c) Fehling' solution (d) Benedict's solution

Short Answer Questions

Q.1. Why ketones are less reactive toward nucleophilic attack as compared to aldehydes?

Q.2. What is the similarity between aldehydes and ketones?

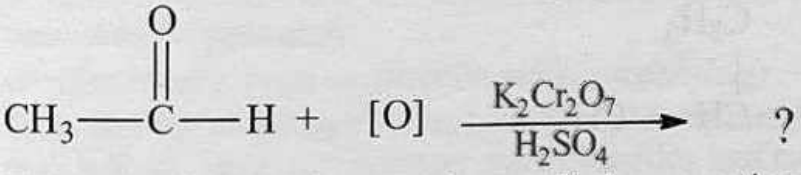
Q.3. What is the difference between an aldehyde and a ketone?

Q.4. Why aldehydes and ketones have higher boiling points than those of ethers and alkanes?

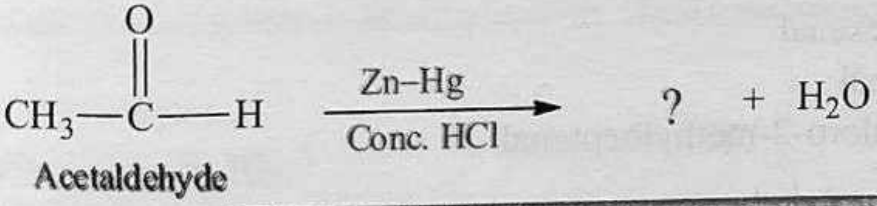
Q.5. Aldehydes have lower boiling points than ketones, why?

Q.6. Which compound has hydrogen bonding, an aldehyde or ketone?

Q.7. What is the product of the following reaction?



Q.8. What is the major product of the reaction given below? What type of reaction is this?



Acetaldehyde

Long Answer Questions

Q.1. What are aldehydes and ketones? Explain nomenclature of aldehydes and ketones.

Q.2. Discuss the structure and reactivity of aldehydes and ketones.

Q.3. What are the physical properties of aldehydes and ketones?

Q.4. Write down three methods for the preparation of aldehydes and ketones?

Q.5. Discuss base and acid catalysed nucleophilic addition reactions.

Q.6. How can aldehyde reacts with the following reagents?

(i) Hydrogen cyanide

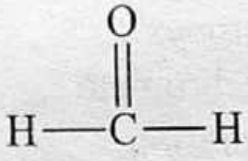
(ii) Grignard's reagent

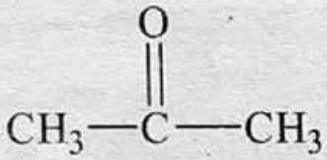
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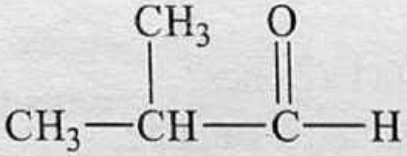
(iii) Ammonia

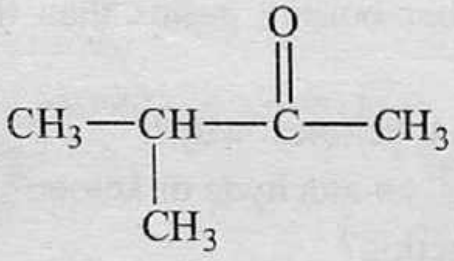
(iv) Primary amines

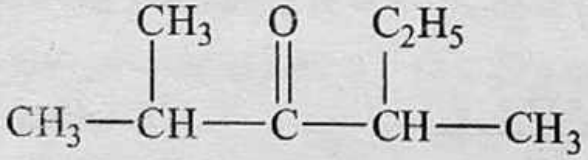
Q.7. What are the IUPAC names of the following compounds?

i) 

ii) 

iii) 

iv) 

v) 

Q.8. Write structural formulas for the following compounds:

i) Butanal

ii) 2-Methyl-2-hexanal

iii) 2-Chlorobutanal

iv) 2-Bromo-3-chloro-2-methylheptanal

v) Butanone

vi) 2,3-Pentadione

vii) 2-Phenyl-3-pentanone

viii) 4-nitroacetophenone

ix) 3-Hydroxybutanal

x) 3-methyl-3-phenylpentanal

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Chapter 20

Carbonyl Compounds 2: Carboxylic Acids and their Functional Derivatives

Major Concepts

20.1 Nomenclature
20.2 Physical Properties
20.3 Structure
20.4 Acidity
20.5 Preparations of Carboxylic Acids
20.6 Reactivity
20.7 Reactions of Carboxylic Acids

Learning Outcomes:

Students will be able to:

- Describe preparation of carboxylic acids by carbonation of Grignard's Reagent, hydrolysis of nitriles, oxidation of primary alcohols, oxidation of aldehydes and oxidation of alkyl benzenes. **(Applying)**
- Discuss reactivity of carboxylic acids. **(Applying)**
- Describe the chemistry of carboxylic acids by conversion to carboxylic acid derivatives: acyl halides, acid anhydrides, esters, amides and reactions involving inter conversion of these. **(Analyzing)**
- Describe reactions of carboxylic acid derivatives. **(Applying)**
- Describe isomerism in carboxylic acids. **(Understanding)**

Introduction

Carboxylic Acids

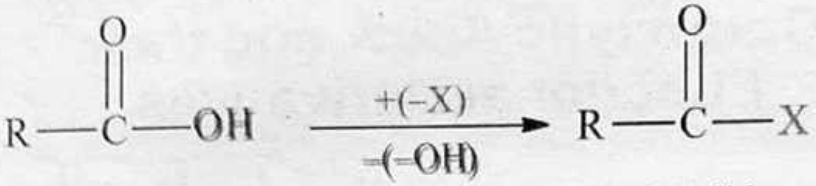
Carboxylic acids are organic compounds containing carboxyl group (—COOH) in their structures. Their general formula is R—COOH, where R stands for some aliphatic or aromatic group. The name carboxyl is obtained from **carb**onyl and hydr**oxyl** because these two groups are present in the carboxylic acids. The most important chemical property of carboxylic acids, as indicated by their names, is their acidity.

Carboxylic Acid Derivatives

Compounds that are obtained by replacing the hydroxyl group (—OH) of the carboxyl group (—COOH) by halogen (—X), alkoxy (—OR), amino ($—NH_2$) and carboxylate (—OCOR) are called carboxylic acid derivatives. There are four types of acid derivatives. These are acyl halides, esters, amides, and acid anhydrides.

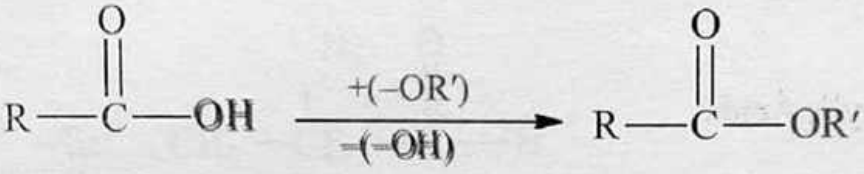
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i) **Acyl halides** are obtained by replacing the hydroxyl group (—OH) of the carboxyl group by halogen (—X). They are also known as acid halides.



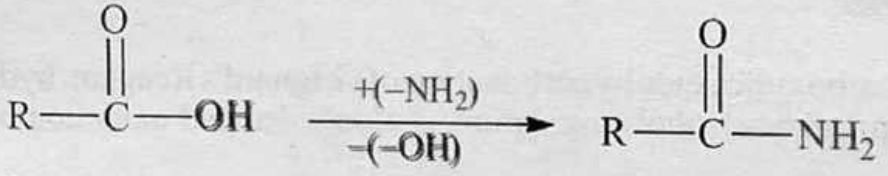
Carboxylic acid — Acyl Halide

ii) **Esters** are obtained by replacing the hydroxyl group (—OH) of the carboxyl group by alkoxy (—OR).



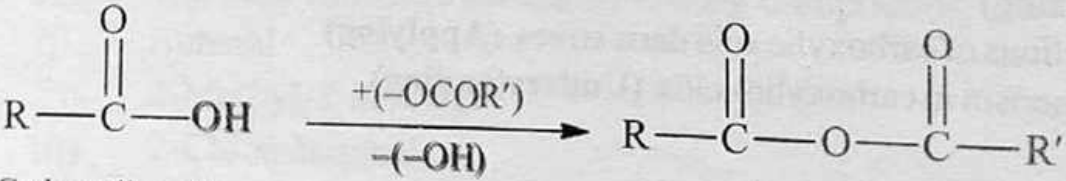
Carboxylic acid — Ester

iii) **Amides** are obtained by replacing the hydroxyl group (—OH) of the carboxyl group by amino ($—NH_2$). They are also known as acid amides.



Carboxylic acid — Amide

iv) **Acid anhydrides** are obtained by replacing the hydroxyl group (—OH) of the carboxyl group by carboxylate (—OCOR).



Carboxylic acid — Acid anhydride

Carboxylic acids and their functional derivatives are the important classes of organic compounds. They are the most abundant of all organic compounds.

20.1 Nomenclature of Carboxylic acids and Functional Group Derivatives

Both common and IUPAC names are used for carboxylic acids and their functional group derivatives.

20.1.1 Nomenclature of Carboxylic acids

20.1.1.1 Common System

Carboxylic acids having six or less carbon atoms are often known by their common names. The common names of carboxylic acids usually derived from the

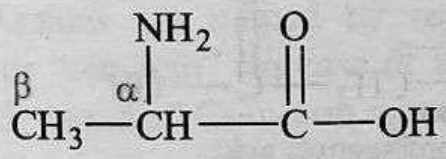
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Latin or Greek word which indicates the original source of the acid. They do not follow any rule except that all common names of acids end in **—ic acid**.

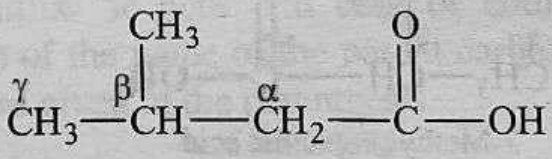
Table 20.1: Common Names and Derivations of Some Carboxylic Acids

Structure	Common Name	Derivation
$HCOOH$	Formic acid	Latin: formica, ant
CH_3COOH	Acetic acid	Latin: acetum, vinegar
CH_3CH_2COOH	Propionic acid	Greek: propion, first fat
$CH_3(CH_2)_2COOH$	Butyric acid	Latin: butyrum, butter
$CH_3(CH_2)_3COOH$	Valeric acid	Latin: valeriana, a flowering plant
$CH_3(CH_2)_4COOH$	Caproic acid	Latin: caper, goat

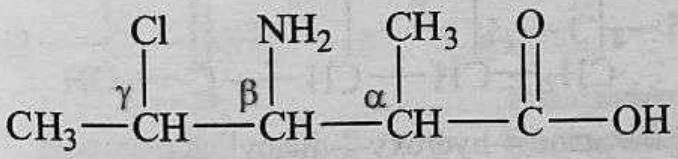
Substituted carboxylic acids are named by indicating the group and the position where such group is bonded. The position of substituents on the chain is indicated by Greek letters α, β, γ, δ, etc. The α-carbon atom is one which is directly bonded to the carbon of carboxyl group. The common names of some substituted carboxylic acids are given below:



α-Aminopropionic acid



β-Methylbutyric acid



β-Amino-γ-chloro-α-methylvaleric acid

Keep in Mind

Formic acid is found in ants, bees, and other stinging insects.
Acetic acid is found in vinegar.
Propionic acid (***pro***, "the first" and ***pion***, "fat") shows some characteristic properties of larger fatty acids.
Butyric acid is found in rancid butter.
Valeric acid got its name from valerian, an herb that has been used as sedative since Roman times.
Caproic acid is found in goat's milk.

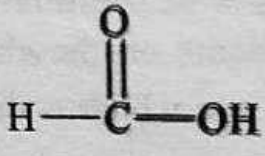
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20.1.1.2 IUPAC System

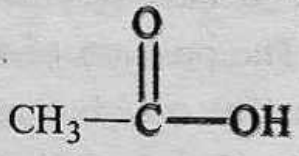
Nomenclature of Monocarboxylic acids

The IUPAC names of carboxylic acids are derived from the names of the corresponding alkanes by replacing the ending **–e** with ***–oic acid***. Hence, the carboxylic acids are named as '***Alkanoic acids.***' For example, if there is one carbon atom in the chain of carboxylic acid, it is derivative of methane and its name is methanoic acid. If there are two carbon atoms in the chain, then it is derivative of ethane and its name is ethanoic acid and so on. Since the carboxyl group lies at the end of the carbon chain, hence there is no need to indicate its position.

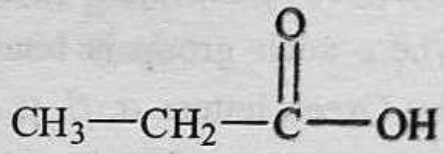
In case of substituted carboxylic acids, find the longest chain containing carboxyl group and number it in such a way that the carbon of carboxyl group is assigned position number one. There is no need to indicate the position of carboxyl group because it must always lie at the end of the carbon chain and it is given position number one. The carboxyl group takes priority over any of the other functional groups when naming them. The IUPAC names of some carboxylic acids are given below:



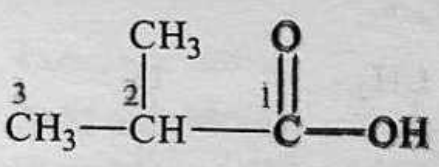
Methan*oic acid*



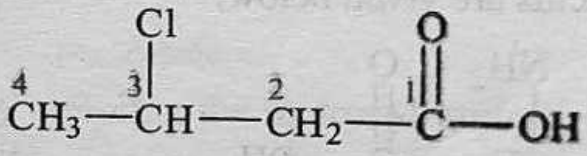
Ethan*oic acid*



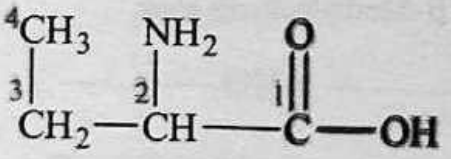
Propan*oic acid*



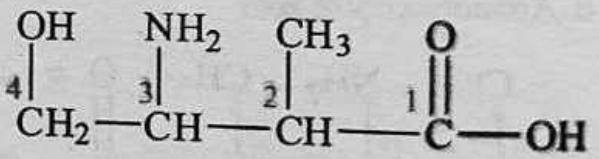
2-Methylpropan*oic acid*



3-Chlorobutan*oic acid*



2-Aminobutan*oic acid*



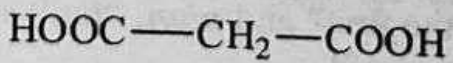
3-Amino-4-hydroxy-2-methylbutan*oic acid*

Nomenclature of Dicarboxylic acids

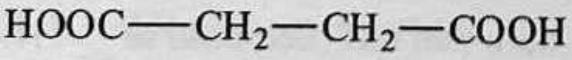
Dicarboxylic acids are also known as "***diacids.***" They have two carboxyl groups in their structures. Dicarboxylic acids are named by adding the suffix –dioic acid to the name of parent alkane. There is no need to indicate the position of carboxyl groups because they lie at the ends of the parent chain.



Ethanedioic acid



Propanedioic acid



Butanedioic acid

The above three diacids are most frequently known by their common names

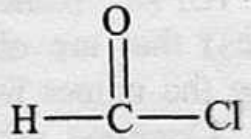
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that have accepted by IUPAC. The common names of ethanedioic acid, propanedioic acid and butanedioic acid are oxalic acid, malonic acid and succinic acid respectively.

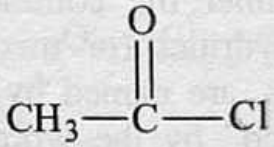
20.1.2 Nomenclature of Carboxylic Acid Derivatives

20.1.2.1 Nomenclature of Acyl halides

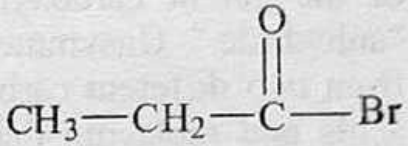
Acyl halides are named by replacing the suffix "ic acid" of the name of the parent carboxylic acid (either the common name or IUPAC name) with "yl halide." Common names of acyl halides are given in the parenthesis.



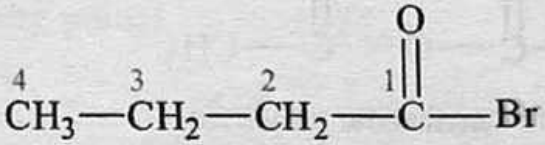
Methanoyl chloride
(Formyl chloride)



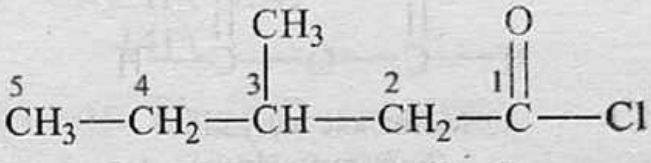
Ethanoyl chloride
(Acetyl chloride)



Propanoyl bromide
(Propionyl bromide)



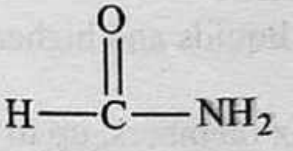
Butanoyl bromide
(Butyryl bromide)



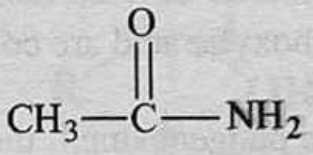
3-Methylpentanoyl chloride
(β-Methylvaleryl chloride)

20.1.2.2 Nomenclature of Amides

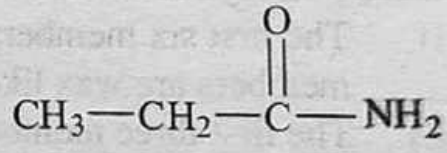
Amides are named by replacing the suffix "ic acid" (in case of common names) or "oic acid" (in case of IUPAC names) of the name of the parent carboxylic acid with "amide." Common names of amides are given in the parenthesis.



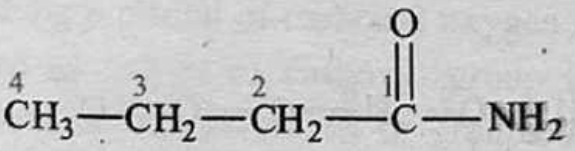
Methanamide
(Formamide)



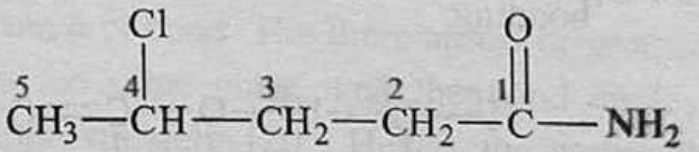
Ethanamide
(Acetamide)



Propanamide
(Propionamide)



Butanamide
(Butyramide)

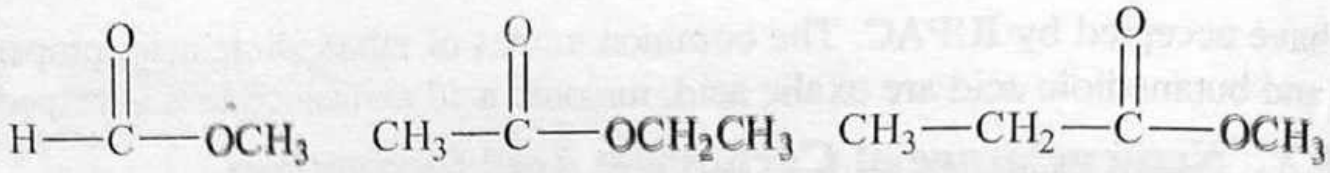


4-Chloropentanamide
(γ-Chlorovaleramide)

20.1.2.3 Nomenclature of Esters

Their names consist of two words. The first word is the name of the alkyl group bonded to oxygen atom. The second word is obtained by replacing the suffix "ic acid"of the name of the parent carboxylic acid (either the common name or IUPAC name) with "ate." Common names of esters are given in the parenthesis.

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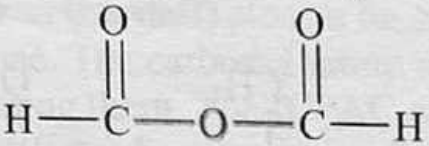
Methyl methanoate
(Methyl Formate)

Ethyl ethanoate
(Ethyl acetate)

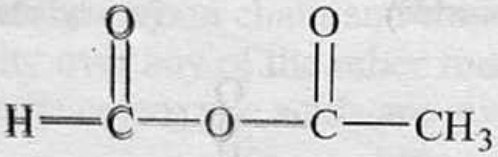
Methyl Propanoate
(Methyl Propionate)

20.1.2.4 Nomenclature of Acid Anhydrides

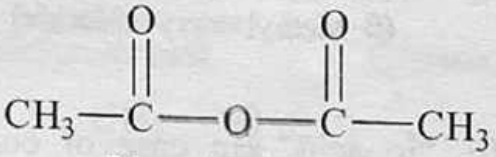
Symmetrical Anhydrides are named by replacing the suffix"acid"of the name of the parent carboxylic acid (either the common name or IUPAC name) with "anhydride." Unsymmetrical Anhydrides (or mixed anhydrides) that are obtained from two different carboxylicacids, are named by alphabetizing the names for both acids and replacing the word "acid" by the word "anhydride."Common names of anhydrides are given in the parenthesis.



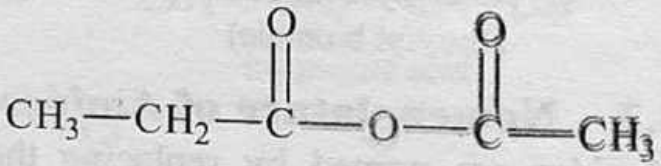
Methanoic anhydride
(Formic anydride)



Ethanoicmethanoic anhydride
(aceticformic anydride)



Ethanoic anhydride
(Acetic anhydride)



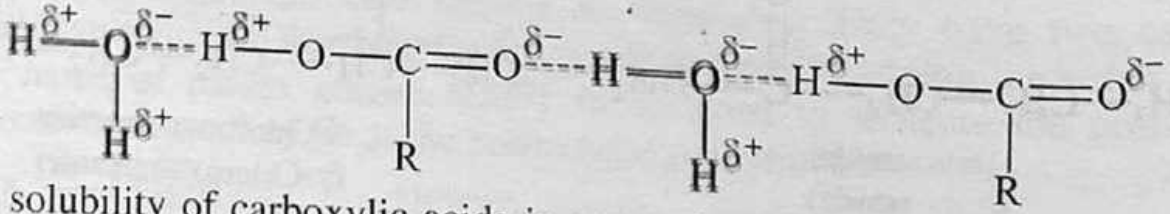
Ethanoicpropanoic anhydride
(Aceticpropionic anhydride)

20.2 Physical Characteristics of Carboxylic Acid

i) The first six members of carboxylic acid are colourless liquids and higher members are wax like solids.

ii) The first three members have pungent smell, the next six members, up to C_9, have a smell of rancid butter. The higher members have almost no smell.

iii) The first four members are completely soluble in water due to hydrogen bonding.



The solubility of carboxylic acids in water decrease when the length of carbon chain increases.

iv) Melting points of carboxylic acids increase irregularly with the increase in molecular masses. The acids with even member of carbon atoms have markedly higher melting points than odd members.

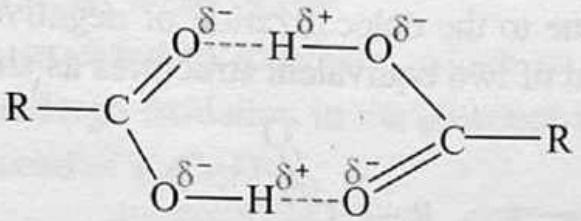
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CH_3CH_2COOH,
(3-Carbons, mp = −21°C)

$CH_3CH_2CH_2COOH$,
(4-Carbons, mp = −7°C)

$CH_3CH_2CH_2CH_2COOH$
(5-Carbons, mp = −35°C)

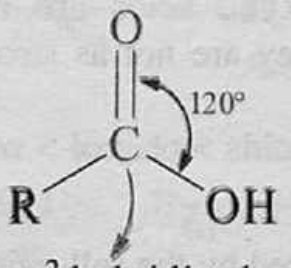
v) The boiling points of carboxylic acids are relatively high due to intermolecular hydrogen bonding. They exist in the form of cyclic dimers.



Formula:	HCOOH	CH_3COOH	CH_3CH_2COOH
Boiling point:	101°C	118°C	141°C

20.3 Structure of Carboxylic Acids and Their Derivatives

The carbon atom of carboxylic acid and carboxylic acid derivatives is sp^2 hybridized. The three sp^2 hybrid orbitals of carbon of carboxyl group forms three sigma bonds, one with carbonyl oxygen, one with oxygen of hydroxyl group and one with hydrogen atom or other group bonded to it.



sp^2 hybridized

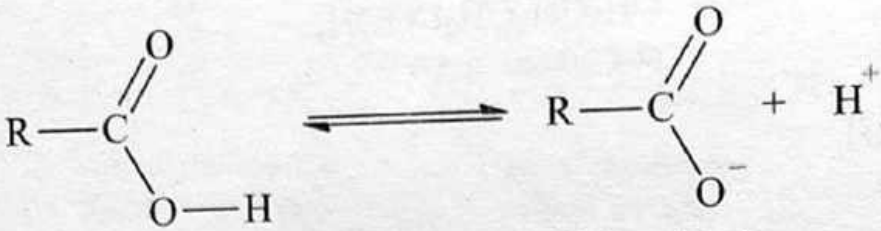
The remaining fourth unhybridized *p* orbital of carboxyl carbon overlaps the remaining *p* orbital of carbonyl oxygen to from a pi bond. The three atoms or groups bonded to carbon of carboxyl group lie in the same plane, and the bond angles between the bonded atoms or groups are approximately 120°. Hence, the carboxyl group shows trigonal planar geometry.

20.4 Acidity of carboxylic Acids

Carboxylic acids are the most acidic organic compounds. The acidic behaviour of carboxylic acid can be explained by the points given below:

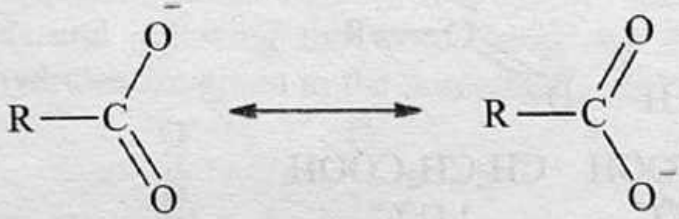
i) The carboxylic acid has acidic behaviour because it has ability to give hydrogen ion in water. As a result of this, a conjugate base, carboxylate ion is produced.

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Carboxylic acid Carboxylate ion

ii) The carboxylate ion is more stable in water than carboxylic acid. The stability of carboxylate ion is due to the delocalization of negative charge. Carboxylate ion is a resonance hybrid of two equivalent structures as shown below:



The conjugate base (carboxylate ion) of carboxylic acid most effectively resonance stabilized than alcohol and phenol. The greater the stability of resonance hybrid, the greater is the strength of acid.

iii) The strength of an acid can also be determined by pK_a values. The greater the value of pK_a, the weaker will be the acid. The pK_a values of HCl, H_2SO_4, CH_3COOH, C_6H_5OH, H_2O and C_2H_5OH are −7, −3, 4.75, 10, 14, and 16 respectively. Hence, carboxylic acids are much stronger acids than water, alcohols and phenols but they are not as strong as mineral acids (HCl, H_2SO_4 etc.).

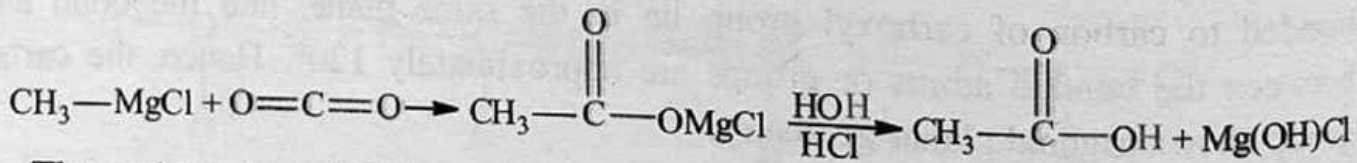
Mineral acids > carboxylic acids > phenol > water > alcohol

20.5 Preparations of Carboxylic Acids

Carboxylic acids are prepared by the following methods:

20.5.1 Carbonation of Grignard's reagent

Grignard's reagents reacts with CO_2 to give addition product which on acid hydrolysis gives carboxylic acids.



The carbonation of Grignard's reagent is a convenient way to convert an alkyl or aryl halide to a carboxylic acid.

20.5.2 Hydrolysis of Nitriles

Alkyl nitriles (alkyl cyanides) react with hot aqueous solution of an acid (mineral acid) or alkali to produce carboxylic acids.

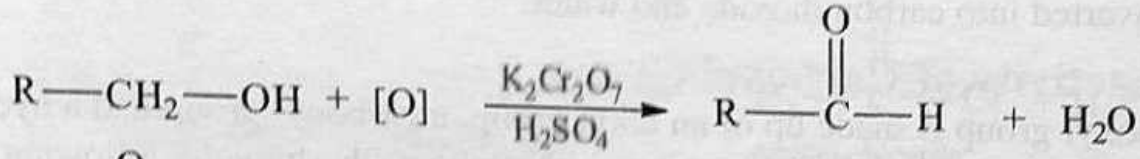
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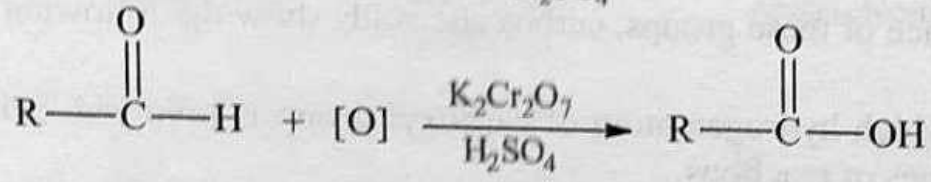


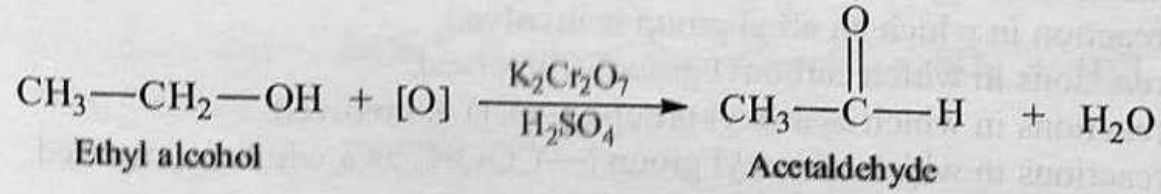


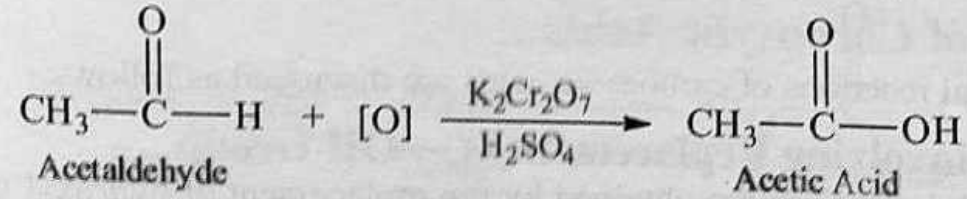
20.5.3 Oxidation of Primary Alcohols

Primary alcohols are oxidized to aldehydes which on further oxidation give carboxylic acids. Alcohols undergo oxidation in the presence of $K_2Cr_2O_7$ and H_2SO_4. $KMnO_4$ can also be used instead of $K_2Cr_2O_7$.



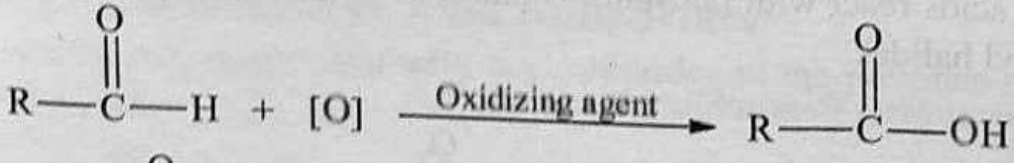


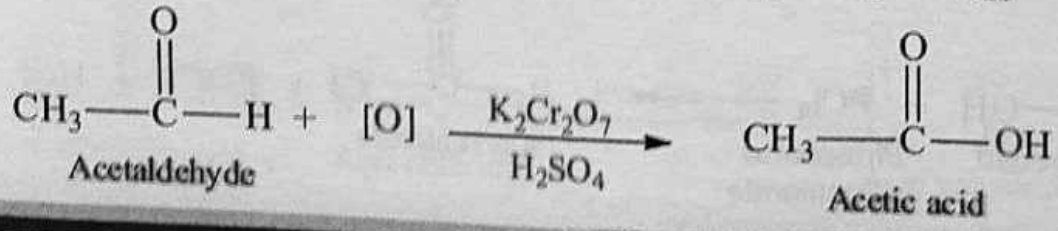




20.5.4 Oxidation of Aldehydes

Aldehydes can be oxidized by mild oxidizing agents such as silver oxide, Ag_2O. Aldehydes can also be oxidized by strong oxidizing agents such as potassium permanganate or potassium dichromate in acidic medium.

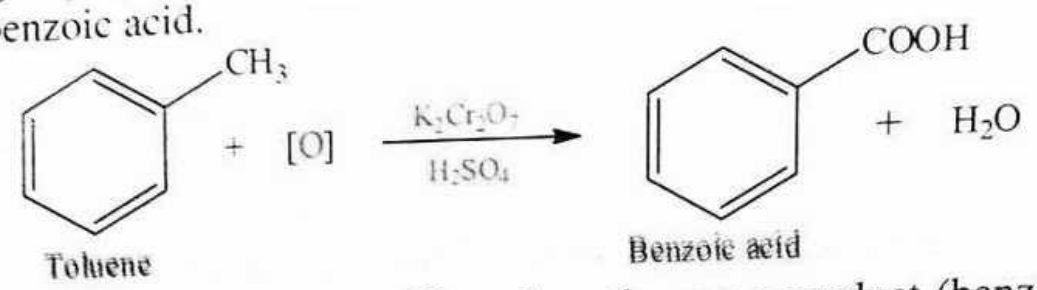




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20.5.5 Oxidation of Alkyl Benzenes

Alkyl groups attached directly to the benzene ring are oxidized into carboxylic acid group by oxidizing agents. For example, toluene is oxidized by oxidizing agents into benzoic acid.



Toluene — Benzoic acid

The alkyl benzenes will produce the same product (benzoic acid) whether the alkyl side chain is methyl, ethyl or any other alkyl group. The rest of the alkyl side chain is converted into carbon dioxide and water.

20.6 Reactivity of Carboxyl Group

Carboxyl group is made up of an alkyl group, a carbonyl group and a hydroxyl group. Due to the presence of these groups, carboxylic acids show the following types of reactions:

i) The reactions in which hydrogen atom of carboxyl group is involved. Salts are formed in these types of reactions.
ii) The reaction in which an alkyl group is involved.
iii) The reactions in which carbonyl group is involved.
iv) The reactions in which hydroxyl group (—OH) is involved.
v) The reactions in which carboxyl group (—COOH) as a whole is involved.

20.7 Reactions of Carboxylic Acids

The important chemical reactions of carboxylic acids are discussed as follows:

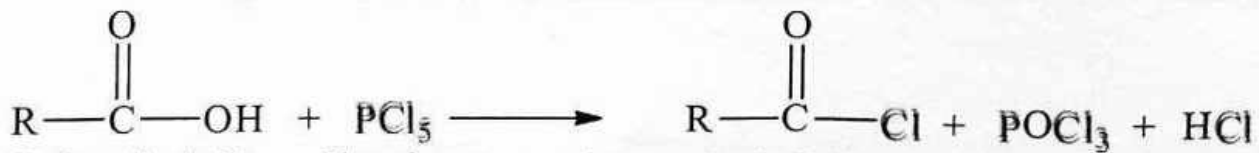
20.7.1 Reactions involving Replacement of —OH Group

Carboxylic acid derivatives are obtained by the replacement of hydroxyl group (—OH) of the carboxyl group (—COOH) by halogen (—X), alkoxy (—OR), amino ($—NH_2$) and carboxylate (—OCOR).

20.7.1.1 Conversion to Acyl Halides (Acid halides)

Carboxylic acids react with phosphorus halide (PCl_5, PCl_3) or thionyl chloride ($SOCl_2$) to give acyl halides.

Reaction with Phosphorus Pentachloride

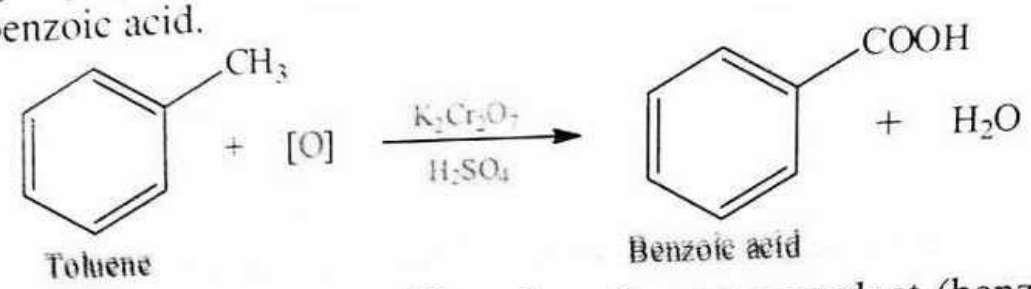


Carboxylic Acid — Phosphorus pentachloride — Acyl chloride

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20.5.5 Oxidation of Alkyl Benzenes

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Toluene — Benzoic acid

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ii) The reaction in which an alkyl group is involved.
iii) The reactions in which carbonyl group is involved.
iv) The reactions in which hydroxyl group (—OH) is involved.
v) The reactions in which carboxyl group (—COOH) as a whole is involved.

20.7 Reactions of Carboxylic Acids

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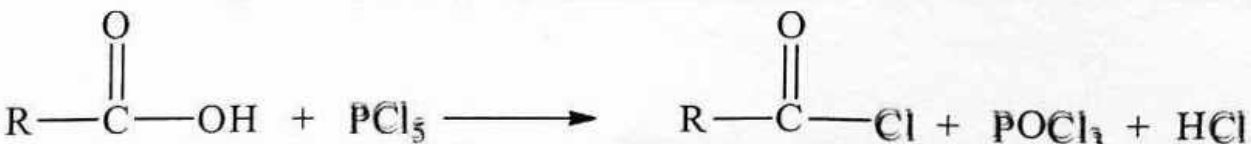
20.7.1 Reactions involving Replacement of —OH Group

Carboxylic acid derivatives are obtained by the replacement of hydroxyl group (—OH) of the carboxyl group (—COOH) by halogen (—X), alkoxy (—OR), amino ($—NH_2$) and carboxylate (—OCOR).

20.7.1.1 Conversion to Acyl Halides (Acid halides)

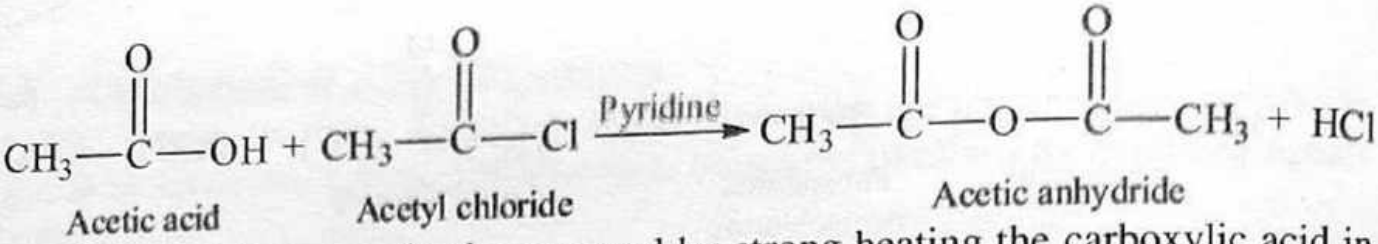
Carboxylic acids react with phosphorus halide (PCl_5, PCl_3) or thionyl chloride ($SOCl_2$) to give acyl halides.

Reaction with Phosphorus Pentachloride

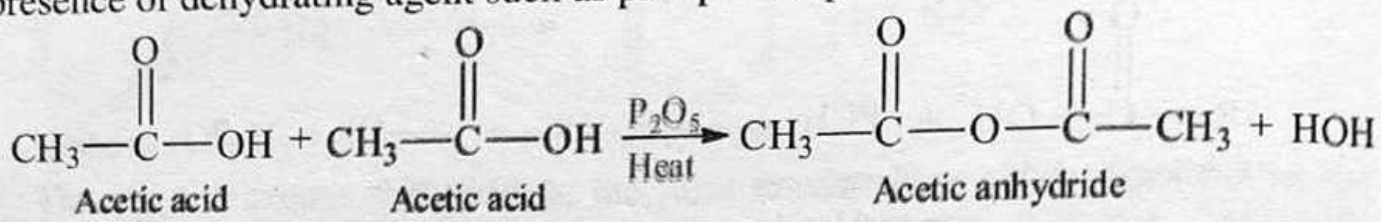


Carboxylic Acid — Phosphorus pentachloride — Acyl chloride

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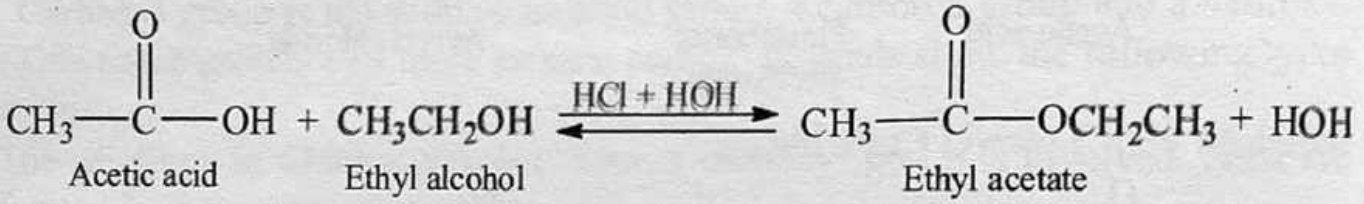


Acid anhydrides can also be prepared by strong heating the carboxylic acid in the presence of dehydrating agent such as phosphorus pentoxide.

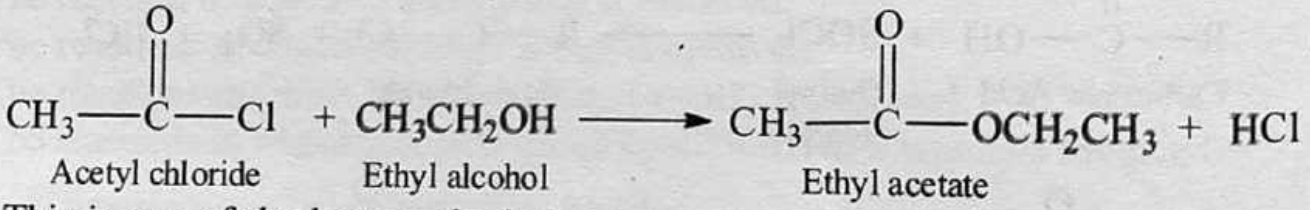


20.7.1.3 Conversion to Esters

Carboxylic acids react with alcohols in the presence of strong acid like H_2SO_4 or HCl to form esters. This reaction is reversible and is known as esterification.



Esters can also be prepared by the reaction of acyl chlorides with alcohols.



This is one of the best methods to prepare an ester and does not need an acid catalyst.

Esters have fruity smell and are used as artificial flavours.

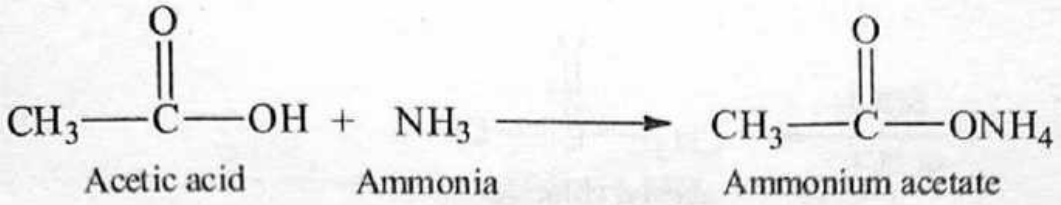
Table 20.2: Esters and their Flavours

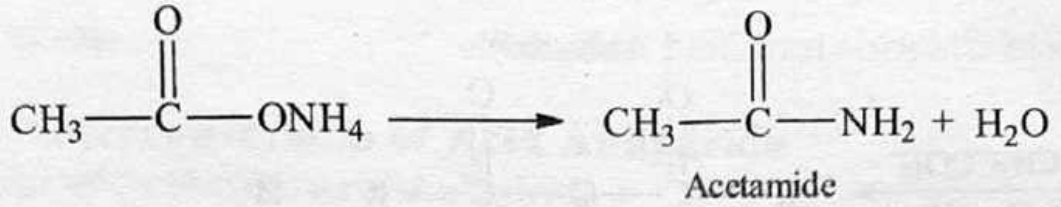
Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Ethyl butyrate	Pine apple
Benzyl acetate	Jasmine	Octyl acetate	Orange
Amyl butyrate	Apricot	Isoamylvalerate	Apple
Isobutyl formate	Raspberry		

20.7.1.4 Conversion to Amides

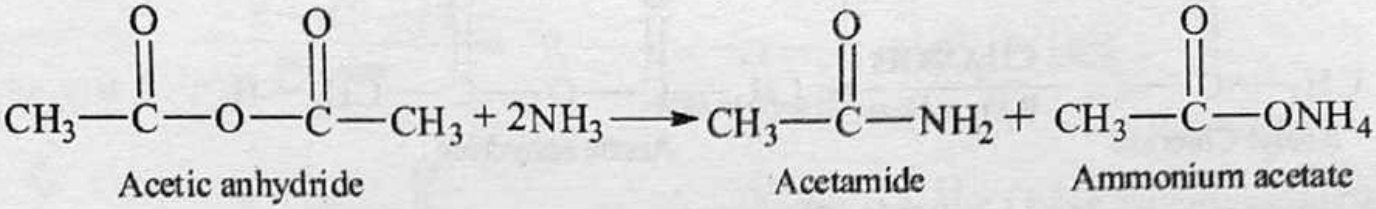
Carboxylic acids react with aqueous ammonia to form ammonium salts of carboxylic acid, which on heating give amides. This is not a good method for the preparation of amides.

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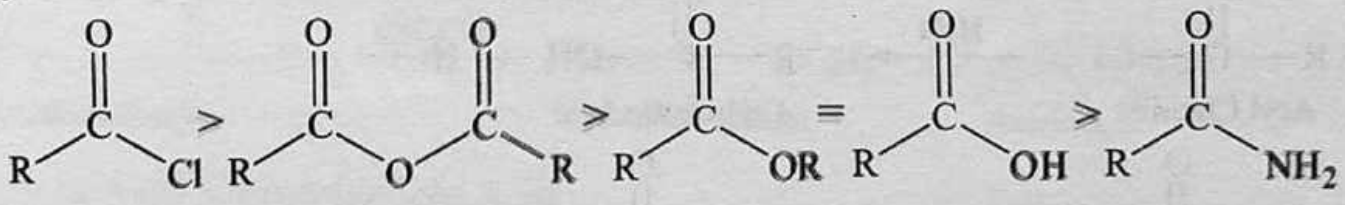


Amides can also be obtained by the reaction of acid anhydrides with ammonia (or amines).



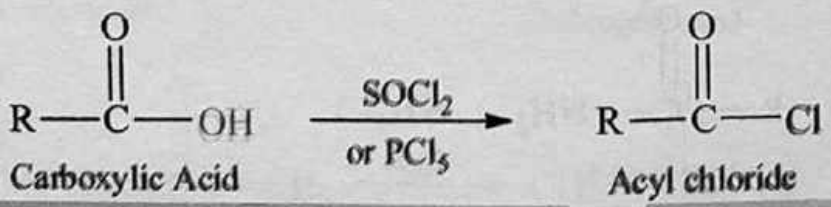
20.7.2 Summary of Reactions that Interconvert Carboxylic Acids Derivatives

Carboxylic acid derivatives are compounds that can be converted to carboxylic acids through simple acidic or basic hydrolysis. The most important acid derivatives are esters, amides, acid halides and acid anhydrides. The carboxylic acid derivatives are a family of closely related functional groups. They all (carboxylic acid and their derivatives) contain carbonyl groups and many of these can be easily interconverted. All of the acid derivatives are converted to carboxylic acids. An acid derivative can be converted to a less reactive derivative and it cannot be converted to a more reactive derivative. For example, esters can be converted to amides, but not into acid halides or anhydrides. The order of reactivity for carboxylic acid and their derivatives is as:

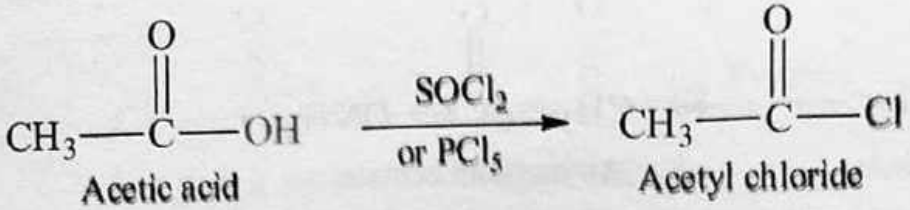


20.7.2.1 Interconversion of Acid Chloride

Conversion of Acid into Acid Chloride

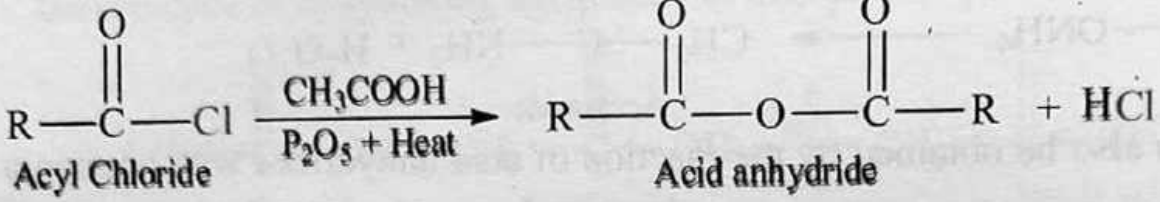


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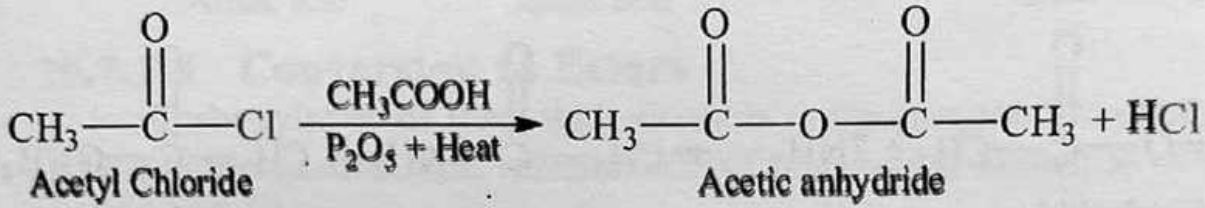


Acetic acid — Acetyl chloride

Conversion of Acid Chloride into Acid Anhydride

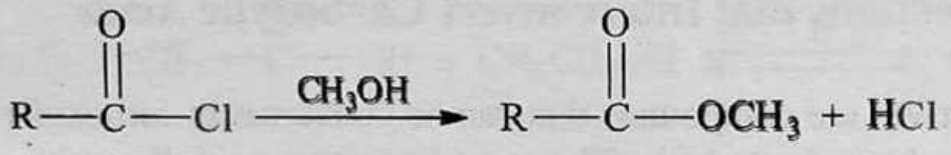


Acyl Chloride — Acid anhydride

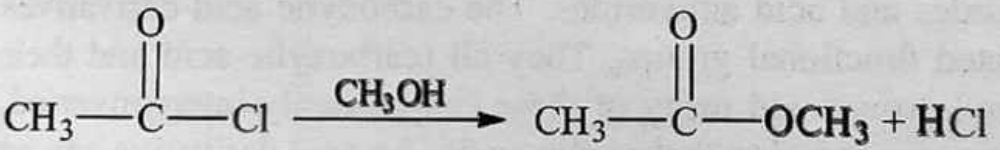


Acetyl Chloride — Acetic anhydride

Conversion of Acid Chloride into Ester

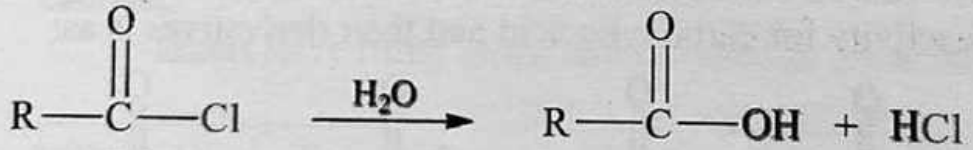


Acyl Chloride — Ester

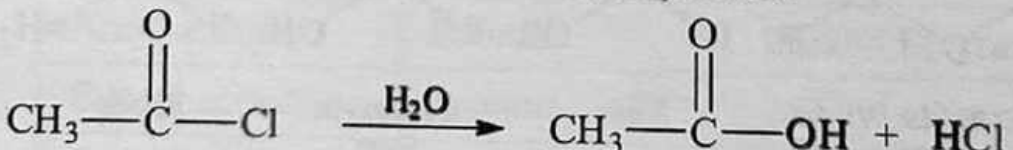


Acetyl chloride — Methyl acetate

Conversion of Acid Chloride into Acid

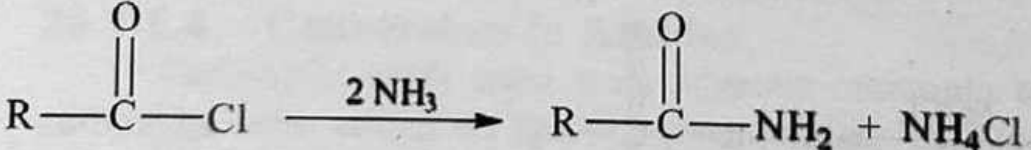


Acyl Chloride — Carboxylic Acid



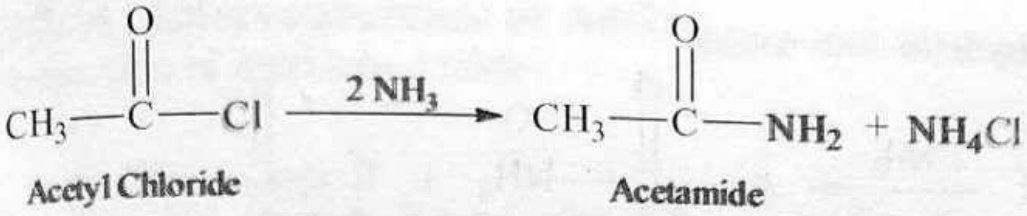
Acetyl Chloride — Acetic Acid

Conversion of Acid Chloride into Amide



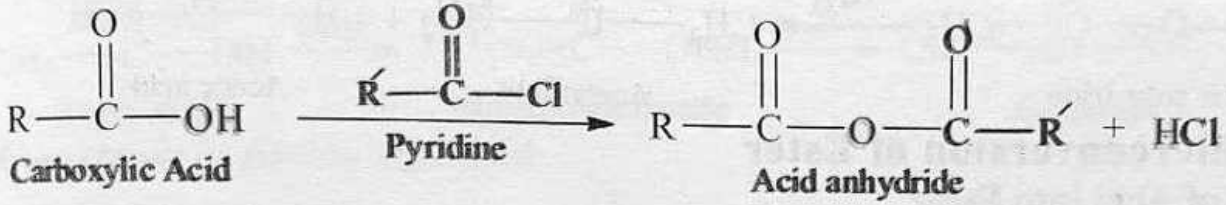
Acyl Chloride — Acyl Amide

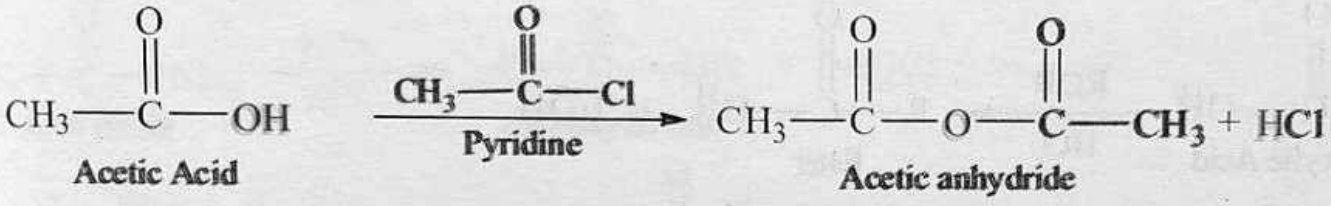
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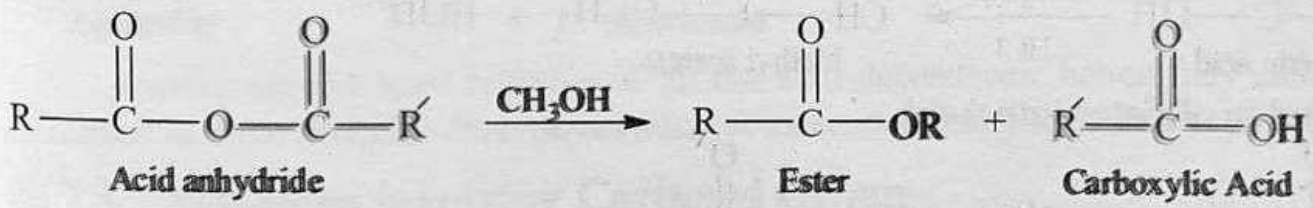
20.7.2.2 Interconversion of Acid Anhydride

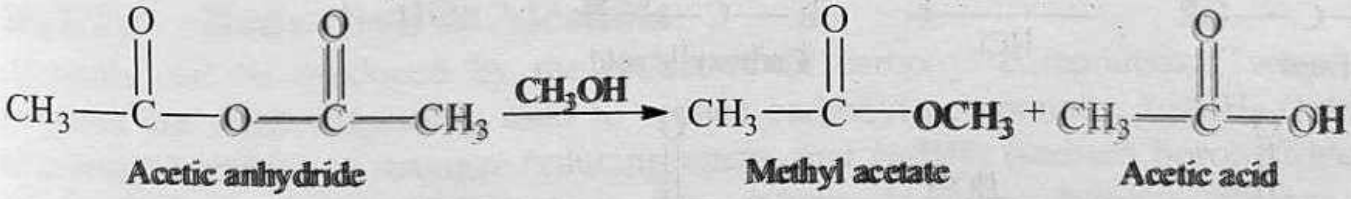
Conversion of Acids into Acid Anhydride



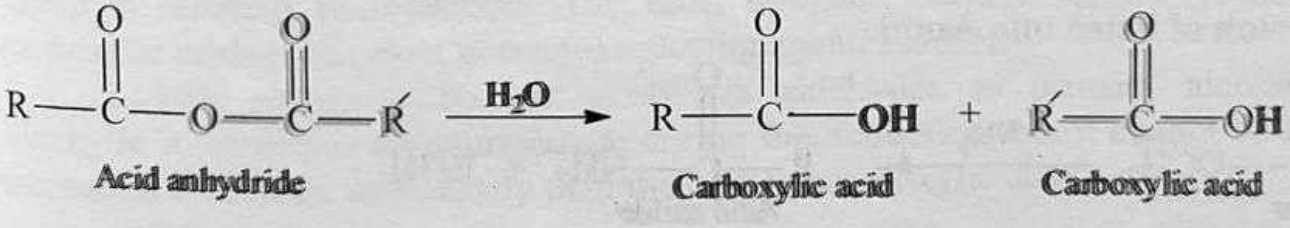


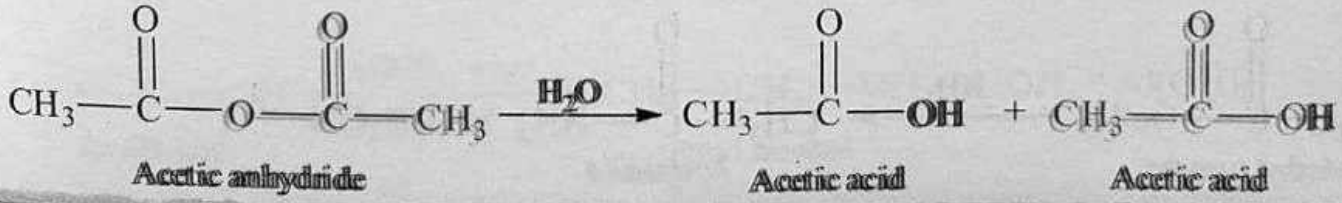
Conversion of Acid Anhydride into Ester





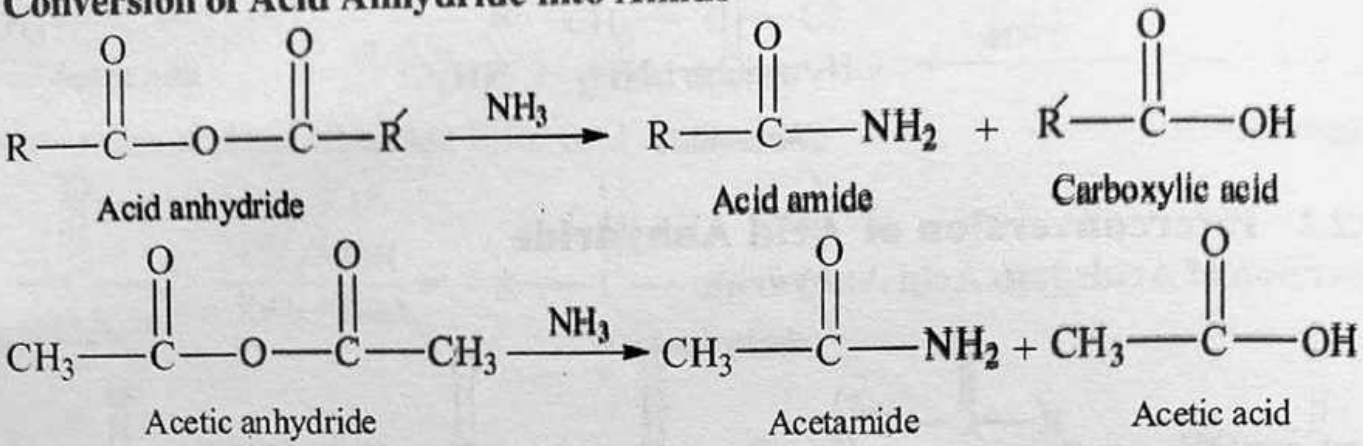
Conversion of Acid Anhydride into Acid





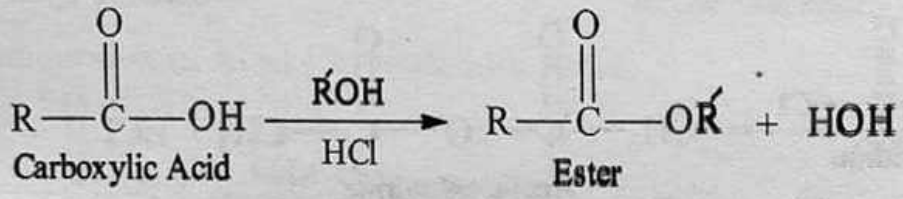
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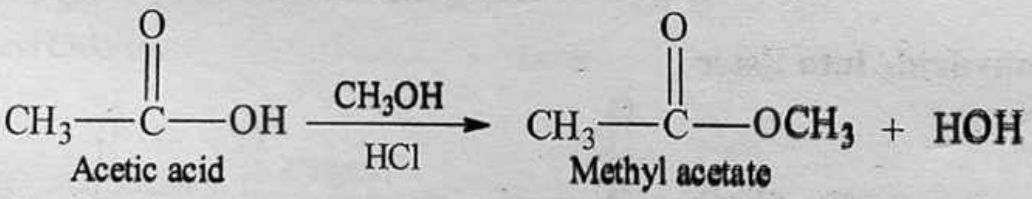
Conversion of Acid Anhydride into Amide



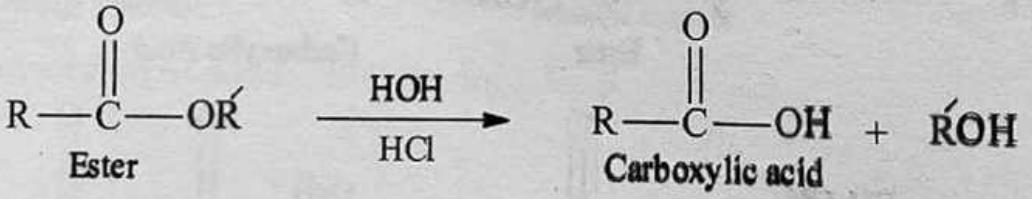
20.7.2.3 Interconversion of Ester

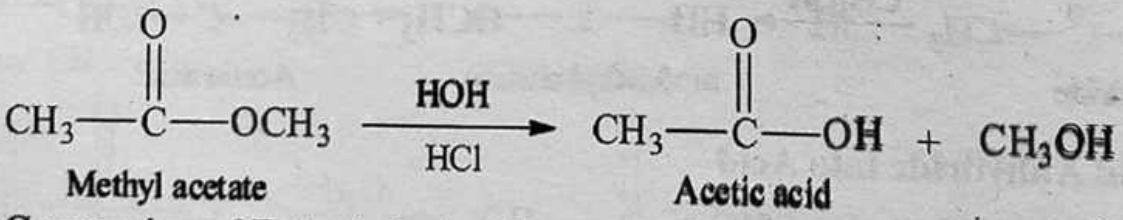
Conversion of Acid into Ester



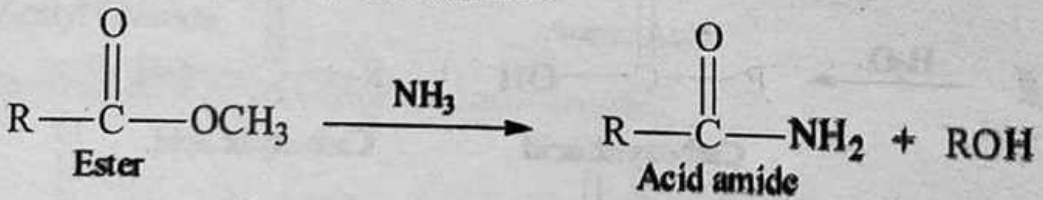


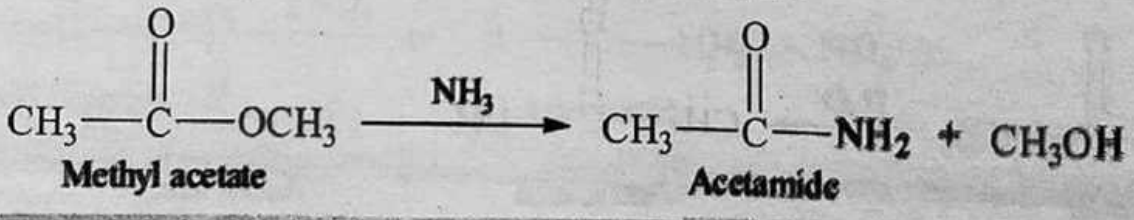
Conversion of Ester into Acid





Conversion of Ester into Amide

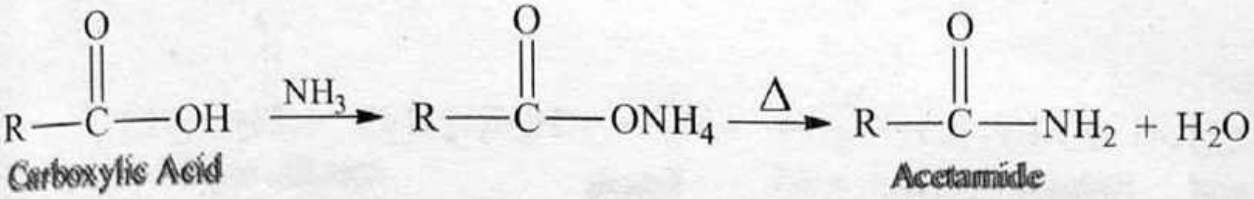




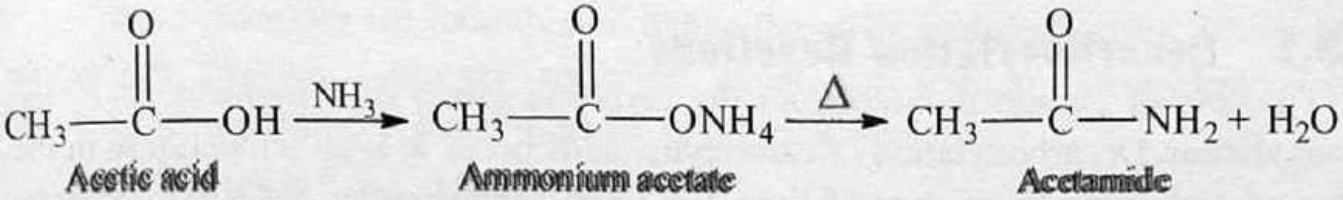
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20.7.2.4 Interconversion of Amide

Conversion of Acid into Amide

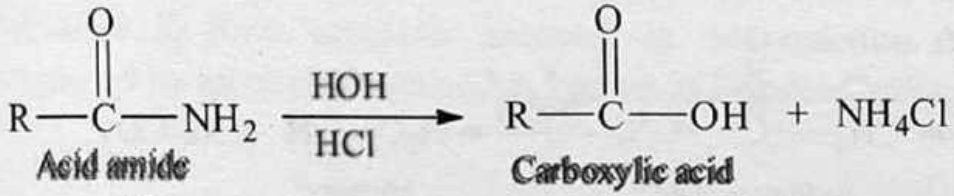


Carboxylic Acid — Acetamide

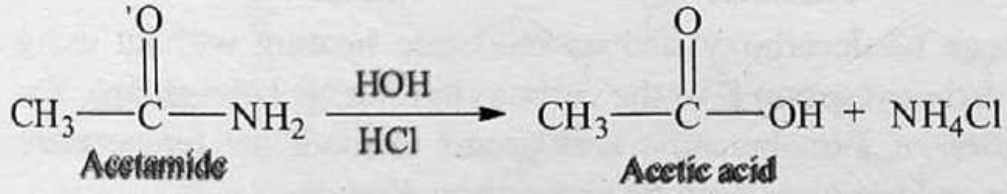


Acetic acid — Ammonium acetate — Acetamide

Conversion of Amide into Acid



Acid amide — Carboxylic acid



Acetamide — Acetic acid

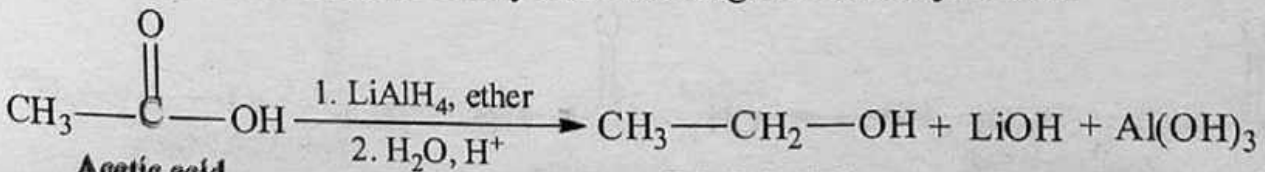
Amides are the least reactive of all the acid derivatives, hence they cannot be converted to more reactive derivatives such as ester, acid anhydride and acyl halides.

20.7.3 Reactions involving Carboxyl Group

20.7.3.1 Reduction to Alcohols

Alcohols can be produced by the reduction of carbonyl compounds. Two reagents are most commonly used to reduce carbonyl compounds, $LiAlH_4$ (lithium aluminum hydride), a stronger reducing agent, and $NaBH_4$ (sodium borohydride), a weaker reducing agent. $NaBH_4$ is used to reduce aldehydes, ketones, alkenes and alkynes but this reagent is not used to reduce carboxylic acids because the carboxyl group is resistant to reduction. The most common reagent for the reduction of carboxylic acids is the most powerful reducing agent, $LiAlH_4$.

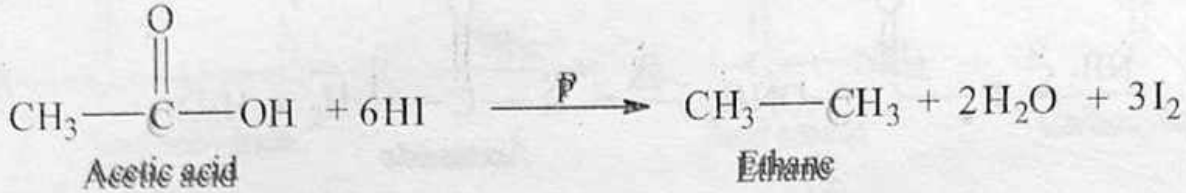
$LiAlH_4$ reduce carboxylic acids via aldehydes to primary alcohols. An aldehyde is formed as an intermediate during this reduction, but it cannot be isolated because it is reduced more easily than the original carboxylic acid.



Acetic acid — Ethyl alcohol

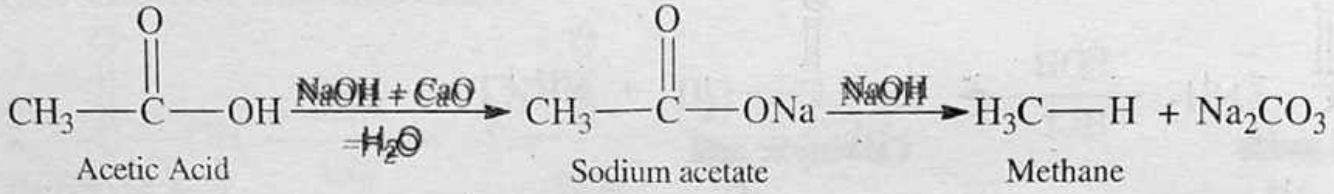
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Carboxylic acids on complete reduction with HI in the presence of red phosphorus give alkanes.

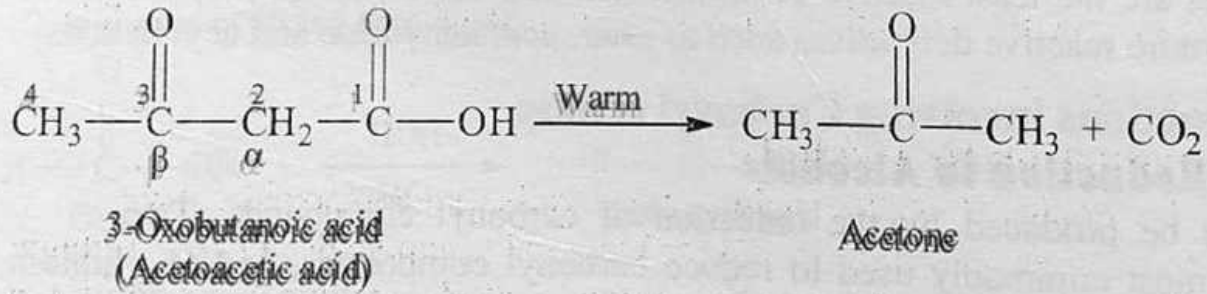


20.7.3.2 Decarboxylation Reactions

The loss of carbon dioxide from the carboxyl group of a molecule is called decarboxylation. Decarboxylation of carboxylic acids occur at high temperature in the presence of soda lime (a mixture of lime, CaO and caustic soda, NaOH) to produce alkanes.



A carboxylic acid can be decarboxylated on moderate heating without using soda lime if it contains a carbonyl group β to the carboxyl group (β keto group). For example, the decarboxylation of 3-oxobutanoic acid occurs at moderate temperature in the absence of soda lime and produces acetone and carbon dioxide.

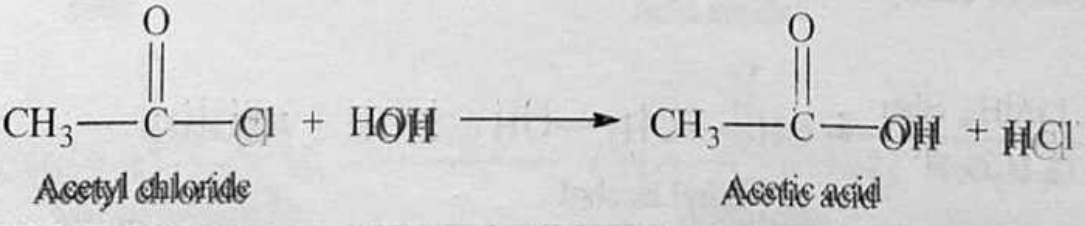


20.7.4 Reactions of Carboxylic Acid Derivatives

20.7.4.1 Reactions of Acyl Halides

Hydrolysis (Reaction with Water)

Acyl halides react spontaneously with water to produce carboxylic acids and HCl. The reaction of low molecular mass acid halides with water is fast and that of high molecular mass acid halides is slow. This is because the higher molecular mass acid halides are less soluble in water.



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Reduction

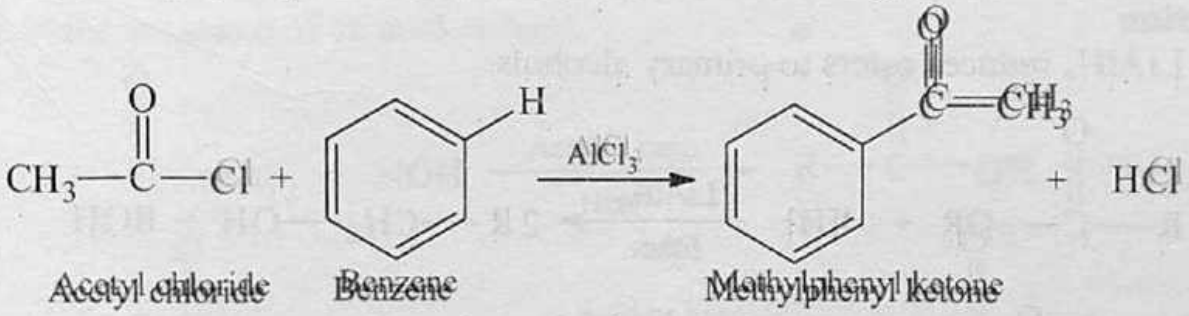
Acyl chlorides are reduced to produce primary alcohols when treated with $LiAlH_4$.



Acid chlorides are more reactive than the other acid derivatives. Either lithium aluminium hydride (stronger reducing agent) or sodium borohydride (weaker reducing agent) converts acid chlorides to primary alcohols.

Friedel-Crafts Acylation

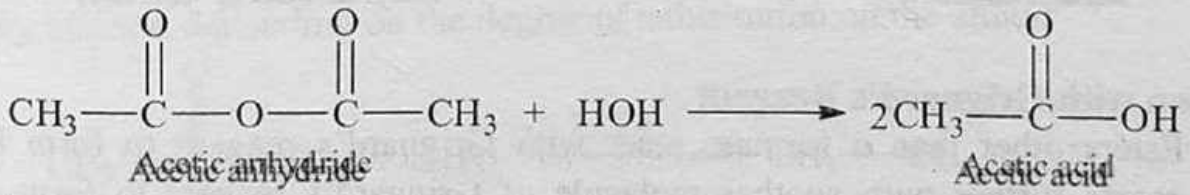
Acid halides react with aromatic hydrocarbons in the presence of aluminum chloride to form aromatic ketones. In this reaction the hydrogen of benzene is replaced by an acyl group and is known as Friedel-Crafts Acylation.



20.7.4.2 Reactions of Acid Anhydrides

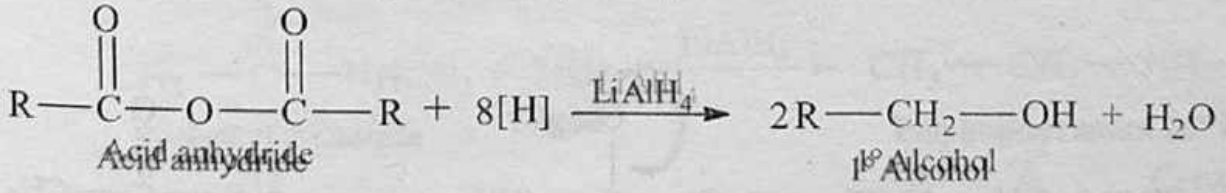
Hydrolysis

Acid anhydrides react with water to produce carboxylic acids.



Reduction

$LiAlH_4$ reduces anhydrides to primary alcohols.



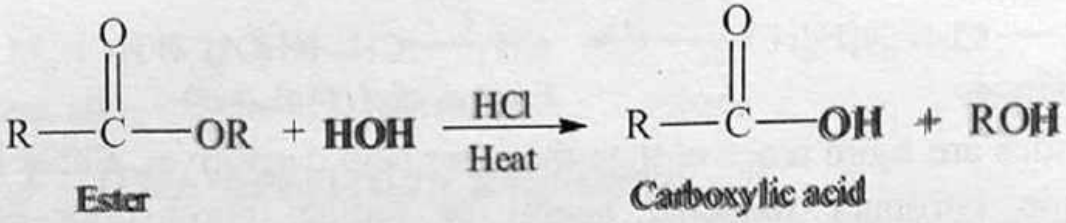


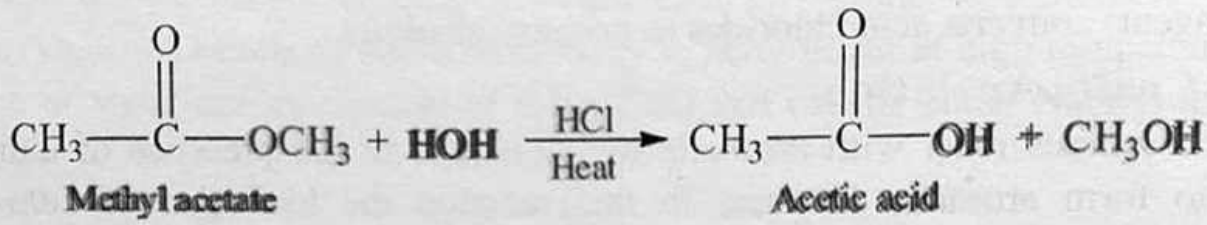
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20.7.4.3 Reactions of Esters

Hydrolysis

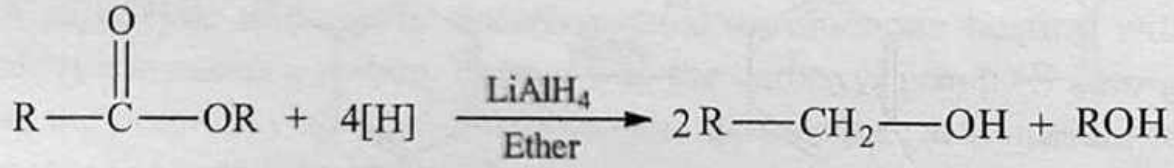
Esters react with water to produce carboxylic acids and water. This reaction is catalyzed by strong mineral acids such as HCl or H_2SO_4.

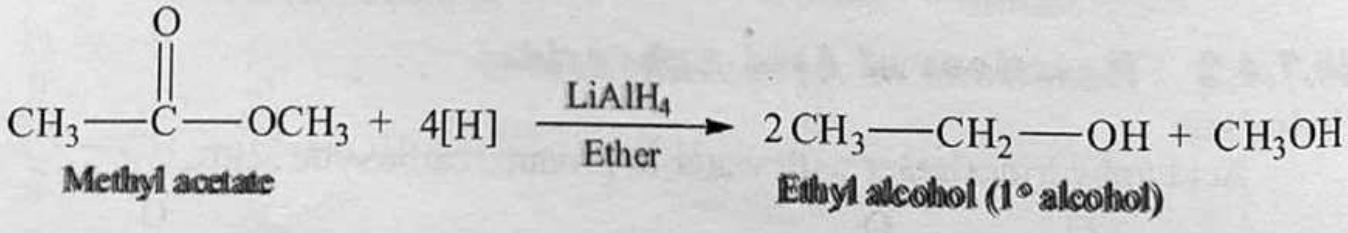




Reduction

$LiAlH_4$ reduces esters to primary alcohols.

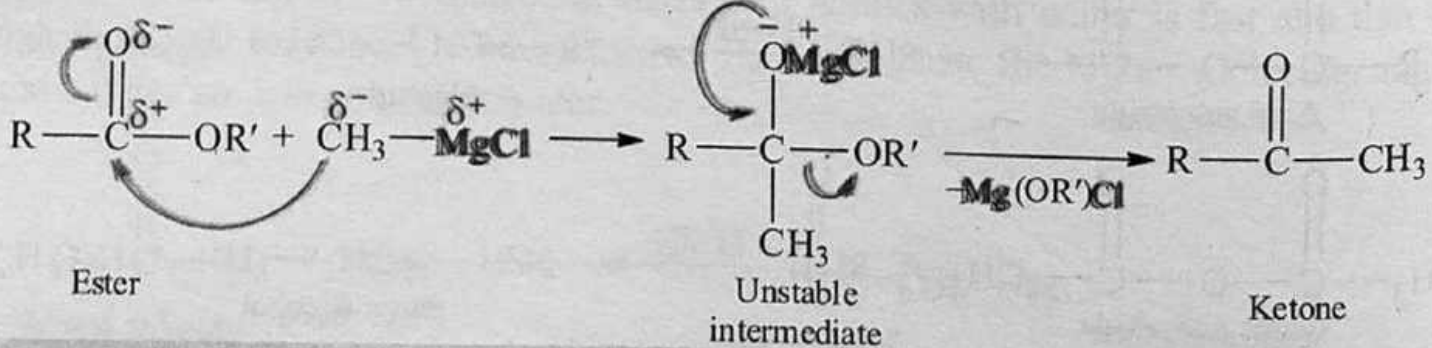




Reaction with Grignard's Reagent

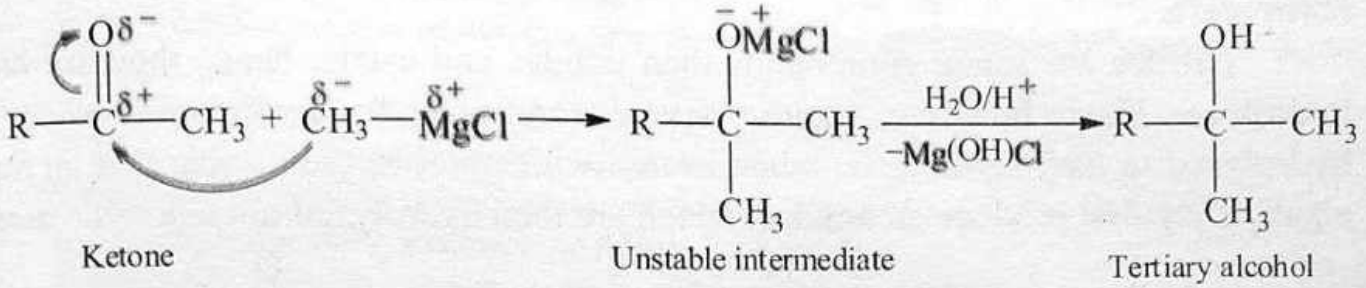
Esters other than a formate react with Grignard's reagent to form ketones which reacts further with another molecule of Grignard's reagent to form tertiary alcohol as a final product.

Step 1:



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Step 2:

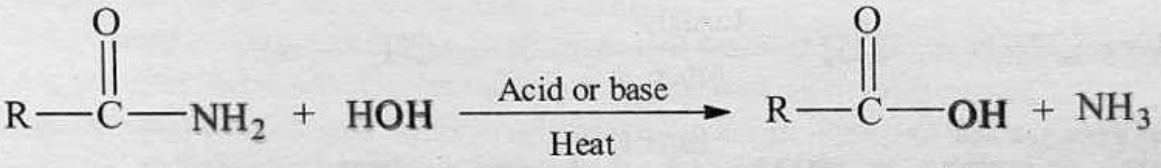


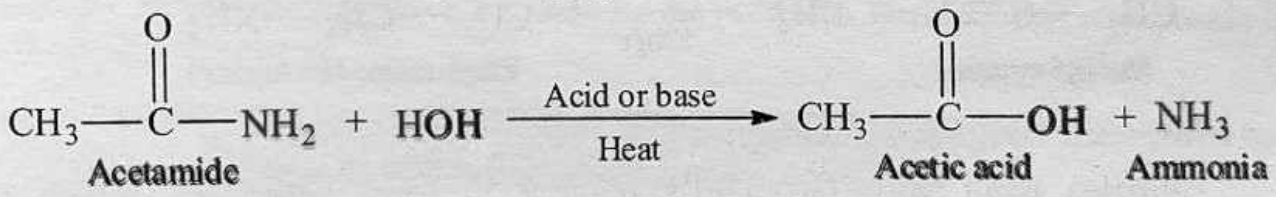
Keep in Mind

The esters namely formates react in the same way with an excess of Grignard's reagents to form secondary alcohols.

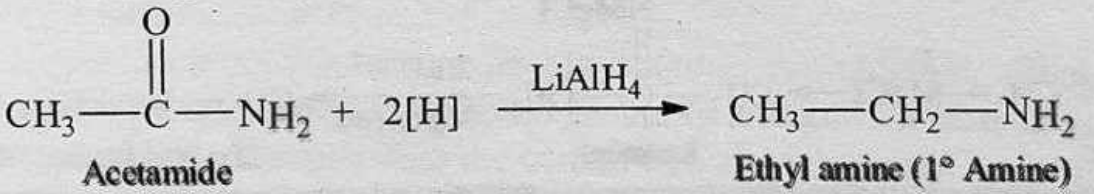
20.7.4.4 Reactions of Amides

Hydrolysis: Amides are the most stable of acid derivatives, and considerably more vigorous conditions are needed for their hydrolysis. Amides do not react with water at normal conditions. Amides do, however, react with water if the reaction mixture is heated in the presence of an acid or base.





Reduction: Lithium aluminum hydride reduces amides to primary, secondary or tertiary amines, depending on the degree of substitution on the amide.





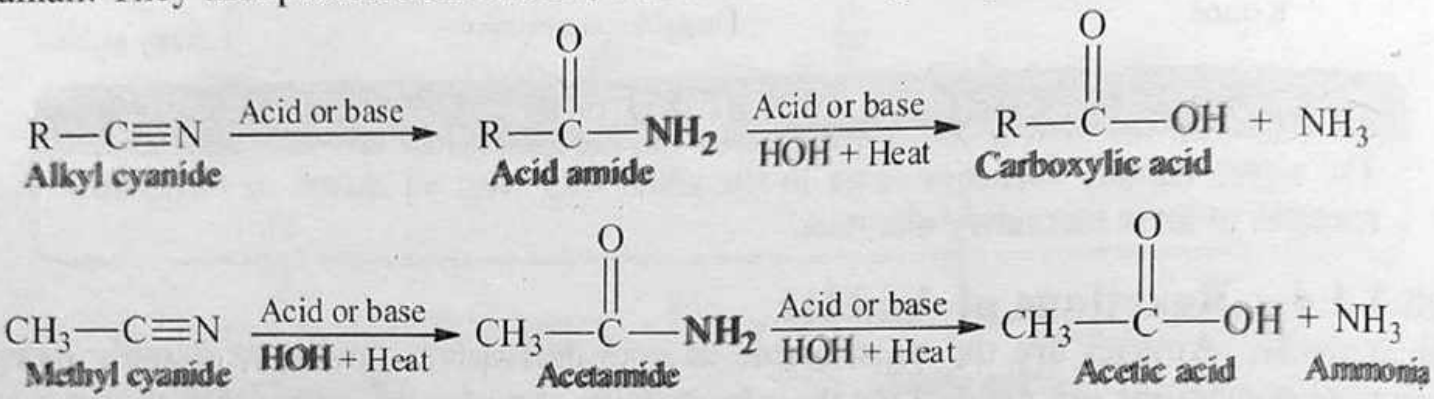


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20.7.4.5 Reactions of Nitriles

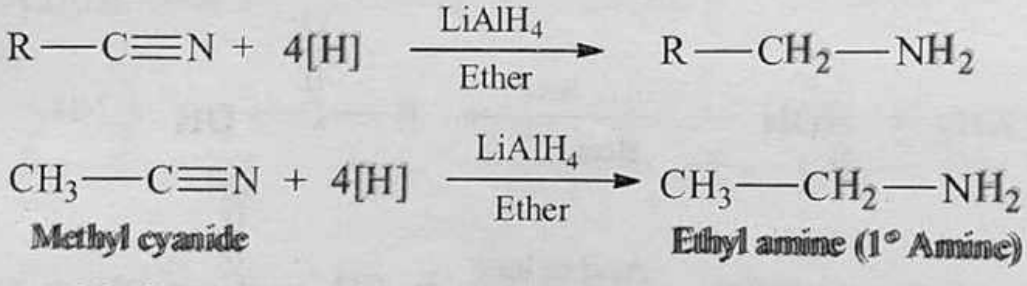
Hydrolysis

Nitriles are stable compounds than amides and esters, hence they are hard to hydrolyze. They, however, require severe conditions for hydrolysis. Nitriles are hydrolyzed to carboxylic acids when heated with water in the presence of an acid or alkali. They first produce an amides, which are then hydrolyzed to carboxylic acids.



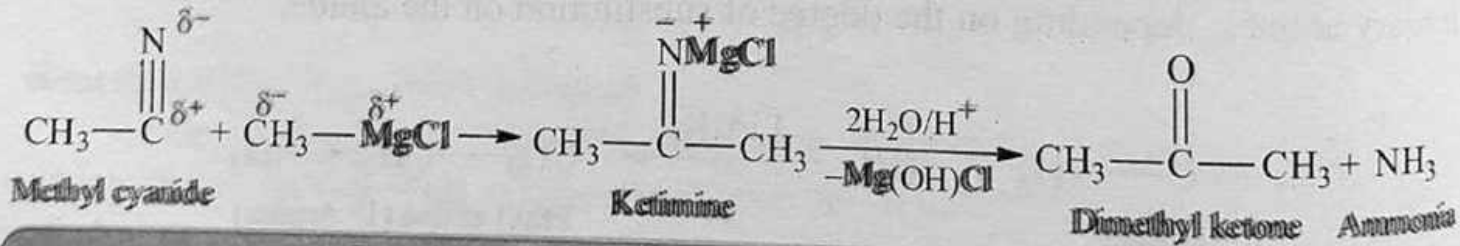
Reduction

Lithium aluminum hydride reduces nitriles to primary amines.



Reaction with Grignard's Reagent

Nitriles react with Grignard's reagent to form ketimines, which on acid hydrolysis gives ketones.



Society, Technology and Science

Sources and Uses of Carboxylic Acids

Most of the simpler saturated carboxylic acids are found in fruits, vegetables and other natural products that give them a distinct flavour or a tinge. Carboxylic acids are primarily used as antibacterial and antifungal preservatives and as flavouring agents in foods and pharmaceutical products. If the acids are not present in foods their taste may bland.

i) **Formic acid** is found in insect stings and nettles. It is used in food preservation.

ii) **Acetic acid** is found in vinegar. It is used in food preservation. It is used in pickles to

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preserve fruits and vegetables. It stops the growth of bacteria.

iii) **Butyric acid** is found in butter. It is responsible for the smell of rancid butter and to the odour of sweat.

iv) **Palmitic acid** is found in palm oil.

v) **Stearic acid** is found in chocolate, waxes, soaps, animal fats and oils.

vi) **Oxalic acid** is found in spinach and some other plant foods including rhubarb. It is used as a cleaning agent for rust stains on fabric and porcelain.

vii) **Citric acid** is found in citrus fruits such as lemons, limes, oranges, grape fruits as well as pineapple and tomatoes. It is also found in tea, cocoa and pepper. It is used as preservative and flavouring agent in both foods and soft drinks.

viii) **Malic acid** is found in many unripe fruits such as green apples and pears. It is also found in plums, currants, etc.

ix) **Tartaric acid** is found in grapes, bananas, potatoes and tamarinds. It is also found in wine and molasses. The tartaric acid in the wine contributes to the tartness of the wine, along with malic acid.

x) **Lactic acid** is found in sour milk such as laban, yougurt, kefir and koumiss. Lactic acid is used as preservative to prevent microbial growth.

xi) **Benzoic acid** is found in berries, plums, prunes, etc.

xii) **Adipic acid** is found in beets and sugar cane.

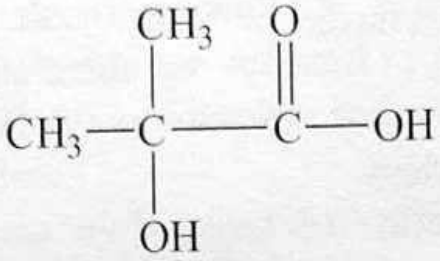
xiii) **Tannic acid** is found in the bark of number of trees. It has been used for tanning. It is now used for the staining of wood and is also used when dyeing cotton.

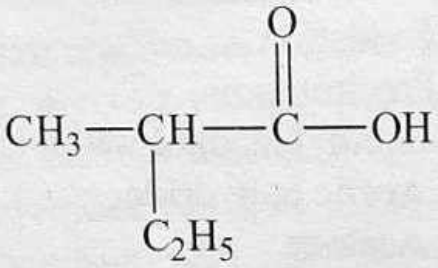
xiv) **Amino acids** are the special form of carboxylic acids. Amino acids are very important because groupings of amino acids make up the proteins. The skin, hair and muscle is composed of protein.

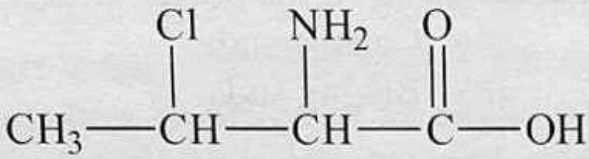
Summary of Facts and Concepts

- Carboxylic acids are organic compounds having carboxyl group (—COOH) as functional group. They are of two types: (i) aliphatic carboxylic acids and (ii) aromatic carboxylic acids.
- In aliphatic carboxylic acids, an alkyl group or hydrogen atom is directly attached with the carbon of carboxyl group. In aromatic carboxylic acids, an aryl group is directly attached with the carbon of carboxyl group.
- Carboxylic acids are prepared by oxidation aldehydes, alcohols and alkyl benzenes. They can also be prepared by hydrolysis of nitriles.
- They have higher boiling points than their corresponding alcohols. Boiling point increases with increase in the molecular mass.
- The reaction of a carboxylic acid with excess alcohol and an acid catalyst is called a Fischer esterification.
- The derivatives of carboxylic acids are: (i) acid halides (ii) acid amides (iii)esters (iv) acid anhydrides.
- Lower members of carboxylic acids are water soluble and have pungent smell.

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iii) 

iv) 

v) 

Q.5. Write structural formulas for the following compounds:

i) Propionic acid
ii) Valeric acid
iii) Lactic acid
iv) Phenylacetic acid
v) 2-Chloro-3-phenylpentanoic acid

Q.6. Describe structure, acidity, and reactivity of carboxylic acids.

Q.7. Write down five physical properties of carboxylic acids.

Q.8. Write down five different methods for preparing carboxylic acids.

Q.9. Write short note on the conversion of carboxylic acids to carboxylic acid derivatives (acyl halides, acid anhydrides, esters and amides).

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Chapter 21

Biochemistry

Major Concepts

21.1 Carbohydrates
21.2 Proteins
21.3 Enzyme
21.4 Lipids
21.5 Nucleic acids
21.6 Minerals of Biological Significance

Learning Outcomes:

Students will be able to:

- Explain the basis of classification and structure-function relationship of carbohydrates **(Understanding)**
- Explain the role of various carbohydrates in health and diseases. **(Understanding)**
- Identify the nutritional importance and their role as energy storage. **(Applying)**
- Explain the basis of classification and structure-function relationship of proteins. **(Understanding)**
- Describe the role of various proteins in maintaining body functions and their nutritional importance. **(Applying)**
- Describe the role of enzyme as biocatalyst and relate this role to various functions such as digestion of food. **(Applying)**
- Identify factors that affect enzyme activity such as effect of temperature and pH.
- Explain the role of inhibitors of enzyme catalyzed reactions. **(Understanding)**
- Describe the basis of classification and structure-function relationship of lipids. **(Applying)**
- Identify the nutritional and biological importance of lipids. **(Applying)**
- Identify the structural components of DNA and RNA. **(Applying)**
- Recognize the structural differences between DNA polymer (double strand) and RNA (single strand).
- Relate DNA sequences to its function as storage of genetic information. **(Applying)**
- Relate RNA sequence (transcript) to its role in transfer of information to protein (Translation). **(Applying)**
- Identify the sources of minerals such as iron, calcium, phosphorous and zinc in nutrition. **(Applying)**

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Introduction

Biochemistry is the study of chemical processes associated with living organisms. Biochemistry is the study of the structures, functions and interactions of biological molecules (or biomolecules) such as carbohydrates, proteins, enzymes, lipids, and nucleic acids, the mechanisms of enzyme action, the chemistry of vitamins and the energy transformations in the cell.

21.1 Carbohydrates

Carbohydrates are the most abundant naturally occurring compounds. They are widely distributed in plants and animals. Plants are the major sources of carbohydrates. About three-fourths of the dry weight of plants and less than 1% of the body weight of animals is made up of carbohydrates. Carbohydrates such as glucose, glycogen and starch are the main sources of energy for our brains and bodies to function properly. Cellulose, the complex carbohydrate, is also used in plants for structural support.

The name carbohydrate means hydrate of carbon and comes from the general formula $C_x(H_2O)_y$. The modern definition of carbohydrates includes polyhydroxyaldehydes or polyhydroxyketones or compounds which give such compounds on hydrolysis are called carbohydrates. For example, glucose, lactose, sucrose, starch etc. They exist mainly in their hemiacetal or acetal forms. Carbohydrates are frequently referred to as saccharides (Sanskrit, *Sarkara*; Greek, *Sakcharon*; Latin, *Saccharum*, sugar) because of the sweet taste of low molecular mass carbohydrates. They are synthesized by photosynthesis in green plants and algae.

21.1.1 Classification of Carbohydrates

They are divided into three major classes:

(i) Monosaccharides (ii) Oligosaccharides

(iii) Polysaccharides

21.1.1.1 Monosaccharides

These are also known as simple sugars or single sugars. The carbohydrates that cannot be hydrolyzed into simpler carbohydrates are called monosaccharides.

$$C_6H_{12}O_6 + H_2O \xrightarrow{H^+} \text{No Reaction}$$

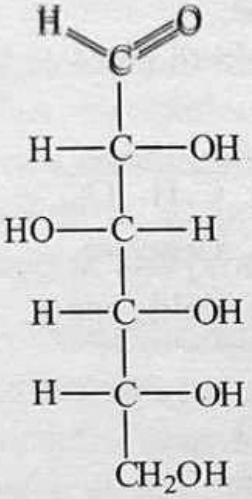
Their general formula is $C_x(H_2O)_y$. For example, glucose, fructose etc. They have three to six carbon atoms. They have sweet taste and are easily soluble in water. Monosaccharides are of two types: aldoses and ketoses.

Aldoses

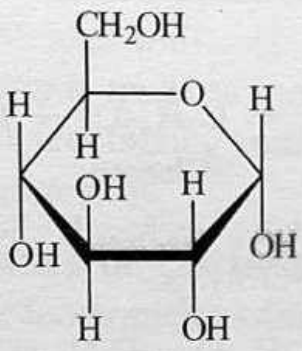
Monosaccharides which have aldehydic group are called aldoses. Examples are glyceraldehyde and glucose.

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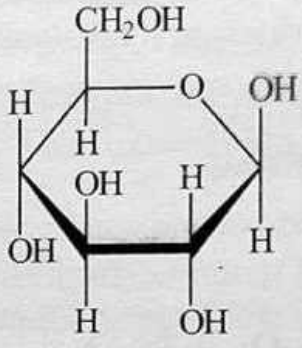
Glucose is also called dextrose, grape sugar or blood sugar. It is present both in free and combined states. In free state, it is present in sweet fruits and honey. It is present in human blood and urine in small amount. In combined state, it is present in disaccharides and polysaccharides. It is the source of energy in our body. The open chain and cyclic structures of glucose are:



Open chain structure



α- D-Glucose



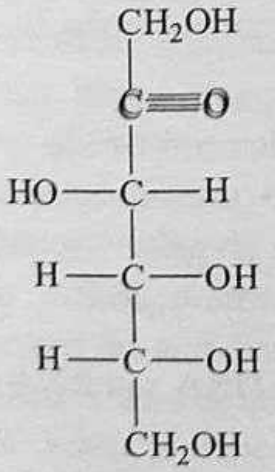
β- D-Glucose

Cyclic structures

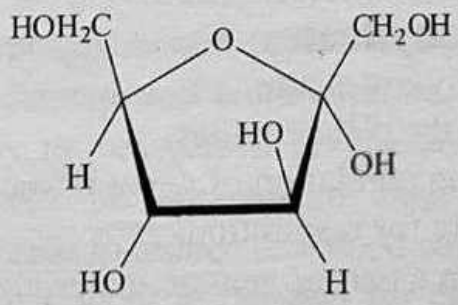
Ketoses

Monosaccharides which have ketonic group are called ketoses. Examples are dihydroxyacetone and fructose.

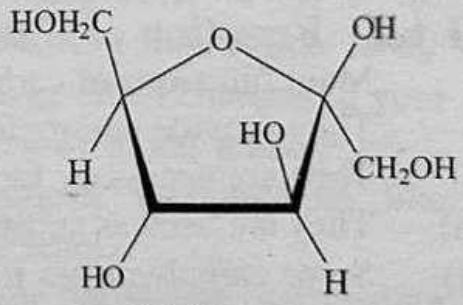
Fructose is found in free and combined states. It is used as sweetening agent in confectionary and as a substitute for cane sugar. The open chain and cyclic structures of fructose are:



Open chain structure



α-D-fructose



β-D-fructose

Cyclic structures

21.1.1.2 Oligosaccharides

The name is derived from Greek word "oligos" meaning "few." These are complex sugars. The carbohydrates which give 2 to 10 molecules of monosaccharides on hydrolysis are called oligosaccharides. Sucrose, raffinose and scorodose are the

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examples of oligosaccharides. On the basis of number of monosaccharide molecules, they are further divided into disaccharides, trisaccharides, tetrasaccharides and so forth. Sucrose, lactose and maltose are disaccharides because they yield two molecules of monosaccharides on hydrolysis.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Raffinose and rabinose are trisaccharides because they yield three molecules of monosaccharides on hydrolysis.

$$\underset{\text{Raffinose}}{C_{18}H_{32}O_{16}} + 2H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} + \underset{\text{Galactose}}{C_6H_{12}O_6}$$

Scorodose and stachyose are tetrasaccharides because they yield four molecules of monosaccharides on hydrolysis.

$$\underset{\text{Stachyose}}{C_{24}H_{42}O_{21}} + 3H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} + 2\underset{\text{Galactose}}{C_6H_{12}O_6}$$

21.1.1.3 Polysaccharides

In Greek "poly" means "many." These are complex carbohydrates. The carbohydrates which give more than 10 molecules of monosaccharides on hydrolysis are called polysaccharides. The most important polysaccharides are starch, glycogen and cellulose. They are polymers of monosaccharides. They may have hundreds or thousands of monosaccharide units. They have relatively high molecular masses. They are tasteless amorphous solids and are called non-sugars. They are water insoluble. The formula of starch and cellulose is $(C_6H_{10}O_5)_n$. The plants store glucose in the form of starch whereas animals store in the form of glycogen in the liver and muscles.

21.1.2 Function of Carbohydrates

Main functions of carbohydrates are:

i) They provide energy for the cell activities.
ii) They are necessary for the regulation of nerve tissue.
iii) They are used as substrate for respiration.
iv) Some carbohydrates form a part of genetic materials like DNA and RNA in the form of deoxyribose and ribose sugars.
v) The glucose (in excess) is converted into glycogen (stored in liver), fats (stored in body) and non-essential amino acids (protein synthesis diet). They are used in times of starvation.
vi) The heart, brain, kidneys and muscles all need carbohydrates to function.
vii) Carbohydrates are constituents of many hormones, vitamins, and enzymes.

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viii) They form components of bio-molecules which have a key role in blood clotting, immunity, fertilization etc.

ix) Some carbohydrates help to clear the gut and prevent constipation.

x) Starch contains fibers which play an important role in the process of digestion.

xi) They are constituents of all the cellular organelles like cell membrane, mitochondria, nucleus, endoplasmic reticulum etc. in one or other way to give structural integrity.

xii) They (cellulose) provide structural support to the plant cells.

xiii) The exoskeleton (outer skeleton) of arthropods (insects, lobsters, crabs,crustaceans, and others) is made of the biological macromolecule chitin, which is a polysaccharide-containing nitrogen. The exoskeleton provides support and protection to arthropods.

21.1.3 Nutritional Importance of Carbohydrates

Carbohydrates are found in foods such as fruits, grains, vegetables, breads and dairy products. Your body uses these foods to make glucose. Glucose is your body's main energy source. They help to fuel your brain, kidneys, heart, muscles and central nervous system. Your body stores excess glucose as glycogen in your muscles and liver for later use, such as during exercise.

Carbohydrates provide nutrients for the good bacteria in our intestines that help us digest our food. They protect our muscles because carbohydrates are the first source of energy for our body, without it, protein and fats from our body will be used.

Low blood sugar (hypoglycaemia) occurs when the glucose levels in the blood drop below normal. While hypoglycaemia is often associated with diabetes, it can be caused by a lack of carbohydrates in healthy people. Symptoms of hypoglycaemia include tiredness, weakness, light-headedness, confusion and hunger.

High blood sugar (Hyperglycaemia) occurs when the glucose levels in the blood rise above normal. Hyperglycaemia makes more serious complication to the body like heart disease, eyes damage and kidney failure. Make small changes in your daily habit and lifestyle surely moves you to get the normal of blood glucose level. Complex carbohydrates should be encouraged than simpler carbohydrate like monosaccharides and disaccharide to reduce the blood sugar level.

Fibre is an essential component in our diet for cancer prevention and healthy digestion. Fibrous (whole grains etc.) foods also reduce the risk of constipation. Without some whole grains, one would need to consume a large amount of fruits, vegetables and legumes to meet daily fibre requirements.

Ketosis occurs in the absence of carbohydrates when glycogen is depleted. Regularly consuming fruits, which contain carbohydrates, and starchy vegetables will

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prevent ketosis from occurring. Ketosis is the normal metabolic process occurs when your body does not have enough carbohydrates from food for your cells to burn for energy, it burns fat in its place. As apart of this process, it makes ketones. If you are eating a balanced diet, your body controls how much fat it burns, and you don't normally make or use ketones.

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Muscular Activities and Glycogen Storage

Glucose is an important source for energy. Energy is required for all kinds of bodily processes. Glucose is stored in the human's body as glycogen. In humans the majority of glycogen is stored in the cells of skeletal muscles (~500 g) and liver (~100 g). However, small amounts of glycogen are also present in the cells of heart, kidneys and brain. The liver will store glycogen for a later time when the body requires it for physical activity. The more carbohydrate a person eats, the more glycogen muscles store (ultimate extent), and the longer the stores will last to support physical activity.

The liver release its glucose into the blood stream to share with other bodily tissues while muscles do not release their glucose into the blood stream directly. During intense activities such as running(marathon race), the muscles glycogen is broken down and released as lactate into the blood. Lactate travels to the liver. The liver convert the lactate back into glucose. Glucose is then return to the muscles to fuel additional activity. The muscles glycogen is important for muscular activities such as running, cycling, weights lifting, climbing hills or stairs, dancing, yoga, football, hockey and push-ups.

Peoples who run out of muscle glycogen during an intense activity such as running, they have to slow down to conserve energy. At this stage, their legs cannot go one in front of the other and they are unable to run anymore. If they continue, their glycogen stores will get so low that their brain will shut down their body down and even jogging will be almost impossible. This can be prevented by eating sufficient quantities of simple carbohydrates both before and during intense activities.

Complex Carbohydrates that Provide Lubrication to Elbow and Knee

Complex carbohydrates (starch and cellulose) are very common in animals, plants, and bacteria. They are constituents of cell membranes, as well as subcellular materials of cells. They are also found in physiological fluids such as blood, tears, milk, and urine.

Many other naturally occurring complex carbohydrates are covalently attached to other biological molecules, such as amino acids, proteins or lipids, by glycosidic linkages of the sugar residues at their reducing ends to form glycoconjugates. They provide lubrication to elbow and knee.

Glucosamine

Clucosamine is an aminosaccaride. It helps in repairing and lubricating joints (elbow, knee and shoulder) and thus can improve flexibility and mobility of joints.

Glucosaminoglycans (GAGs)

Glycosaminoglycans such as chondroitin sulphate (most abundant GAG) are jelly-like

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substances and are found in cartilage, tendons and connective tissues. It helps lubricate the surfaces of joints. Other glycosaminoglycans such as hyaluronic acid are found in synovial fluid (a viscous and slippery fluid found in cavities of synovial joints) that lubricate the joints. The chondroitin sulphate and hyaluronic acid both reduce the friction between the cartilage and other tissues of joints especially elbows and knees and help you to move about freely.

Proteoglycans (Mucoproteins)

Proteoglycans are proteins that are covalently bonded at multiple sites along the protein chain to glycosaminoglycans. They are found in connective tissues and serve as joint lubricants.

21.2 Proteins

The high molecular mass organic compounds which on complete hydrolysis give amino acids are called proteins (Greek, Proteios = first). Proteins are present in all the living organism. Life is impossible without protein. They are present in skin, hair, wool, feathers, nails, horns, hoofs, nerves etc.

The %age of elements in proteins is:

C = 51%, H = 7%, O = 23%, N = 16%, S = 1-3%, P = < 1%

They may have copper, iodine, manganese and zinc.

21.2.1 Classification of Proteins

Proteins are classified into three types on the basis of physical and chemical properties: Simple proteins, compound proteins and derived proteins.

Simple proteins

The proteins which give only amino acids or their derivatives on hydrolysis are called simple proteins. Examples of such proteins are albumins, globulins, legumin, glutelins, histones, collagen etc. They are the most abundant proteins in the animals and form about 25-35% of body protein.

Albumins are found in blood, egg white, wheat, etc.

Globulins are found in blood, muscle, potatoes, etc.

Legumin and collagen are found in connective tissues of body.

Glutelins are found in wheat and rice.

Histones are found in thymus gland, pancreas and nucleoproteins.

Compound or Conjugated Proteins

The proteins which give an amino acid and non-protein group on hydrolysis are called compound proteins. They are also known as conjugated proteins. The non-protein group is called prosthetic group. For example, phosphoproteins are conjugated (attached) with phosphoric acid and lipoproteins are conjugated with lipids such as cholesterol, fatty acids.

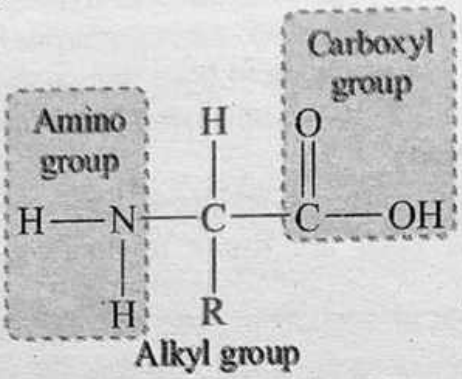
Derived Proteins

The proteins which are derived from simple and conjugated proteins are called derived proteins. For example, poly-peptides and proteases enzymes.

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21.2.2 Structure of Proteins

Let us start by looking at the structure of amino acid:



The amino acids are generally represented using three letters. They can also be represented using one letter for easier convention as given in the image below.

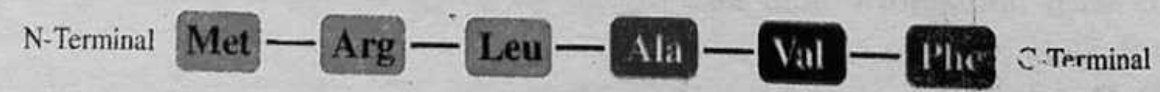
G	Glycine	Gly
A	Alanine	Ala
L	Leucine	Leu
M	Methionine	Met
F	Phenylalanine	Phe
W	Tryptophan	Trp
K	Lysine	Lys
Q	Glutamine	Gln
E	Glutamic acid	Glu
S	Serine	Ser

P	Proline	Pro
V	Valine	Val
I	Isoleucine	Ile
C	Cysteine	Cys
Y	Tyrosine	Tyr
H	Histidine	His
R	Arginine	Arg
N	Asparagines	Asn
D	Aspartic acid	Asp
T	Threonine	Thr

There are four types of proteins on the basis of structure: primary, secondary, tertiary, and quaternary structures.

Primary Structure

The sequence of the amino acids in the polypeptide chain is called primary structure. The primary structure is held together by peptide bonds that are made during the process of protein biosynthesis. The sequence is described by starting with the first amino acid found at the amino terminal (N) and ending with the last amino acid found on the carbonyl terminal (C).



Understanding the primary structure of proteins is important because many genetic diseases result in proteins with abnormal amino acid sequences, which cause

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improper folding and loss or impairment of normal function. The best example of primary structure is hemoglobin.

Secondary Structure

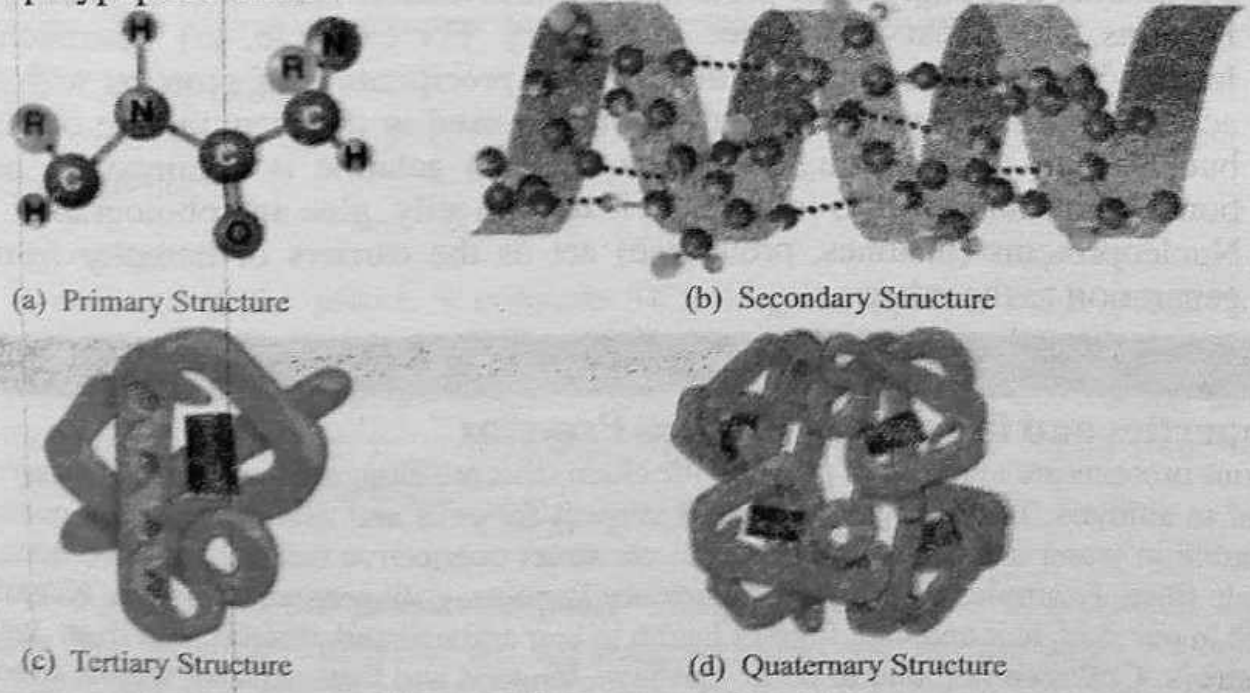
The regular coiled or zigzag structures of polypeptide chains which are held by hydrogen bonding between —NH group and —CO group are called secondary structures. Myoglobin is the good example of secondary structure.

Tertiary Structure

The three-dimensional twisting and folding of the polypeptide chains results in the tertiary structure. The best example of the tertiary structure of protein is myoglobin. Insulin, like all other proteins, has primary, secondary and tertiary structures.

Quaternary Structure

The structure which is formed by the polymerization of two or more tertiary structures is called quaternary structure. The polypeptides may be similar or different in them. Most proteins are made from only one peptide chain so they have primary, secondary and tertiary structures, but not quaternary structure. All those proteins have quaternary structure, which are made from more than one peptide chain. Haemoglobin and collagen are among those proteins which have quaternary structures. Collagen consists of three polypeptide chains while haemoglobin consists of four polypeptide chains.



(a) Primary Structure (b) Secondary Structure

(c) Tertiary Structure (d) Quaternary Structure

Figure 21.1: Structures of Proteins

Every protein in your body has a primary, secondary and tertiary structure, but only some proteins have a quaternary structure.

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21.2.3 Properties of Protein

i) They contain carbon, hydrogen, oxygen and small amount of sulphur.
ii) They are complex biological molecules and are composed of amino acids. Amino acids are linked together by polypeptide bonds.
iii) They are biological catalysts and catalyse chemical reactions in living cells.
iv) They provide structural support to the cells.
v) They secrete hormones.
vi) They are amphoteric in nature and react with both acids and bases.
vii) Proteins can be denatured. Denaturing of protein is the disruption of the structure (secondary, tertiary and quaternary structures) of protein by heat, change in pH or by using strong oxidizing and reducing agents. The coagulation of the protein is the most common observation in the denaturing process. For example, the coagulation of albumin (the major component of egg white) occurs when egg is heated.

21.2.4 Importance of Protein

i) Protein is essential for the formation of protoplasm.
ii) Proteins play an important role in the contraction of muscles, digestion of food and clotting of blood.
iii) Almost all enzymes are proteins and they acts as organic catalysts.
iv) Haemoglobin, a protein, transports O_2 from lungs to the cellular tissues.
v) Insulin, a protein, regulates glucose metabolism.
vi) Myosin, a protein, present in muscles.
vii) Protamine, a strongly basic protein, present in nucleic acids (i.e. in sperm cells)
viii) Proteins have great importance in industry. For example, (a) manufacture of leather by tanning of hides is done by the precipitation of proteins with tannic acid, (b) casein, a protein found in milk, is used in the manufacture of buttons, buckles and in the sizing of papers, and (c) gelatine is obtained by heating bones, skins and tendons in water. It is used in jelly, glue and photography.
ix) Nucleoproteins (histones, protamine) act as the carriers of heredity from one generation to the other.

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Properties and function of Fibrous Proteins

Fibrous proteins are made up of polypeptide chains that are elongated in shape. They are only found in animals. They provide structural support for cells and tissues. They are generally insoluble in water and are usually used to construct connective tissues, tendons, bone and muscle fibre. Examples of fibrous proteins are keratins, collagens and elastins. **Keratin** is found in our skin, hair and nail. It gives health to hair and nail and protects skin from damage and stress. **Collagen** is found in bone, cartilage, tendons and ligaments for tensile strength. **Elastin** is found in connective tissues and is responsible for elastic properties. It allows many tissues in the body to resume their shape after stretching or contracting. It helps skin to return to its original position when it is poked or pinched.

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21.3 Enzymes

Enzymes are proteins that act as catalysts to increase the rate of chemical reactions. These reactions include respiration, photosynthesis and forming new proteins. Examples of enzymes are lipase, zymase, glycosidase and isomerase. They are produced by living cells only but they catalyse (speed up) chemical reactions occurring inside and outside of living cells. Without enzymes, many chemical processes happen at a very slow rate; at such a slow rate that existence of life is practically not possible. An enzyme increase the rate of chemical reaction between 10^4 to 10^{20} times. Enzymes are specific in their action. An enzyme catalyses only one type of reaction not others. For example, sucrase will hydrolyse only sucrose and glucokinase can catalyse only glucose. Enzymes have two parts, namely the protein component (part) and the non-protein component. The protein part of the enzyme is known as apo-enzyme while the non-protein part of the enzyme is known as co-enzyme or co-factor.

21.3.1 Role of Enzyme as a Biocatalyst

A natural substance especially an enzyme that initiates or increases the rate of chemical reaction in a living body is called biocatalyst. Enzymes play an important role in the metabolism, respiration, digestion of food and other important life processes. Our body produces two types of enzymes: the digestive enzymes and the metabolic enzymes. The digestive enzymes are responsible for digestion of food and metabolic enzymes are responsible for all biochemical reactions that occur in the cell of our body. The digestive enzymes and their functions are given below:

21.3.1.1 Amylase

This enzyme is made in two places and are divided into salivary amylase and pancreatic amylase.

Salivary Amylase

It is found in the saliva. It converts 30% of carbohydrates such as starch and sugar present in our food into simple sugars in the mouth. That is why you are advised to chew food for a long time. If you chew food (bread) for a long time, it starts to taste sweet because the amylase present in the saliva breaks down the starch into simple sugars like glucose and fructose.

Pancreatic Amylase

It is present in the pancreatic juice. The pancreatic juice is produced by the pancreas. The pancreatic amylase has the same action as salivary amylase.

21.3.1.2 Lipase

It is present in the pancreatic juice. It is used to break down dietary fats into smaller molecules called fatty acids and glycerol.

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Digestion of fat in the small intestine is helped by bile (bile acid), made in the liver. Bile is secreted into the intestine, where it breaks down the fat into small droplets that are easier for the lipase enzymes to work on. Bile is not an enzyme.

21.3.1.3 Protease

Protease is a general term used for three main enzymes, namely pepsin, trypsin and chymo-trypsin. Pepsin is present in the gastric juice of stomach. It breaks proteins into peptides. The trypsin and chymotrypsin are produced in the pancreas. They are released into small intestine through the pancreatic duct. When partially digested food moves from your stomach into your intestine, trypsin and chymotrypsin complete protein digestion, producing simple amino acids.

Keep in Mind

- The substances like vitamins, minerals and water are not digested because they are already small enough to be absorbed by the body without being broken down.
- The digestive enzymes cannot break down dietary fibre that is why the body cannot absorb it.

21.3.2 Factors Affecting Enzyme Activity

The factors that affect the activity of enzyme are:

21.3.2.1 Concentration

It can be explained in two ways:

Enzyme Concentration

The rate of reaction increases with an increase in the concentration of enzyme. For example, the rate of digestion increases by increasing the concentration of pepsin (an enzyme).

Substrate Concentration

The rate of enzymatic reaction is also directly proportional to the concentration of substrate.

21.3.2.2 Temperature

The enzyme activity increases with rise in temperature up to 45°C. The enzymes being protein in nature are denatured and become inactive at the temperature above 45°C. They are completely destroyed at 100°C. The activity of enzyme is reduced at low temperature (0°C) but they are not destroyed. The optimum temperature (The temperature at which enzyme activity is maximum) of enzymes in the body of mammals is about 37°C to 40°C. The optimum temperature is different for different enzymes.

21.3.2.3 Effect of pH

Changes in pH will greatly affect the activity of enzymes. The pH at which enzyme activity is maximum is called optimum pH. The optimum pH of salivary amylase is 6.4 to 6.9. The optimum pH of pepsin of stomach is 1.4. It is inactive in

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neutral and alkaline solutions. The optimum pH value of enzymes has never been found above 10.

21.3.2.4 Effect of Other Substances

The enzyme action is increased or decreased by the presence of other substances. These substances are: (i) Co-enzymes, (ii) Activators, (iii) Inhibitors

Co-enzymes

The non- proteinaceous part of the enzyme is called co-enzyme and the proteinaceous part of enzyme is called apo-enzyme.

Enzyme = Coenzyme + Apoenzyme

Vitamins are the examples of co-enzymes. The certain enzymes are unable to function without co-enzymes.

Activators

Inorganic substances which increase the activity of an enzyme are called activators. For example, Mg^{2+} and Zn^{2+} ions act as activators for the enzyme phosphatase and carbonic anhydrase respectively.

Inhibitors

The substances which either reduce (inhibit) or destroy the enzyme activity are called inhibitors. For example, sulpha drugs, penicillin and streptomycin act as inhibitors and cure many infections.

21.3.2.5 Radiation

Enzymes are generally inactivated by UV light, β–, γ–and X- rays.

21.3.3 Industrial Application of Enzymes

Enzymes are the most proficient catalysts. Enzymes have a wide variety of applications in industries. They are used in food, beverages, cosmetics, detergents, leather, agriculture and medicines. They are also used in biofuels and biopolymers. Some of the important industrial applications of enzymes are as follows:

21.3.3.1 Food Industry

They are used to process carbohydrates, proteins and fats. The enzymes that are used in food processing include amylase, lactases, cellulases and lipase. Amylase, lactases, and cellulases are used to break complex sugars into simple sugars. Lipase is used to break lipids into fatty acids and glycerol.

21.3.3.2 Beverage Industry

They are used to increase juice yield and decrease energy consumption. The pectinase, an enzyme, is used in fruit juice manufacture to break pectins and makes juice less viscous. The cellulases and hemicellulases are used to break the plant cell wall for efficient liquefaction. The number of enzymes such as neutral proteases,

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alpha amylase, beta-glucanase, cellulases etc. are used in the industrial production of alcoholic beverages like beer, wine, brandy, whiskey and rum.

21.3.3.3 Detergent Industry

Enzymes such as proteases, lipases, amylases and cellulases are added to some detergents to break or remove the dirt and stains from the cloth fibres.

21.3.3.4 Leather Industry

Enzymes can be applied during different steps of the leather production process: soaking, dehairing, dying etc. Proteases are used to remove hair from hides. These hides are then treated with pancreatic enzymes to increase the softness of leather.

21.3.3.5 Paper Industry

The amylases, xylanases, cellulases, laccase, lipase and ligninases are the most important enzymes that are used in the pulp and paper processes. They are used to lower viscosity, coating paper, remove colour, smooth fibres, enhance water drainage, and for softness of paper.

21.4 Lipids

The naturally occurring heterogeneous group of organic compounds of animals and plants which are soluble in organic solvents (acetone, benzene, CCl_4 etc.) but insoluble in water are called lipids. Examples are fats, oils, waxes etc. The word 'lipid' is derived from Greek word 'Lipas' which means fats. The fats and oils are the most important lipids found in nature. Lipids which are solid at ambient temperatures tend to be referred as "fats" while those which are liquid are called "oils".

21.4.1 Classification of Lipids

They are classified into the following types:

Simple Lipids

The esters of fatty acids with glycerol are called simple lipids. Examples are common fats and oils.

Compound Lipids

The lipids which have radicals in addition to fatty acids and alcohols are called compound lipids. Examples are glycerol, phospholipids, lipoproteins etc.

Derived Lipids

The lipids which are obtained by the hydrolysis of simple or compound lipids are called derived lipids (or **associated lipid**). For example, sterols, vitamin D, terpenes etc.

Edible Lipids

The lipids which have fats, oils and waxes are called edible lipids.

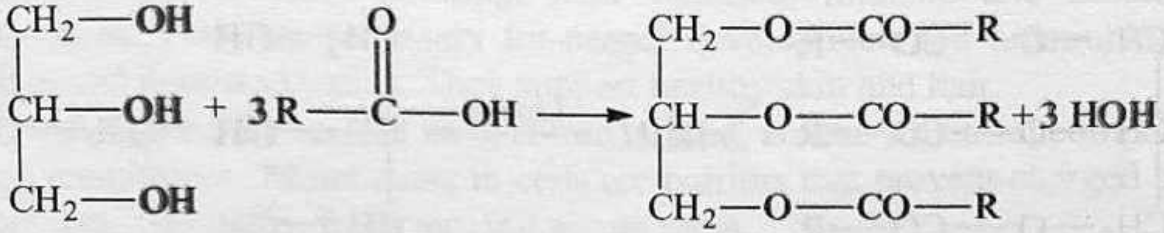
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Steroids

The lipids which have high molecular mass tetracyclic compounds are called steroids. Cholesterol is the example of steroids.

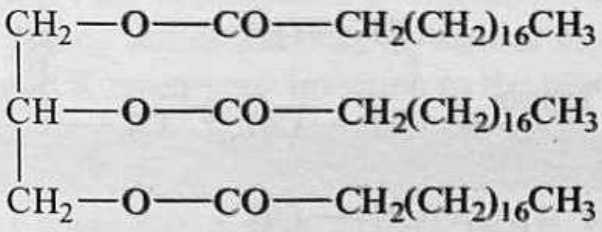
21.4.2 Structure of Lipids (Fats and Oils)

Fats and oils are the triesters of glycerols with fatty acids. They are known as triglycerides or glycerides. Lipids have no single common structure. We will discuss the structure of the most common lipid namely triglycerides. Triglycerides contain a glycerol molecule attached to three fatty acid "tails".



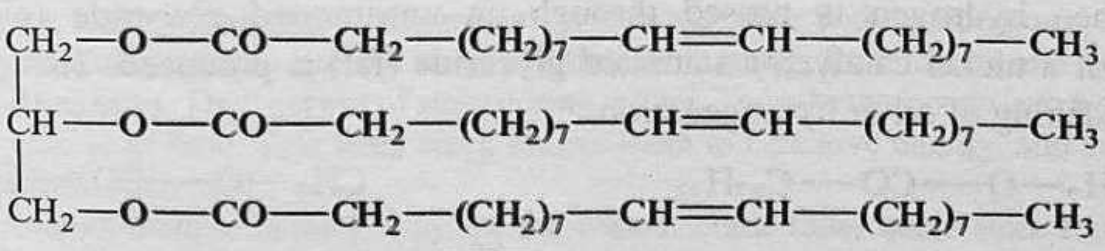
Glycerol Fatty acid Triglyceride

The common oils and fats are the mixture of saturated and unsaturated triglycerides. The solids or semi-solids triesters of long chain saturated fatty acids with glycerol at room temperature are known as fats.



(Fat Molecule)

The liquid triesters of long chain unsaturated fatty acids with glycerol at room temperature are known as oils.



(Oil Molecule)

21.4.3 Properties of Lipids

Physical Properties

i) Pure fats and oils are colourless, odourless and tasteless.

ii) They may either be liquid or non-crystalline solids.

iii) They are insoluble in water but are readily soluble in organic solvents.

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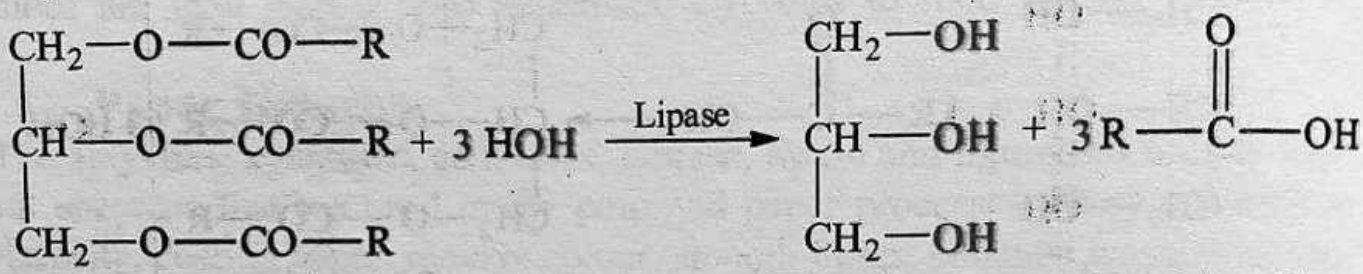
iv) They form emulsions when shake with water in the presence of a base like NaOH.

v) They are poor conductors of heat and electricity and act as excellent insulators for the animal body.

Chemical Properties

Hydrolysis

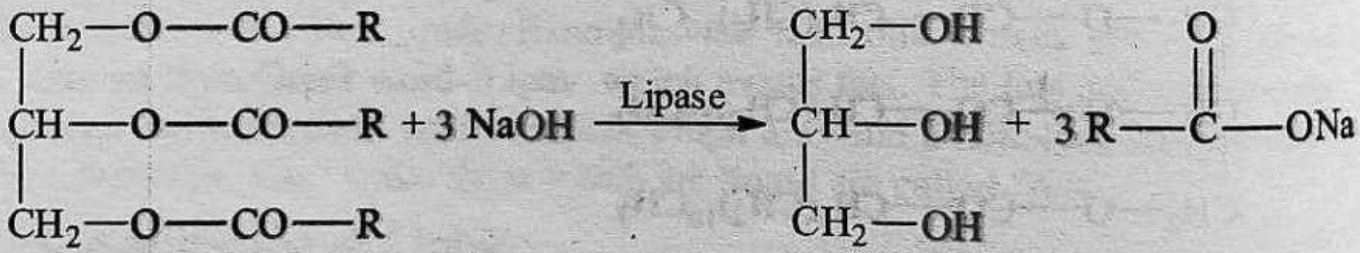
The oils and fats give glycerol and fatty acid on hydrolysis in the presence of enzyme lipase.



Triglyceride — Glycerol — Fatty acid

Saponification

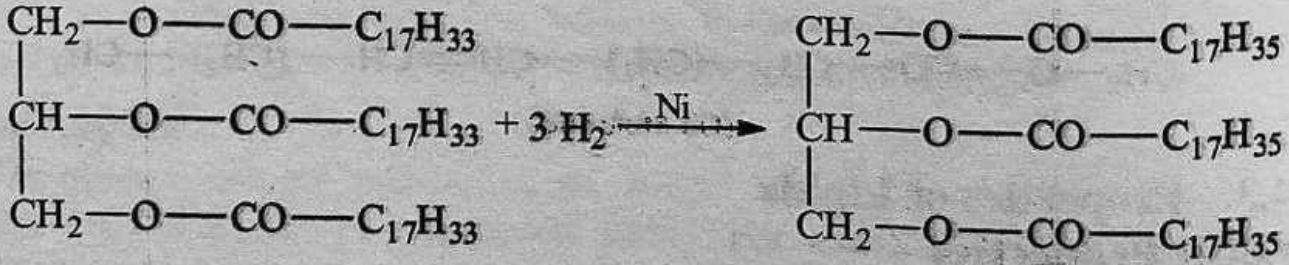
The reaction of fats or oils with NaOH to give soap and glycerol is called saponification.



Triglyceride — Glycerol — Soap

Hardening of Oils

When hydrogen is passed through an unsaturated glyceride (oil) in the presence of a nickel catalyst, a saturated glyceride (fat) is produced. This process is called hardening of oil or hydrogenation.



Glycerol trioleate (an oil) — Glycerol trioleate (a fat)

This reaction is used for the production of vegetable ghee or margarine. Hardened oils are also used for making soap and candles.

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21.4.4 Nutritional and Biological Importance of Lipids

Lipid play an important role in living organisms.

i) The main role of lipids in your body is to provide energy for muscles and body processes. Fat contains 9 calories per gram, whereas protein and carbohydrate contain only 4 calories per gram.

ii) Lipids provide energy to digest and absorb food properly.

iii) The essential lipids (linoleic and alpha-linolenic) cannot be synthesized in your body and must be obtained from diet. They are necessary for regulation of blood pressure, blood clotting, liver function, immune and inflammatory responses. They are necessary for proper development and functioning of the brain and nervous system. They support healthy skin and hair.

iv) Phospholipids, the second most common lipid, are the structural components of cell membranes. Membranes in cells are barriers that prevent charged particles and large molecules from moving across them.

v) Cholesterol, a steroid lipid, serves as the starting material for other important molecules in the body, including vitamin D and bile acids, which aid in the digestion and absorption of fats from dietary sources.

vi) Cholesterol is also used in the synthesis of sex hormones

vii) They are components of the nervous system.

viii) Lipids act as carriers of natural fat-soluble vitamins such as vitamin A, D, E and K from your intestine to the blood stream.

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Hibernating Animals (Polar bear, reptiles and amphibians) Accumulate Fat to Meet Energy Resources during Hibernation

The food (insects and green plants) is unavailable during the winter months, the animals either need to migrate to warmer regions or hibernate. Hibernation is the state of inactivity of animals during winter. During hibernation, the animals will reduce their body temperature, heart rate, breathing rate and metabolic rate. All kinds of animals hibernate, from insects and amphibians to birds and primates. They get out of sight during winter. The hibernators go into a deep sleep for a long period of time. This deep sleep allows them to conserve energy, and survive the winter with little or no food.

Most hibernators prepare in some way for the winter. Some hibernators store food in their burrows (tunnels used by small animals such as rabbit) or dens (caves used by wild animals such as lion), to eat when they awake for short periods. Many eat extra food in the autumn while it is abundant. The food in hibernating animals is stored as body fat to be consumed in the winter for energy. The fat is rich and efficient source of energy and can store a lot of energy in a small space. For example, one gram of fat contains 9 kcal while one gram carbohydrate and protein contain 4 kcal. The hibernating period of animals depends on different factors: species, time of the year and individual's body condition. Animals can put themselves into a deep sleep for few days, weeks or months.

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21.5 Nucleic Acids

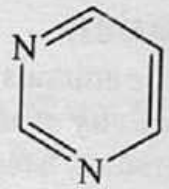
The high molecular mass biopolymers of nucleotides are called nucleic acids. They are present in the nucleus of all eukaryotic living cells as well as in viruses. They are the carriers of necessary hereditary information. They were first isolated from the nuclei of puss cells (white blood corpuscles) in 1869 by Friedrich Miescher. They were named nucleic acids because: (i) they are present in the nucleus (ii) they are acidic in the nature.

21.5.1 Structural Components of DNA and RNA

The two main classes of nucleic acids are DNA and RNA. DNA is the master blueprint for life and constitutes the genetic material in all free-living organisms and most viruses. RNA is the genetic material of certain viruses, but it is also found in all living cells, where it plays an important role in certain processes such as the making of proteins. The DNA and RNA are formed by large number of nucleotides. Nucleotides contain nitrogenous bases, pentose sugars and phosphoric acids in ester linkage.

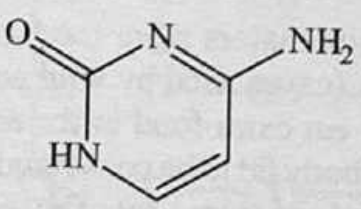
21.5.1.1 Nitrogenous bases

Nitrogenous bases are purine and pyrimidine derivatives. Pyrimidine derivatives (bases) have single rings. Pyrimidine has two nitrogen atoms at C1 and C3 of a six membered ring.

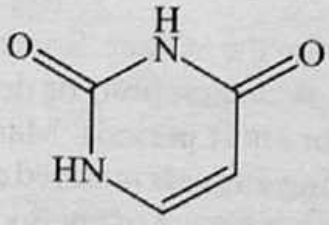


Pyrimidine

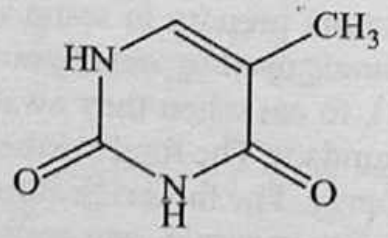
The pyrimidine derivatives consist of cytosine, thymine and uracil.



Cytosine



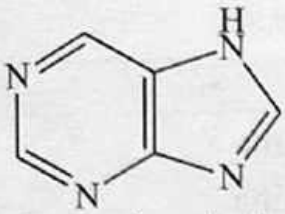
Uracil



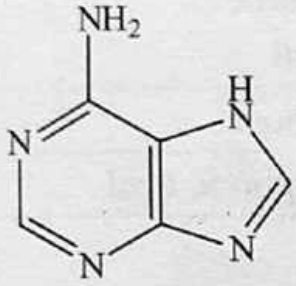
Thymine

Purine derivatives (bases) have double rings. It has one pyrimidine ring and an imidazole ring ($C_3H_4N_2$).

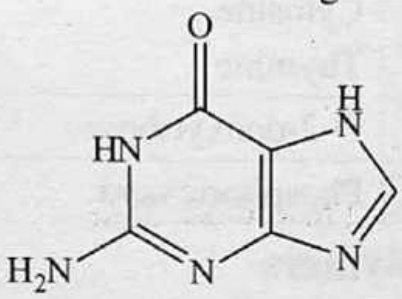
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The purine derivatives consist of adenine and guanine.



Adenine



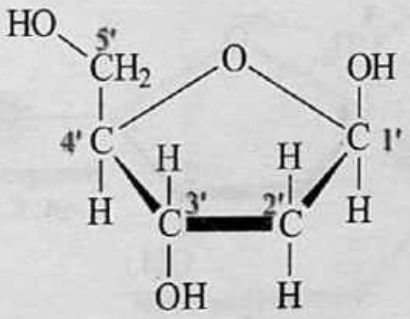
Guanine

Keep in Mind

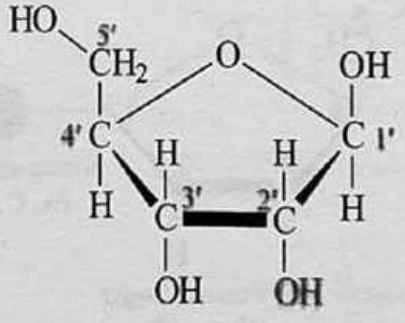
The four different bases in DNA are cytosine (C), Thymine (T), Adenine (A) and Guanine (G), while in RNA, thymine is not present and its place is taken by Uracil (U).

21.5.1.2 Pentose Sugar

Each nucleic acid has a different carbohydrate (sugar). The sugar in DNA is D-2-deoxyribose while the sugar in RNA is D-ribose.



Deoxyribose

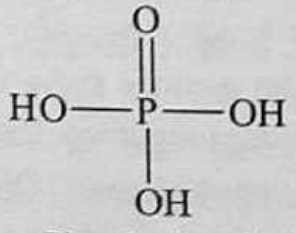


Ribose

By convention, the carbon atoms in the sugar are numbered from the original carbonyl position on the chain using a number plus the prime symbol (′). For example, in the deoxyribose sugar, the hydroxyl groups are boded to the 1′ (pronounced as "one prime), 3′ (three prime) and 5′ (five prime) carbon positions.

21.5.1.3 Phosphoric Acid

It forms phosphodiester bonds between nucleotides.



Phosphoric acid

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Table 21.1 : Components of DNA and RNA

	DNA	RNA
Purines	Adenine Guanine	Adenine Guanine
Pyrimidines	Cytosine Thymine	Cytosine Uracil
Pentose	D-2-deoxyribose	D-ribose
Acid	Phosphoric acid	Phosphoric acid

21.5.2 Nucleic Acid Polymers

The nucleic acids (DNA and RNA) are polymers of nucleotides. As you know, components of each nucleotide are pentose sugar, phosphate group and nitrogenous base. The pentose sugar is the central component of the nucleotide. The nitrogenous base is attached to the number 1 carbon (right point) of the sugar. The phosphate is attached to the number 5 carbon (left point) of the sugar.

Nucleotide = Nitrogenous base + Pentose sugar + Phosphate group

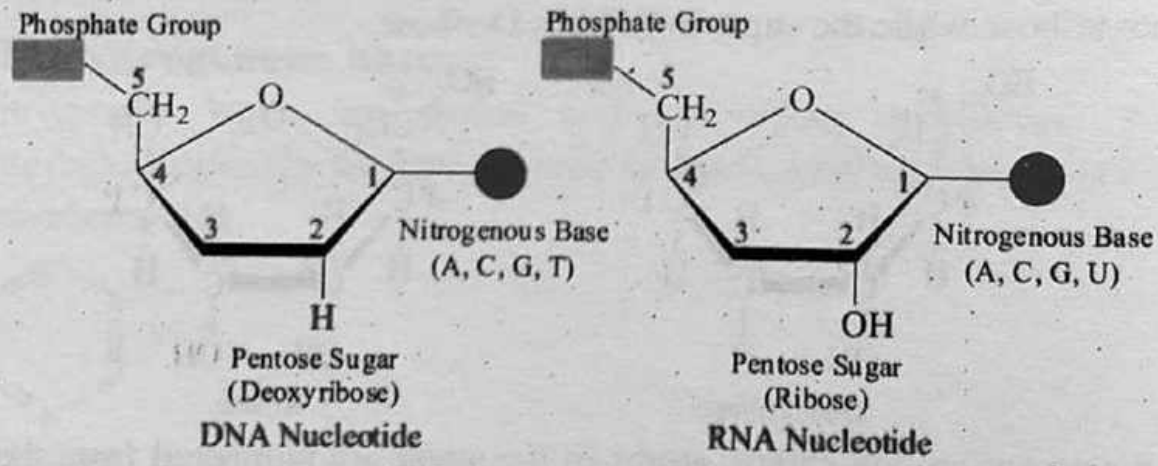


Figure 21.2: Three Parts of a Nudeotide

Nucleotides can link together by the formation of phosphate ester bonds. The hydroxyl group of a phosphate on one nucleotide undergoes a condensation reaction with the hydroxyl group on the carbohydrate ring of another nucleotide. The process may continue, building up nucleic acid molecules. These are polymers called polynucleotides. A covalent bond in RNA or DNA that holds a polynucleotide chain together by joining a phosphate group at position 5 in the pentose sugar of one nucleotide to the hydroxyl group at position 3 in the pentose sugar of the next nucleotide is called phosphodiester bond (or phosphodiester linkage). DNA is polydeoxyribonucleotide while RNA is polyribonucleotide.

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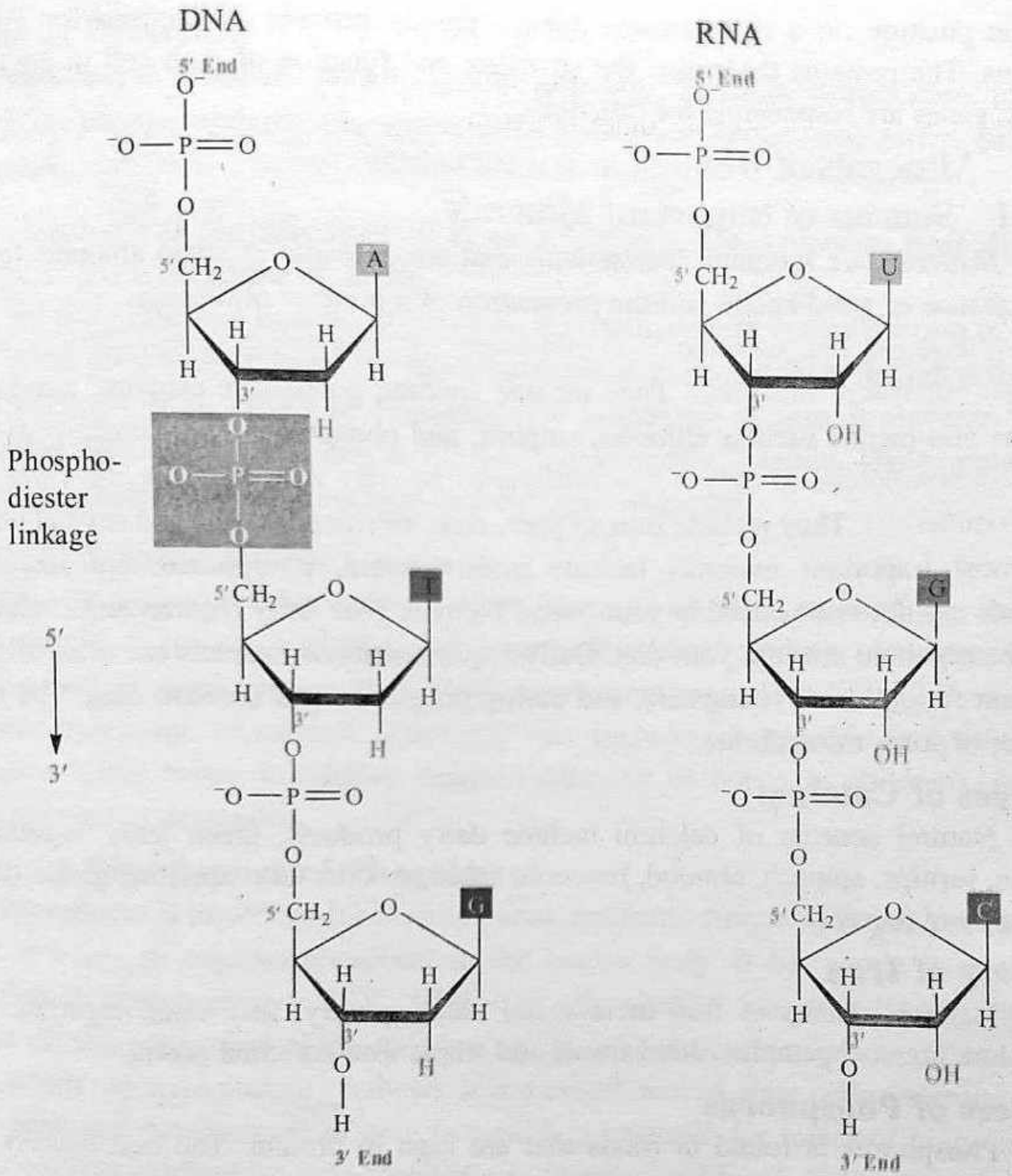


Figure 21.3: Phosphodiester linkages in the DNA and RNA

21.5.3 Storage of Genetic Information

Nucleic acids are macromolecules that carry out two main functions in the cell: storage of genetic information and synthesis of proteins. Two types of nucleic acids specialize in these functions: deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA is the genetic material that stores the biological information in sequences of four bases of nucleic acid that are, adenine, thymine, cytosine and guanine. The sequence of bases forms genes. Genes are located on chromosomal thread which runs along the entire length of chromosome. Each gene occupies a

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specific position on a chromosome. Genes mainly provide instructions for making proteins. The proteins determine the structure and function of each cell in the body. Hence, genes are responsible for inheritance.

21.6 Minerals of Biological Importance

21.6.1 Sources of Important Minerals

Minerals are inorganic compounds that are essential in small amounts for the maintenance of good health and the prevention of a number of diseases. The minerals that are required in amounts of 100 milligrams or more per day are called the major minerals (or macro minerals). They include sodium, potassium, calcium, manganese and the non-metals such as chlorine, sulphur, and phosphorus. The minerals that are required in amounts of only a few milligrams per day are called the trace minerals (micro minerals). They include iron, copper, zinc, selenium, iodine and several others. The most important minerals include iron, calcium, phosphorus and zinc. The minerals are not synthesized in your body. To meet your daily requirements, minerals must be obtained through your diet. Daily requirements of minerals are often slightly different for children, youngsters, and during pregnancy and breastfeeding. The main sources of some minerals are:

Sources of Calcium

Natural sources of calcium include dairy products, green leafy vegetables, salmon, turnips, spinach, almond, broccoli, cabbage, kale, tofu, apricots, garlic, dates, sardines and papaya.

Sources of Iron

Natural sources of iron include red meat, poultry, fish, liver, legumes, egg yolk, dark green vegetables, dried fruits, and whole iron-enriched grains.

Sources of Phosphorus

Phosphorus is found in foods that are high in protein. The best sources are dairy product, nuts, seeds, legumes, meat, and fish.

Sources of Zinc

Zinc is found in meats, mushrooms, liver, poultry, seafood, nuts, whole grains, soybeans, milk and other dairy products.

Sources of Magnesium

The natural sources of magnesium are nuts, seeds, whole grains, apricots, beans, green leafy vegetables, potatoes, banana, milk, and spinach. Magnesium is found especially in plant foods.

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Sources of Potassium

Potassium is found in spinach, apples, tomatoes, bananas, strawberries, fresh orange juice, papaya, apricots, pineapple, dried fruits, rice, cucumbers, garlic, ginger and legumes.

21.6.2 Biological Significance of Iron, Calcium, Phosphorus and Zinc

Biological Significance of Iron

Iron is an essential mineral. It plays an important role in the production of red blood cells of your body. It helps red blood cells to carry oxygen from the lungs to all parts of the body. It also plays an important role in immune system. It prevents you from feeling tired. The lack of iron in red blood cells causes anaemia. The symptoms of anaemia include weakness, tiredness and shortness of breath.

Biological Significance of Calcium

Calcium is essential for building strong bones and teeth in children and teens. It helps muscles to contract and relax. It is important in blood clotting, blood pressure regulation and immune system. It supports nerve transmission and blood pressure regulation. Symptoms of calcium deficiency may include osteoporosis (a condition that causes brittle bones in adults), rickets (softening of bones in children), poor growth and mental depression.

Biological Significance of Phosphorus

Phosphorus is important for healthy bones and teeth. Above 80% phosphorus is located in bones as calcium phosphate in the human body. It has a role in energy production as components of ATP. ATP is readily used to fuel your body's many functions. It is a component of the complex nucleic acid structure of plants (DNA and RNA), which regulates protein synthesis. It is a constituent of plant cells, essential for cell division and development of new tissues. It is essential for repair of body cells and tissues. It is required for acid-base balance (regulate pH level) in the body. It has a role in the working of the body's muscular system and is therefore important to the beating of the heart.

The deficiency of phosphorus is relatively uncommon. Phosphorus deficiency may cause bone diseases such as rickets in children and osteomalacia (softening of bones) in adults especially in pregnant women. An improper balance of phosphorus and calcium may cause osteoporosis (a disease that causes the bones to become weaker and easily broken). The symptoms of phosphorus deficiency may include poor formation of teeth, irregular breathing pattern, joint stiffness and pain.

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Biological Significance of Zinc

Zinc is an essential element. It is important for normal growth, wound healing, the nervous system, and especially for defensive (immune) system. It is needed for cell division, tissue growth and repair. It plays a role in the breakdown of carbohydrates. It enhances the action of insulin. It is important for proper sense of taste and smell. A lack of zinc may be associated with skin problems, slow healing of wounds, loss of appetite, weight loss and decreased ability to taste food.

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Hormones and Their Functions

Hormones are chemical substances that act as a chemical messengers in the body. They are secreted by specific organs and glands and are travel to their target organs in the bloodstream or other body fluids. Hormones control and regulate various biological activities such as growth, development, reproduction, energy use and storage, and water and electrolyte balance. For example, insulin is a hormone that is secreted from pancreas and helps to lower glucose levels in the bloodstream and promote the storage of glucose in liver, muscle and other body tissues. Hormones can be classified into three groups based on their chemical structure: cholesterol-derived hormones, amino acid-derived hormones and peptide (or protein) hormones.

The cholesterol derived hormones are steroid hormones. They are secreted by adrenal cortex, male and female gonads and the placenta during pregnancy.

The amino acids derived hormones are derived from the amino acids tyrosine and tryptophan. Examples of amino acid-derived hormones include epinephrine, norepinephrine and thyroxine. Epinephrine and norepinephrine are synthesized in the medulla of the adrenal glands and thyroxine is produced by the thyroid gland.

Peptide or protein hormones are made from amino acids by specialized endocrine glands. Examples of Peptide hormones are insulin, glucagon, leptin, ADH and oxytocin.

Insulin as Protein Hormone whose deficiency leads to Diabetes Mellitus

Diabetes mellitus is disease in which insulin is either not produced by the pancreas (type 1 diabetes) or is produced in insufficient amounts (type 2 diabetes). Insulin is an important protein hormone that facilitates glucose transport, promotes glucose storage, stimulates protein synthesis and enhances free fatty acid uptake and storage. Insulin is often described as a "key," which unlocks the cell to allow sugar to enter the cell and be used for energy. The insulin deficiency leaves too much sugar in the blood and causes diabetes mellitus (DM). Symptoms of diabetes mellitus include frequent urination, fatigue, weight loss, excessive thirst and hunger. Diabetes mellitus causes serious health complications including kidney failure, heart disease, stroke and loss of sight. The treatment includes changes in diet, oral medications, and in some cases, daily injections of insulin.

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Summary of Facts and Concepts

- Macromolecules are made up from small subunits, called monomers.
- Macromolecules are of two types (i) organic macromolecules (ii) inorganic macromolecules.
- Organic macromolecules are also of two types: (i) biological macromolecules (ii) non-biological macromolecules.
- Biological macromolecules are called life molecules. They are also known as biopolymers or natural macromolecules. Examples of biopolymers are: carbohydrates, proteins, lipids, DNA, RNA, etc.
- Carbohydrates are the most abundant biopolymers found on earth.
- Carbohydrates are further classified into three major classes: (i) monosaccharides, (ii) oligosaccharides (iii) polysaccharides.
- Glucose is an aldose and is known as dextrose. It is also known as grape sugar or blood sugar. It is present in honey and sweet fruits.
- Sucrose is oligosaccharides and is found in sugarcane, sugar beet and pineapple.
- Starch is polysaccharides and is present in wheat, rice, maize, potatoes and barley.
- Proteins are the building blocks of amino acids and are essential components of all living organisms.
- Lipids are high molecular mass organic compounds of animals and plants origin that are soluble in organic solvents.
- Steroids are lipids that have high molecular mass tetracyclic compounds. The most important steroid in the body is cholesterol.
- Oils and fats are the most important lipids found in nature.
- Enzymes are proteins that catalyse chemical reactions in living organisms. They are also known as biological catalysts.
- Nucleic acids are the high molecular mass biopolymers of nucleotides. They are present in the nucleus of all living cells as well as in viruses. They are the carriers of necessary hereditary information.
- Minerals are inorganic compounds that are essential in small amounts for the maintenance of good health and the prevention of a number of diseases.

Multiple Choice Questions

Q. **Select one answer from the given choices for each question:**

i) A large molecule that is made up of small repeating units is called:

(a) Isomer (b) Monomer

(c) Micromolecule (d) Macromolecule

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ii) Which one of the following is a macromolecule?
(a) Amino acids (b) Sugars
(c) Lipids (d) Proteins

iii) $C_{12}H_{22}O_{11}$ is the chemical formula of:
(a) Blood sugar (b) Glucose
(c) Fructose (d) Cane sugar

iv) The most abundant biopolymer on the earth is:
(a) Proteins (b) Lipids
(c) Carbohydrates (d) Nucleic acids

v) The reaction between fat and NaOH is known as:
(a) Hydration (b) Saponification
(c) Esterification (d) Fermentation

vi) Which one of the following is the example of conjugated proteins?
(a) Albumins (b) Histones
(c) Phosphoproteins (d) Poly-peptides

vii) Proteins are essential for:
(a) Formation of protoplasm (b) Digestion of food
(c) Manufacture of buttons (d) All of the these

viii) Which one of the following transports oxygen from lungs to the cellular tissues:
(a) Haemoglobin (b) Nucleoprotein
(c) Albumins (d) Globulins

ix) Which one of the following enzymes is present in the pancreas?
(a) Pepsin (b) Trypsin
(c) Zymase (d) Isomerase

x) The mineral, which is essential for immune system:
(a) Iron (b) Zinc
(c) Magnesium (d) Calcium

Short Answer Questions

Q.1. Why boiling points of saturated fatty acid is higher than unsaturated fatty acid?
Q.2. What do you mean by carbohydrate?
Q.3. What happens when you eat too much protein?
Q.4. Why do weightlifters take amino acids?
Q.5. Where enzymes are found?
Q.6. Where are enzymes produced in the body?

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Q.7. What are the three main functions of lipids?
Q.8. Why are lipids a better source of energy?
Q.9. Can lipids dissolve in polar solvents like water or not?
Q.10. What is the best solvent for lipids?
Q.11. What are the two main types of nucleic acids?

Long Answer Questions

Q.1. What is biochemistry? Discuss in four to five lines.
Q.2. What are carbohydrates? Explain briefly.
Q.3. Explain various classes of carbohydrates.
Q.4. Write down main functions of carbohydrates.
Q.5. What is the Nutritional Importance of Carbohydrates?
Q.6. What are proteins? Describe different classes of proteins.
Q.7. Write a short note on the properties of proteins. Discuss the importance of protein.
Q.8. What are enzymes? Explain the role of enzymes as a biocatalyst.
Q.9. What are the factors that affect enzyme activity? Discuss.
Q.10. What are the commercial uses of enzymes.
Q.11. What are lipids? Describe the classification of lipids.
Q.12. Explain the structure of lipids.
Q.13. Explain briefly the physical and chemical properties of lipids.
Q.14. What is the nutritional and biological importance of lipids?
Q.15. What are nucleic acids? What are the structural components of DNA and RNA?
Q.16. What are sources and biological significance of minerals? Describe briefly.

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Chapter 22

Industrial Chemistry

Major Concepts

22.1 Introduction: Introduction to Chemical Process Industry and Raw Materials used.
22.2 Safety Considerations in Process Industries
22.3 Dyes
22.4 Pesticides
22.5 Petrochemicals
22.6 Synthetic Polymers (PVC and Nylon)
22.7 Cosmetics: Lipstick, Nail Varnish and Remover, Hair Dyes

Learning Outcomes:

Students will be able to:

- Discuss the importance of the chemical industries in the economy of Pakistan. **(Analyzing)**
- Describe the raw materials available in Pakistan for various chemical industries. **(Applying)**
- Describe the chemical processes of addition and condensation polymerization. **(Understanding)**
- Interpret difference between petrochemical and chemicals derived from them. **(Understanding)**
- Describe the fractional distillation and refining of Petroleum. **(Understanding)**
- List the various raw materials for Petrochemical industry. **(Analyzing)**
- Identify the important fractions. **(Analyzing)**
- Describe the basic building block processes in Petrochemical technology. **(Understanding)**
- Describe the Petrochemical process technology. **(Understanding)**
- List some major petrochemicals. **(Applying)**
- Discuss types and applications of hair dyes. **(Applying)**
- Describe the formation and uses of PVC and Nylon. **(Applying)**
- Describe preparation and applications of various cosmetics like nail varnish, nail polish remover and lipsticks. **(Understanding)**
- Describe types and applications of synthetic adhesives. **(Understanding)**

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Introduction

Industrial chemistry is the branch of chemistry which is concerned with using physical and chemical processes towards the transformation of raw materials into useful and profitable products. These products are used both as consumer goods and as intermediates for the manufacture of other, more complex products, such as household appliances, automobiles etc. It plays an important role in our society. It has increased the standard of living of people. Life at present without the benefits of industrial chemistry would be problematic and of low quality. Industrial chemistry is also helpful in bringing prosperity of the nation by increasing the exports, which helps in bringing wealth and earning valuable foreign exchange for the country.

22.1 Introduction to the Chemical Industry and Raw Materials Used

22.1.1 Introduction to Chemical industry

The branch of economic activity that is concerned with the processing of raw materials and manufacture of goods in factories is known as industry. The industries that produce chemicals are called chemical industries. They convert raw materials such as oil, natural gas, air, water, metals, and minerals into thousands (more than 70,000) different products that we use in our day-to-day life.

The chemical industry has touched all our aspects of life like agriculture, environment, food, hygiene, décor, transportation etc. The chemical industry provides:

i) The chemicals such as preservatives, taste enhancers and flavours play an important role in our food. These chemicals help the food to be edible and increase the shelf life (the period of time that a product can be stored and remain fresh, useful or suitable for consumption).

ii) Fertilizers and pesticides to the farmers, which are essential for the crop production.

iii) Polymers and plastics, which are used in clothing, home décor, PVC piping, water tanks and many other things.

iv) Medicines and drugs for saving life of peoples and animals.

v) Toiletries such as soaps, detergents, shampoos, body wash, face wash, toothpaste, toothbrush, deodorant and many more products that we use every day.

The chemical industry is a very important contributor to the wealth of a country. The chemical industry has many challenges which must be overcome in order to help society to maintain and improve its standard and sustainable way of living.

In the Pakistan the average growth in chemical industry sector is recorded to about 10.01% during 2014-15 and 2015-16 eras. The major chemical industries of the

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country include sulphuric acid (the king of chemicals), soda ash, caustic soda, paints, varnish, petrochemicals, polymer and plastic products, fertilizers, cement, limestone, gypsum, soaps and many more.

The table 22.1 shows some important chemical sector products (Source: Economic Survey of Pakistan, 2015-16) so the reader can imagine the quantity of their production.

Table 22.1: Production of Selected Items

Year	Soda Ash (Tonnes)	Sulphuric Acid (Tonnes)	Caustic Soda (Tonnes)	Chlorine Gas (Tonnes)	Plants & Varnishes (Tonnes)	Polishes, Creams & Footwear (mln. Grams)
2014-15	325.6	50.5	127.7	13.4	33142	675.1
2015-16	345.6	63.5	161.9	12.2	40162	681.9

Mostly these products are used up inside the country and saves up the valuable foreign exchange, but some amount is also exported and thus foreign exchange is earned bringing up the prosperity of the country.

22.1.2 Raw Materials used in Chemical Industries

All chemicals are derived from raw materials available in nature. The price of chemicals depends on the availability of their raw materials. Major chemical industries have therefore developed around the most plentiful raw materials. The natural environment is the source of raw materials for the chemical industry.

Raw Materials from the Atmosphere

The atmosphere is a useful source for raw materials. The six important industrial gases that are nitrogen, oxygen, argon, neon, krypton and xenon are separated from liquid air by fractional distillation. Nitrogen is the most abundant gas and oxygen is the second most abundant gas found in the atmosphere. The other gases are found in much smaller proportions.

Raw Materials from the Hydrosphere

Seawater is also a useful source of raw materials. Several useful substances such as sodium chloride, magnesium, bromine and sodium hydroxide are obtained from seawater. Sodium chloride is an important raw material and is obtained by evaporating it out from sea water. The electrolysis of aqueous solution of sodium chloride (brine) produces three useful products that are hydrogen, chlorine and sodium hydroxide. The electrolysis of molten sodium chloride produces two useful products that are sodium and chlorine.

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Raw Materials from the Lithosphere

Lithosphere provides minerals. Minerals are natural compounds formed through geological processes. Minerals are very important to us because many of the elements such as gold, silver, copper, aluminium and iron are obtained from the earth's crust in the form of mineral ores. They are used to make automobiles, airplanes, computer chips, windows and many more valuable things of our interest. In addition to minerals and ores, the products obtained from lithosphere are coal, natural gas and crude petroleum. They are important in meeting our energy needs.

Lithosphere is a source of many valuable gemstones such as diamond, amethyst, etc. Gemstones are used in jewellery and other adornments.

Raw materials from the biosphere

Before industrialization, we got a majority of our materials from the biosphere. Now it is estimated that we get 70% of all the materials from the lithosphere. The oils, fats, waxes, resins, sugar, leather, cotton, wool, silk and other natural fibres are examples of products obtained from biosphere.

22.2 Safety considerations in Process Industries

Chemical industries during the manufacture of materials involve the processing of reactive chemicals, flammable liquids, vapours, gases and powders. The safety record of the chemical industry is good but uncontrolled fires, explosions and chemical reactions can result in hazardous situations. A strategy is required that ensures that the chemical manufacturing activities are carried out safely. The objective of the strategy is to establish and maintain safe manufacturing practices in a manner that is compatible with the plant design, the operating conditions, production demands, commercial requirements and economic factors.

The following safety considerations will help you to ensure the health and safety of workers and eliminating chances of damage to machinery and equipment in the process industries.

i) The proper safety training should be given to all workers prior to permitting them to go to work.

ii) Government has to make number of legislations in order to ensure industrial safety.

iii) The safety committee should be made that can help in creating safety consciousness.

iv) Increase the communication in the workplace. This will encourage employees to communicate about potential problems effectively with one another. This can make the work place safer by reducing potential hazards.

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v) Take regular breaks while working in industry. Taking regular breaks help you stay fresh and able to stay more alert when working.

vi) Use tools and machines properly and avoid shortcuts. Shortcuts may lead to workplace injury. Furthermore, regularly clean and inspect tool and equipment to ensure that it is safe.

vii) Keep clear access to equipment shutoffs in case you need to quickly stop them from functioning. In addition, place equipment in proper storage areas after use. It will help keep the work area and emergency exits clear.

viii) Wear the correct safety equipment such as safety googles, hard hats, gloves or full-face mask for a task. Additionally, check that your safety equipment is safe. It significantly reduces your chance of getting injured.

ix) Extra care should be made for the receipts, storage, handling and disposal of chemicals and other hazardous materials.

x) Fire extinguishers and fire buckets should be provided at all fire hazardous locations. The extinguishers should be inspected, serviced and maintained.

xi) Inspection and maintenance of your equipment should be scheduled regularly so that your equipment is not only safe to use, but its lifetime is also extended.

xii) Clear passageways and clean spills to prevent employees from tripping or slipping. Likewise, check your workplaces to make sure there are no holes, loose boards, or nails projecting from the floor.

xiii) Combustible materials should be stored away from sources of ignition. Furthermore, store combustible waste in metal containers and discard it daily.

Industries that have increased risk of workplace accidents must be extra attentive about potential workplace hazards. They have to implement key safety measures to keep their workers happy, healthy and productive.

22.3 Dyes

Dyes are organic compounds that are widely used for imparting colour to various substrates such as paper, leather, fur, hair, drugs, food, cosmetics, waxes, greases, plastics and textile materials.

Dyes are normally water-soluble or water dispersible organic compounds that are capable of being absorbed into the substrate destroying the crystal structure of the substance. The dye molecules are usually chemically bonded to the surface and become a part of the material on which it is applied. The dyes must have high colour intensity. The colour intensity of the dye molecule depends on how strongly it absorbs radiation in the visible region, which extends from 400 to 800 nm. The dye should be resistant to the action of water, dilute acids and alkalies (all the detergents and soaps are alkaline in nature).

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22.3.1 Chemical Composition of Dye

A 'ye is made up of two kinds of parts: Chromophores and Auxochromes.

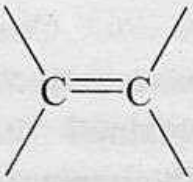
Chromophores

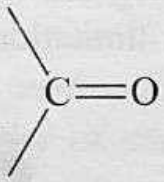
They are unsaturated groups. An organic compound looks coloured due to presence of these groups. The important chromophores are:

i) Nitroso group, —NO

ii) Nitro group, $-NO_2$

iii) Azo group $-N=N-$

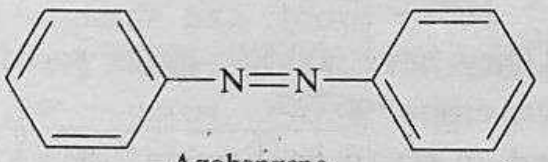
iv) Ethylene group 

v) Carbonyl group 

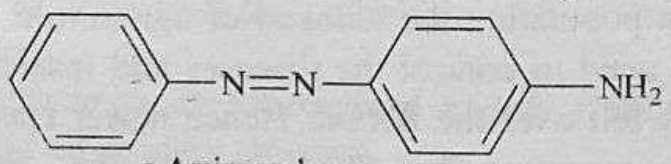
The intensity of colour increases with the number of chromophores or the degree of conjugation. The compounds that have chromophore groups are called chromogen.

Auxochromes

The groups that deepen or intensify the colour in the presence of chromophore are called auxochromes (colour intensifying groups). Example of auxochromes are hydroxyl group (—OH), carboxyl group (—COOH), sulphonic acid group ($-SO_3H$), amino group ($-NH_2$), secondary amine group (—NHR) and tertiary amine group ($-NR_2$). These groups impart no colour in the absence of chromophore. A chromogen without an auxochrome can never act as a dye. For example, azobenzene although red coloured yet is not a dye; on the other hand, *p*-amino azobenzene is a yellow dye.



Azobenzene



p-Aminoazobenzene

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22.3.2 Classification of Dyes

There are several ways for classification of dyes. They are classified based on their source, application, structure and nature of their respective chromophores.

Classification Based on Source of Dyes

There are two types of dyes on the basis of source: natural dyes and synthetic dyes.

Natural Dyes

The dyes derived from biological sources such as plants (roots, berries, bark, leaves, seeds, stem, and flowers), insects (cochineal, lac and tyrian purple), or minerals (iron oxide and buff) are called natural dyes. Other organic sources include fungi and lichens. The prominent examples of natural dyes are alizarin (red dye) and indigo (blue dye). Logwood is a natural dye obtained from plants. Tyrian purple is obtained from animals and Prussian blue is an inorganic dye obtained from naturally occurring minerals. The natural dyes have the limitations that they have limited shades and are not durable.

Synthetic Dyes

The man-made dyes that are manufactured in the laboratory or industry are called synthetic dyes. These dyes are made from petroleum, sometimes in combination with mineral-derived components. The first man-made organic aniline dye, mauveine, was discovered by William Henry Perkin in 1856. Synthetic dyes are used everywhere in everything from clothes to paper and from food to wood. This is because they are cheaper to produce, brighter, more colour-fast, and easy to apply to fabric. Examples are acid dyes, azo dyes, basic dyes, mordant dyes, etc.

Keep in Mind

Mordant dye, a colourant that combines with dye and fibre. They are available commonly in the form of salts from metals such as chromium, tin, copper, aluminium and iron. The metal ion acts as a bridge between the dye and fibre. These dyes are economical and are generally used to produce dark shades such as dark blues, dark greens and blacks. They are most readily used to dye the natural protein fibres, particularly wool; and sometimes the synthetic fibres particularly nylon.

22.4 Pesticides

The pesticides are the certain chemicals used to control pests, insects, weeds, fungus etc. They are generally used on fruit, vegetable and horticulture crops.

Although traditional pest control methods were in application since long in history, but with the increase in human population the demand of agriculture based food stuff increased many times and a need to control the diseases and insects that destroy a large part of vegetative crops felt over the period. Hence newer chemical methods were developed for the purpose. In this respect the famous

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Dichlorodiphenyltrichloroethane (DDT) was synthesized in 1943, which was found to be effective against many insects like mosquitoes. Due to its hazardous nature DDT is no longer used now a days, and other chemicals of similar nature but with more safety nature were synthesized of which Aldrin, dieldrin, heptachlor, mirex, chlordane, biphenanthrine, tetramethionineetc. are important which have targeted action rather than global insecticidal nature, that is they control only desired species and do not affect the good helping insects and pests.

Classification of Pesticides

The Pesticides are classified on the basis of their action on specific species that spread disease or affect the crops. Thus some important types of pesticides are:

Insecticides: The insecticides are the substances that are used to control insects.

Fungicides: The fungicides are the substances that are used to control the fungus.

Herbicides: These are the chemicals that are used to control unwanted herbs in the crops.

Miticides: The miticides are used to kill mites and ticks of the crops.

Rodenticide: A large quantity of crop is damaged by the rodents like rats, mice, raccoons. Moreover birds and big mammals also affect the crops adversely. These are controlled by the use of chemicals called rodenticides.

Nematicides: These are the chemicals that control the action of harmful nematodes. The nematodes are tiny hair like worms that live in earth and feed on plant roots and the juices from plant roots.

Repellents: These are certain chemicals that repel the harmful pests, insects and other mammalians.

22.5 Petrochemicals

The chemicals derived from petroleum products and used for a variety of commercial purposes are called petrochemicals.

Petrochemicals can be converted into thousands of industrial and consumer products, including plastics, paints, rubber, pesticides, cosmetics, fertilizers, detergents, dyes, textiles and solvents.

22.5.1 Raw Materials for Petrochemicals

A raw material, also known as a feedstock or most correctly unprocessed material, is a basic material that is used to produce goods, finished products, energy, or intermediate materials which are feedstock for future finished products.

Petrochemicals are derived mainly from two feedstocks that are natural gas liquids and oil refinery streams.

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Natural Gas Liquids (NGL)

Natural gas liquids are obtained from natural gas processing plants. They are mainly ethane, propane and butanes. They are cracked at high temperatures to yield the primary petrochemicals such as ethylene, propylene, butylenes and butadiene.

Oil Refinery Streams

Oil refinery streams are obtained from the fractional distillation of crude oil. They include naphtha, kerosene oil or gas oil. They are cracked to produce higher ratios of propylene, butylenes and butadiene plus the aromatic products benzene, toluene, xylenes along with other co-products. Primary petrochemicals are reacted to form secondary petrochemicals, other chemical products, or polymerized to form synthetic resins. These in turn are incorporated into a great variety of industrial and consumer products.

Interesting Information

Feedstocks are the raw hydrocarbons obtained from crude oil refining by distillation, thermal and catalytic processes. Natural gas and refinery products are the major source of feedstocks for petrochemicals.

Primary raw materials are naturally occurring substances that have not been subjected to chemical changes after being recovered. Examples of primary raw materials for petrochemicals include: olefins (ethylene, propylene and butadiene) aromatics (benzene, toluene, and xylenes); and methanol.

Secondary raw materials or intermediates are generally produced by chemical conversion of primary raw materials to form more complicated derivative products. Example of secondary raw materials for petrochemicals include ethylene glycol, polyvinyl acetate, polyvinyl chloride, polyethylene resins, phenol formaldehyde resins, etc.

Final products are obtained from secondary raw materials. Examples are detergents, dyes, cosmetics, solvents, polymers, fertilizers, etc. Final products satisfy our basic needs (clothing, shelter, food, health, etc.) and also provide luxury consumer items.

Feedstock ⇒ Primary petrochemicals ⇒ Secondary petrochemicals ⇒ Final products

22.5.2 Classification of Petrochemical Feedstocks

Petrochemical feedstocks can be classified into three general groups: olefins, aromatics and synthesis gas.

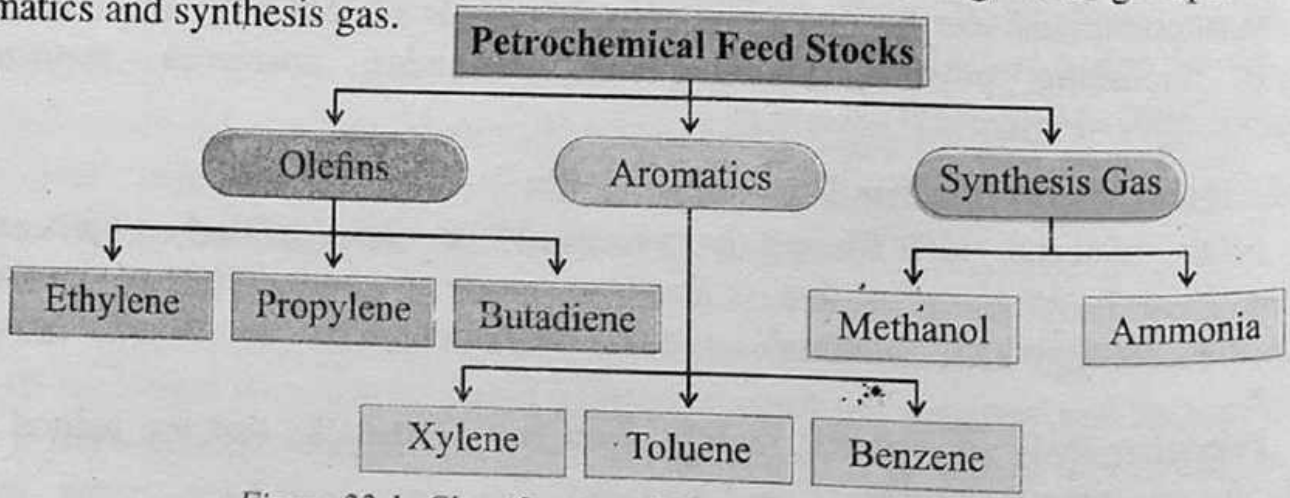


Figure 22.1: Classification of Petrochemical Feed Stocks

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Olefins

The major components of olefins are ethylene, propylene and butadiene. Ethylene is used in the manufacture of antifreeze, detergents, plastics and synthetic rubber. Propylene is used in the manufacture of resins, fibres and numerous other chemical products. Butadiene is widely used in the production of synthetic rubbers and polymer resins.

Aromatics

The major components of aromatic hydrocarbons are benzene, toluene and xylene. These aromatic petrochemicals are used in manufacturing of secondary products like synthetic detergents, polyurethanes, plastic and synthetic fibres.

Synthesis Gas (Synthetic Gas)

Synthesis gas comprises of mixture of carbon monoxide and hydrogen. This mixture is used in the manufacture of ammonia and methyl alcohol. The ammonia is further used in the production of urea fertilizer.

22.6 Synthetic Polymers

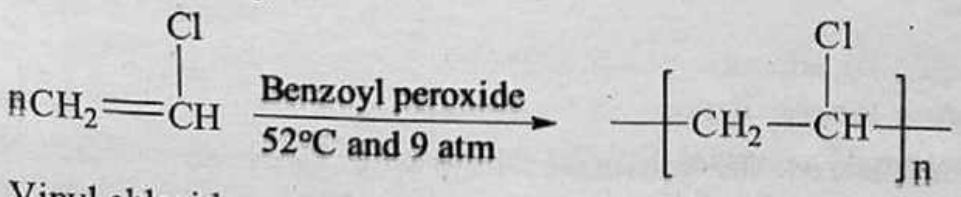
Polymers or so-called macromolecules are high molecular mass compounds which are formed either by the addition of many smaller molecules (monomers), as polyvinylchloride (PVC), or by the condensation of many smaller molecules (monomers) with the removal of water or alcohol, as nylon. The process by which monomers are converted into polymers is called polymerization. Polymers may be divided into two types that are natural polymers and synthetic polymers.

Natural polymers also known as biopolymers are derived from natural sources. Examples of natural polymers are silk, rubber, cellulose, wool, starch, proteins, DNA, etc.

Synthetic polymers are man-made polymers and are prepared by a chemical reaction, often in a lab. Examples of synthetic polymers are polyethylene, PVC, synthetic rubber, nylon, etc.

22.6.1 Formation and Uses of PVC

Polyvinyl chloride commonly abbreviated as PVC is formed by the addition of vinyl chloride monomer units at 52°C and 9 atmosphere pressure in the presence of benzoyl peroxide catalyst.



Vinyl chloride

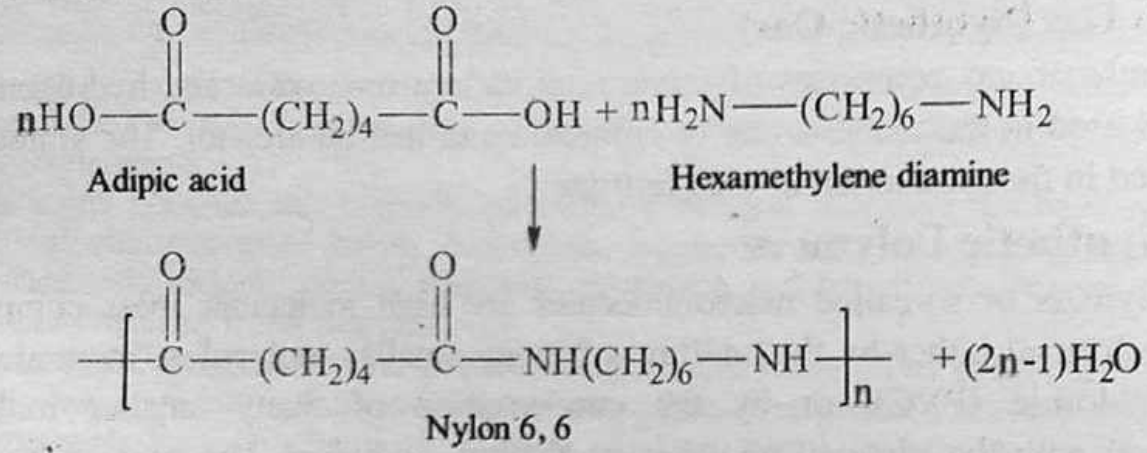
Polyvinyl chloride

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PVC is the most widely used plastic after polyethylene. It is used in the manufacture of pipes, floor coverings (tiles), bottles, electrical wiring and cables, window frames, blood storage bags, stationary, seat coverings, packaging, credit cards, synthetic leather, rain coats, shower curtains and many other useful materials.

22.6.2 Formation and Uses of Nylon

Nylons are high molecular mass polyamides. They are of various types such as nylon 4,6; nylon 6; nylon 6,6; nylon 6,12; nylon 12; etc. They are the most popular synthetic polymers. Nylon 6,6 (read as nylon six, six) is the well-known example of nylon. It is prepared by the condensation reaction of adipic acid and hexamethylene diamine at about 252°C.



Nylon 6, 6

Nylon 6,6 got its name from its monomers, adipic acid and hexamethylene diamine, each of them providing six carbon atoms.

Nylon has incredible properties. They have high strength, medium stiffness and resistance to high temperature (+85°C), fuel and lubricants and most of the chemicals. It is also used in collaboration of other materials (e.g. with cotton) for more strength and durability of the product and is believed to be as strong as the steel metal.

Nylons are used:

i) In the manufacture of carpets, textile fibres and bristles of brushes
ii) In dress socks, swimwear, activewear, shorts, track pants, windbreakers and bedspreads.
iii) For making elastic hosiery
iv) As a substitute for metals in bearings and gears
v) For food packaging
vi) For making rope.
vii) In tyre cord.

22.7 Cosmetics

We define cosmetics as: the substances used to enhance your natural beauty and to promote good health. The cosmetics may also be defined as: any substance to

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be rubbed, poured, sprinkled, or sprayed on or introduced into or applied to any part of the human body, for cleaning, beautifying, promoting- attractiveness or altering the appearance. Cosmetics are useful for making the skin feel soft, healthy and flawless. Colour cosmetics products are designed to add colour to the skin and thereby enhance the appearance of good health and youth. The colours (pigments) make prominent the cheeks, lips and eyes. These are the colours that make cheeks rosy, lips ruby and eyes smoky. Colour cosmetics applied to the face to enhance its appearance are often called make-up or makeup (For example, lipsticks, eye liners, nail varnish, powder, etc.). Recent research has shown that makeup helps in protection from harmful rays of the sun. The first known people who used cosmetics to enhance their beauty were the Egyptians. Currently cosmetics play an important role for both men and women. Cosmetics are available in the form of creams, lipsticks, shampoos, hair dyes, body wash, eye liners, eye shadows, perfumes, sunscreens, talcum powder, toothpastes, nail varnish and remover, etc.

22.7.1 Lipsticks

Lipstick is one of the inexpensive cosmetic products and is most widely used by women to give an attractive colour and appearance to lips. They are manufactured as moulded sticks. They are made from waxes, oils, pigments and emollients. Other important additives are antioxidants, preservatives and fragrances. The waxes used include beeswax, carnauba, candelilla wax, and ozokerite. Oils used include castor oil, coconut oil, mineral oil, vegetable oil or petrolatum (petroleum jelly). Some of the important emollients that are used in lipsticks are cocoa butter, shea butter, vitamin E, and aloe vera.

The wax gives lipstick its shape and ease of application. Oils are added to reflect light and provide shine. Oils give lipstick the ability to be easily applied, keeping the wax soft enough for it to be spread easily. Pigments are the colours. They give colour to the lipsticks and improve the appearance of the lips. Emollients are used to soften and smooth the surface of lips.

Other important additives are antioxidants and preservatives. Antioxidants are used to prevent the lipsticks from becoming rancid. Preservatives are used to extend the shelf life of lipsticks. Many manufacturers add little fragrance (perfume) to give it a nice smell when it is being applied.

22.7.2 Nail Varnish

Nail varnish is applied to the fingernails or toenails to colour them or make them shiny. It is used mainly by women. Nail varnish protect and beautify the nail plates. The correct name of nail varnish is nail lacquer. However, the terms nail varnish, nail polish, nail enamel, nail paint and nail lacquer are used interchangeably.

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These products are sold in liquid form in small bottles and are applied by painting the nail with a tiny brush. Nail varnish is a flexible lacquer that does not easily crack and flake with nail movement. People want brands of nail varnish that are easy to apply, dry quickly, glossy looking and last a long time without chipping.

There is no single formula for nail varnish. Nail varnish is made up of many different chemicals. The four major ingredients in most nail varnish brands are resins, plasticizers, organic solvents and colouring agents.

Resins, types of polymers, are the thickening and hardening agents that serve as colourless nail protector. There are two types of resins that are used in nail varnish, which are hard glossy resins (e.g. nitrocellulose) and soft pliable resins (tosylamide / formaldehyde resin).

Plasticizers (e.g. camphor, dibutyl phthalate, adipates) make the polish more flexible after drying and increase its durability.

Solvents are used to dissolve the ingredients and make the polish spreadable. The most common organic solvents are ethyl acetate and butyl acetate. It must dry quickly to increase the ease of the nail polish application.

Colouring agents (pigments) are used to create the colour of each polish. A combination of naturally occurring and synthetic pigments are mixed together to create varying shades.

Sometimes, nail polish also contains particles such as mica, bismuth, pearl essence (guanine) and aluminium powder as sparkling and reflective particles. These particles are used to give shimmery look to the polish.

22.7.3 Nail Varnish Remover

Nail varnish (or nail polish) remover is a powerful solvent that can quickly remove polish from the nails, cuticles, and surrounding skin. Nail polish remover works by moisturizing the dried nail polish and returns it to its liquid state. Nail polish remover mainly consists of volatile organic solvents such as ethyl acetate (a common solvent for nail varnish itself) or acetone. They may contain oils, scents and colouring. Acetone is one of the main components in nail polish remover. It is found naturally in the environment and is produced in the factories. It is a colourless, flammable liquid that evaporates easily. The nail polish removers that contain acetone work very quickly and effectively. But acetone can be harmful to our nails and skins. Acetone can irritate nose, eyes, throat, lungs and skin. It can cause our nails to become dry and brittle. Acetone can also remove artificial nails made of acrylic or cured gel. It is therefore, necessary to find the mild non-acetone nail polish remover to make sure the strongest, healthiest nails possible. The industry has formulated many acetone alternatives for polish removers that contain a variety of different solvents. Ethyl acetate and butyl acetate are the two most commonly used solvents for nail polish remover currently. Both solvents are colourless, volatile liquids. These solvents are less harsh and toxic than acetone.

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22.7.4 Hair Dyes

Hair dyes (also hair colours) are chemicals that are used to change the hair colour. The preferred professional term for hair dye is hair colour.

The first safe commercial hair colour was created in 1909 by French chemist, Eugene Schuller, using the chemical paraphenylenediamine. This compound is present in all colouring products along with ammonia and peroxide in varying proportions. Most hair dyes, in general, contain dyes, modifiers, antioxidents, alkalizers, soaps, ammonia, wetting agents, fragrance, and a variety of other chemicals used in small amounts that impart special qualities to hair (such as softening the texture) or give a desired action to the dye (such as making it more or less permanent). The dye chemicals are usually amino compounds. Metal oxides, such as titanium dioxide and iron oxide, are often used as pigments as well.

Types of Hair Dyes

Hair dyes are classified by the types of colour molecules used and the length of time that they last. There are three main types of hair dyes and they are temporary hair dyes, semi-permanent hair dyes and permanent hair dyes.

Temporary Hair Dyes

These dyes only coat the surface of the hair. They cannot penetrate into the hair shaft. They are easily removed with one or two washings. Temporary hair dyes do not contain ammonia, meaning the hair shaft is not opened up during processing and the natural colour of hairs is retained once the product washes out.

Semi-permanent Hair Dyes

Semi-permanent hair dyes have smaller molecules than those of temporary hair dyes and so can penetrate the surface of the hair into the cuticle layer. These dyes are generally not formulated with ammonia, so they should not require any development. These dyes will last for five to ten washings and so last longer than temporary dyes.

Permanent Hair Dyes

The most common hair colour is permanent hair colouring. These involve a change in hair colour that is "permanent" or at least until new hair grows. They contain ammonia and hydrogen peroxide. Ammonia opens the cuticle and hydrogen peroxide used as developer. The dyes used are actually dye precursors. Their molecules are monomers and are smaller than that of semi-permanent and permanent hair dyes. They are able to penetrate into the hair all the way to the cortex. The shades of permanent hair dyes are often more natural-looking. However, permanent hair dyes can be more damaging to your hair. The chemicals used are stronger and the mixture usually has to be left on for a longer period of time.

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Permanent hair dyes are usually packaged with a developer, which is in a separate bottle. The developer is most often based on hydrogen peroxide, with the addition of small amounts of other chemicals.

Side Effects of Hair Dyes

The chemicals used in hair dyes remain at safe levels. However, some of the ingredients found in hair dye such as resorcinol and parabens are suspected to be endocrine-disrupting chemicals.

22.7.5 Adhesives

An adhesive, also known as glue, is a substance that is applied to one surface, or both surfaces, of two separate objects that binds them together and resists their separation. You use an adhesive to pack gifts, re-join broken materials, connect parts of toys, mend shoes, or paste a photograph into an album. Adhesives have been used successfully in a variety of applications for centuries. Currently, adhesives are more important than ever in our daily lives, and their usefulness is increasing rapidly.

Types of Adhesives

There are two types of adhesives on the basis of origin: natural adhesives and synthetic adhesives.

Natural Adhesives

Natural adhesives are those adhesives that are produced or extracted from natural resources such as plants or animals. Examples of natural adhesives are starch, dextrin, casein glues, blood albumin glue, natural gums, bees wax and resin (tree sap). They are inexpensive, easy to apply and have a long shelf life. They develop tack quickly but have low strength properties. Natural adhesives have been used since earliest times. Ancient Egyptians used flour paste in the making of papyrus (paper reed) and glue made from animal skin and bones for woodworking. Natural adhesives are still popular and useful but have been replaced for most applications by synthetic adhesives. Natural adhesives are still used in corrugated board, envelopes, bottle labels, book bindings, cartons, furniture, and laminated film and foils.

Synthetic Adhesives

Synthetic adhesives are those that are not found in nature and are designed and manufactured by chemists in the laboratory or factory. Synthetic adhesives can be classified on the basis of chemical composition as thermosetting, thermoplastic, elastomeric or alloys (hybrid) of these.

Thermosetting adhesives

They are essentially infusible and insoluble. They show good heat and solvent resistance. These materials have good creep (flow-under-load) resistance. They show little elastic deformation under load at elevated temperature.

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Thermosetting adhesives are recommended for use at temperatures from 93–260°C. They are used for high load assemblies and severe service conditions such as heat, cold, radiation etc. Examples are epoxies, polyesters, polyamides and phenolics. Most materials can be bonded with thermosetting adhesives, but the emphasis is on structural applications. These adhesives are usually available as solvent-free liquids, pastes and solids. They are available as one-part and two-part systems. The two part systems have longer shelf lives.

Thermoplastic Adhesives

They are fusible and soluble. They can soften or melt when heated without undergoing any chemical change. These material have poor creep resistance and fair peel strength (measure of the bond strength of a material). They hardens upon cooling from a melt state, or by evaporation of a solvent. Wood glues are thermoplastic emulsions that are common house hold items. They harden by evaporation of water from an emulsion.

Thermoplastic adhesives are not usually recommended for use at above 66°C, although they can be used up to 90°C in some applications. They are normally used for low load assemblies under mild service conditions. The materials most commonly bonded are non-metallic materials, especially wood, leather, plastics and paper. They are not usually used for structural applications. Examples are polyvinyl alcohol, polyvinyl acetates (PVA), cellulose acetate, polyamides, cyanoacrylates and polyacrylates. They are available as one-part system.

Elastomeric Adhesives

Elastomeric adhesives are based on synthetic or naturally occurring polymers. They have great toughness and elongation. These adhesives are made from polymeric resins that are capable of high degrees of extension and compression. They return rapidly to their initial dimensions and shape after the load is removed. They are generally used for their high degree of flexibility and good peel strength. Their bond strengths are relatively low, but flexibility is excellent. These adhesives are used in unstressed joints on lightweight materials, so they cannot be considered structural adhesives. Most of these adhesives are modified with synthetic resins for bonding rubber, fabric, foil, paper, leather and plastic films. They are also used as tapes. Elastomeric adhesives may be

Keep in Mind

Peel strength is the measure of the bond strength (adhesive strength) of two bonded materials such as tape, rubber, plastic, textile, wood, paper, foil, plastic films and leather. The strength of bond is calculated through a peel test. Peel test is used to measure the average force required by the unit width to separate bonded materials at a constant speed. Peel tests can be performed with different angles. Peel tests at 90° and 180° are commonly used. Special equipment such as force measurement instruments and materials testing machines are used to perform these tests. The peel tests can be done on pockets, trays, cans, jars, and pouches.

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supplied as solutions in organic solvents, water dispersions, pressure-sensitive tapes and single or multiple part solvent-free liquids or pastes. Examples are natural rubber, nitrile rubber, neoprene, polysulphide and silicones.

Hybrid Adhesives

Adhesive hybrids are made by combining thermosetting, thermoplastic, or elastomeric resins into a single adhesive formulation. The thermoset resin chosen for its high strength is plasticised by the second resin which is usually a thermoplastic or elastomer, thus making the alloy tougher, more flexible and more resistant to impact. These adhesives are generally stronger over wider ranges of temperature than other adhesives. They are suitable as structural adhesives and are used where the highest and strictest end-use conditions must be met (irrespective of cost), such as in military applications. Materials bonded include metals, ceramics, glass and thermosetting plastics. They also have a tendency to bond well to oily substrates. It is believed that the oil on the substrate is adsorbed into the formulation and acts as another flexibilizer in the adhesive system. Examples are epoxy-phenolics, epoxy-nylon, epoxy-polysulphide and nitrile-phenolic.

Summary of Facts and Concepts

- Industries form the backbone of economy of a country and is directly related with the prosperity of a nation.
- An important point in establishing an industry is that the cost of the product must be low so the consumers find it easy to use it.
- To keep the cost low, the raw materials used in industries should be cheap and available easily.
- The chemical industry provides the material and chemical for most of the other industries.
- Many of the chemicals and materials (like cement, fertilizers, drugs, polymers etc.) are needed in bulk and are provided by the chemical industry sector.
- A chemical dye is a substance that is used to colour the different commercial products which makes it attractive, so the buyers like them.
- The chemical dye molecule consists of two parts, one of the part is a substance which produces the colour and is called the **"Chromogen"**, and the second part of molecule which regulates the solubility of the dye called **"Auxochrome"**.
- The pesticides are the chemicals which are used to control pests, insects, weeds, fungus and even the rodents to increase the yield of agriculture products.
- Petrochemicals are chemical derived from petroleum products. Examples of petrochemicals are rubbers, plastics, fibres, detergents, solvents and paints.

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- The prosperity of a nation is also determined by the use of its petroleum products.
- Fibres from the natural sources only cannot meet the needs of humans and artificial fibres are prepared to meet their needs.
- Polymers are the compounds which are formed by the large number of smaller repeating units called monomers.

Multiple Choice Questions

Q. Select one answer from the given choices for each question:

i) Which one of the following statements is true regarding chemical industries?
(a) Chemical industries provide medicines and drugs for saving life of peoples
(b) Chemical industries are located near automobile industries
(c) Chemical industries provide fish and plants to the farmers
(d) Chemical industries provide infra structure for industries

ii) Which of the following statements is/are correct?
(a) Herbicides are used for killing unwanted plants
(b) Nylon was first introduced as an early substitute for silk
(c) Excessive use of fertilizers is good for the fertility of soil
(d) Cotton is an artificial fibre of almost pure cellulose

iii) Adhesive that become soft on heating are:
(a) Thermosetting (b) Thermoplastic
(c) Elastomeric (d) Hybrid

iv) Natural adhesives are also known as:
(a) Bioadhesives (b) Synthetic adhesives
(c) Spray adhesives (d) Fabric adhesives

v) Which one of the following is a synthetic fibre?
(a) Wool (b) Cotton
(c) Silk (d) Polyester

vi) What is the fuel that is mostly used to run the buses, trucks and trains?
(a) Petrol (b) Diesel
(c) Kerosene (d) Bitumen

vii) Ethylene is used in the manufacture of:
(a) Fertilizers (b) Plastics
(c) Silks (d) PVC

viii) Nail polish remover contains:
(a) Benzene (b) Acetone
(c) Acetic acid (d) Benzoic acid

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ix) Henna usually gives you a shade of:

(a) Golden yellow (b) Bluish green

(c) Reddish brown (d) Light pink

x) The term petrochemical refers to the chemicals derived from

(a) Gasoline oil only

(b) Natural gas only

(c) Crude petroleum only

(d) Natural gas liquids and oil refinery streams

Short Answer Questions

Q.1. What do you know about chemical industry?

Q.2. Where do colour dyes come from?

Q.3. How do pesticides affect human health?

Q.4. What are the most commonly used pesticides?

Q.5. What are the four major ingredients in nail varnish?

Q.6. What are primary and secondary raw materials?

Q.7. Write down the name of three main fossil fuels?

Q.8. Give some of the important examples of synthetic and natural polymers.

Q.9. Name the four most commonly used cosmetic products.

Q.10. What type of nail polish remover works quickly and effectively?

Q.11. Define resins. What are the different types of resins used in nail varnish?

Q.12. Why is wax used in lipstick?

Q.13. Is there any other name for nail polish?

Q.14. What chemicals make up nail polish?

Q.15. Give names of less harsh and toxic nail polish removers.

Q.16. Name the four different types of synthetic adhesives.

Q.17. What is the difference between glue and adhesive?

Long Answer Questions

Q.1. What is industrial chemistry? Discuss the importance of industrial chemistry.

Q.2. What is the role of chemical industries in the economy of a country?

Q.3. Discuss various raw materials that are used in chemical industries.

Q.4. Explain how the lithosphere is an important source of natural raw materials for the chemical industry?

Q.5. How chemical process safety can be managed in industries?

Q.6. What are dyes? What is the chemical composition of dyes? How are they classified on the basis of origin?

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Q.7. What are pesticides? Describe its types.

Q.8. What is meant by petrochemicals? Describe different types of petrochemicals in detail.

Q.9. What are polymers? What are natural and synthetic polymers?

Q.10. Write down the formation and uses of PVC and Nylon?

Q.11. What are cosmetics? Explain the role and uses of cosmetics.

Q.12. Describe preparation and applications of lipsticks.

Q.13. Describe preparation and applications of nail varnish and nail varnish remover.

Q.14. What are hair dyes? What ingredients are most commonly used in hair dyes?

Q.15. Discuss types and applications of hair dyes.

Q.16. What are adhesives? Explain different types of adhesives.

Q.17. Explain types and applications of synthetic adhesives.

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Chapter 23

Environmental Chemistry

Major Concepts

23.1 Chemistry of the Troposphere
23.2 Chemistry of the Stratosphere
23.3 Water Pollution and Water Treatment
23.4 Green Chemistry

Learning Outcomes:

Students will be able to:

- Recognize various chemical reactions occurring in the atmosphere. **(Understanding)**
- Recognize that the release of COx, SOx, NOx, VOCs are associated with the combustion of hydrocarbon based fuels. **(Applying)**
- Outline problems associated with release of pollutants including acid rain and the formation by free radical reactions of hazardous inorganic and organic compounds e.g., PAN. **(Analyzing)**
- Describe causes and impacts of urban smog. **(Analyzing)**
- Explain greenhouse effect and global warming as resulting in climate change. **(Analyzing)**
- Explain the build upto and recognize the adverse effects of ozone in the troposphere. **(Applying)**
- Describe the role of CFCs in destroying ozone in the stratosphere. **(Applying)**
- Describe the role of ozone in the stratosphere in reducing the intensity of harmful UV radiation reaching the earth. **(Understanding)**
- List possible alternatives to the use of CFCs. **(Applying)**
- Recognize and describe various water pollutants. **(Applying)**
- Explain the various parameters of water analysis. **(Applying)**
- List some major products of the petrochemicals industry, together with their uses. **(Applying)**

Introduction

Environmental chemistry is the study of various chemical phenomena that occur in the natural places such as air, water and soil. Environmental chemistry can be defined as: the study of sources, reactions, effects, transport and fate of chemical substances in the air, water and soil as well as their effects on human health and natural environment. Environmental chemistry is related with chemistry, physics,

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agriculture, life sciences, medical sciences, public health, sanitary engineering etc.

Environment and its Segments

Environment is everything that is around us. It belongs to all the living beings and thus is, important for all. The environment consists of four segments: lithosphere (from the Greek "lithos" for *stone*), hydrosphere (from the Greek "hydor" for *water*), biosphere (from the Greek "bios" for *life*, course or way of living) and atmosphere (from the Greek "atmos" for *vapour* and "sphaira" for *globe*).

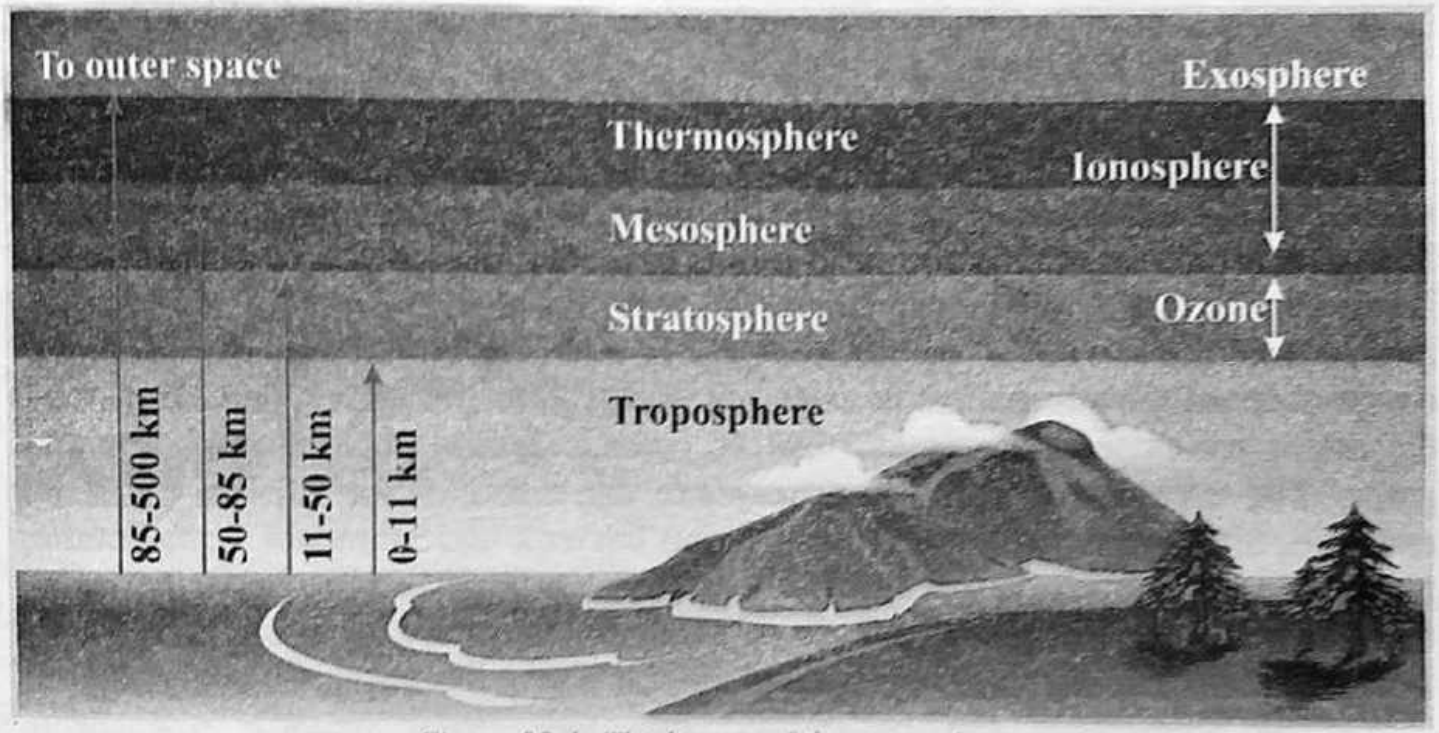


Figure 23.1: The Layers of the atmosphere

Lithosphere

The upper rigid and rocky layer of earth's crust is called lithosphere. It includes soil, earth, rocks and mountains. The soil is the most important part of lithosphere. The soil mainly consists of complex mixture of minerals, organic matter and water. Soil is used as a medium for agricultural production of crops. It extends to the depth of 100 km.

Hydrosphere

The water containing part of our earth is called hydrosphere. It includes oceans, rivers, lakes, streams, polar icecaps, glaciers and groundwater reservoirs. The earth is called blue planet because about 75% of the earth's surface is covered by water that appears blue from space. Oceans are large bodies of salt water and contain about 97% of all water on earth. Salt water is unusable by most land animals, including humans. About 2% of the earth's water is stored in glaciers and polar ice caps. However, only about 1% of the total earth's water is available as a fresh water.

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It includes surface water, rivers, lakes, streams and ground water. The fresh water is used for irrigation (30%), thermal power plants (50%), industry (12%) and for domestic purposes (8%).

Biosphere

It consists of the region of earth where all living species exist above as well as below sea level (about 10000 m below sea level to 6000 m above sea level). Thus, the biosphere denotes the entire realm of living organisms and their interactions with other three segments of the environment, viz., lithosphere, hydrosphere and atmosphere.

Atmosphere

Atmosphere is the protective layer of gases surrounding the earth. It helps in sustaining life on the earth and protecting the earth from the dangerous cosmic rays from outer space. It screens the dangerous ultraviolet radiations coming from the sun. It plays an important role in maintaining the heat balance of the earth by absorbing the infrared radiation emitted by the sun and re-emitted from the earth. The major components of the atmosphere are nitrogen (78.08%) and oxygen (20.94%), whereas the minor components are argon (0.93%), carbon dioxide (0.03%) and some trace gases. The component gases of atmosphere are essential for life on earth. For example, nitrogen is used by nitrogen fixing bacteria and ammonia manufacturing plants (for the preparation of fertilizer), oxygen supports life on earth and carbon dioxide is essential for photosynthesis of plants. Furthermore, it is a carrier of water from oceans to land. Its thickness is about 500 km above the surface of the earth.

The atmosphere can be divided into four major regions: troposphere, stratosphere, mesosphere and thermosphere.

Table 23.1: Regions of Atmosphere

Region	Altitude range (km)	Temperature range (°C)
Troposphere	0 to 11	15 to –56
Stratosphere	11 to 50	–56 to –2
Mesosphere	50 to 85	–2 to –92
Thermosphere	85 to 500	–92 to 1200

23.1 Chemistry of the Troposphere

Troposphere is the nearest to the earth's surface extending up to 11 km. It accounts for about 70% of the atmospheric mass. In this region of atmosphere, the humans live and most of the biological activities occur. In this region all the dramatic events of weather (breezes, winds, storms, clouds, lightning, rain, and sunny skies) occur. The jet aircrafts flying at an altitude of about 10 km is still in the troposphere,

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although near upper limits of troposphere. The temperature in this region decreases uniformly with increasing altitude, reaching a minimum of about −56°C at about 11 km. The important chemical species in this region are nitrogen, oxygen, carbon dioxide and water vapours. Due to the force of gravity, molecules making up the atmosphere are most concentrated near earth's surface. Atmospheric pressure decreases with increasing altitude. The average value of pressure at sea level is 760 torr and at 100 km altitude is 0.0023 torr. The troposphere is the most easily disturbed by human activities and has the greatest effect on the earth's surface conditions. Among those effects, air pollution, acid rain, and global warming are particularly important.

Keep in Mind

Primary pollutants are directly emitted from a source. Examples are total suspended particulates (tiny particles of smoke, dust, fumes, etc.) and oxides of carbon, nitrogen and sulphur. They are emitted from chimneys of industrial units and exhaust of automobiles. **Secondary pollutants** are created in the atmosphere as a result of chemical reactions such as oxidation, photochemical reactions, and oxidation that involve primary pollutants. Examples are: hydrogen peroxide, ozone, peroxyacetyl nitrate (PAN), sulphuric and nitric acids and their salts.

23.1.1 Chemical Reactions in the Atmosphere

The atmosphere contains various gases. The numerous chemical and photochemical reactions occur in the atmosphere. The chemical reactions initiated by sunlight are called photochemical reactions. These reactions depend upon composition, temperature, pressure, humidity and intensity of sunlight. Evidently different processes will be observed under variable atmospheric conditions. Diatomic oxygen (O_2) plays an important role in the troposphere and ozone (O_3) plays an important role in the stratosphere.

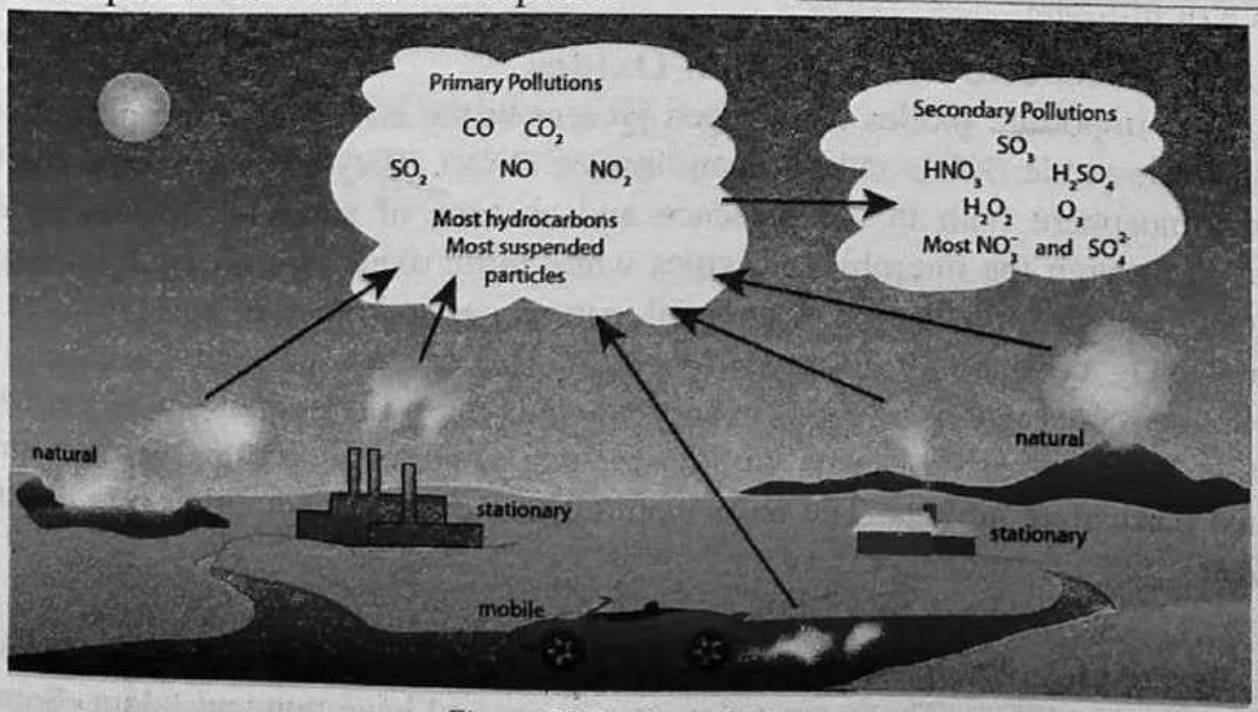


Figure 23.2: Air pollution

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The important chemical reactions that occur in the atmosphere are:

23.1.1.1 Reaction of Oxygen

About 21% by volume of the gas in the atmosphere is oxygen. Oxygen plays a key role in the atmosphere (troposphere) because it is very reactive and acts as a strong oxidizing agent. The presence of large amount of oxygen makes the atmosphere thermodynamically oxidizing. In the atmosphere, oxygen is produced by photosynthesis and this oxygen is consumed by animals through respiration. The important chemical reactions of oxygen in the atmosphere are:

Rusting of iron

Iron and steel rust when they come into contact with oxygen and water vapours.

Iron + Oxygen + Water $\longrightarrow$ Hydrated iron (III) oxide (rust)

Formation of ozone

Diatomic oxygen absorbs an ultraviolet photon and produces two free radicals such as oxygen atoms.

$$O_{2(g)} \xrightarrow{h\nu} O^{\bullet}_{(g)} + O^{\bullet}_{(g)}$$

These free radicals react with another molecule of diatomic oxygen to produce triatomic oxygen (ozone).

$$O^{\bullet}_{(g)} + O_{2(g)} + M(N_2 \text{ or } O_2) \longrightarrow O_{3(g)} + M$$

Where, M is the third body that absorbs excess energy liberated by the ozone formation, and thereby stabilize the ozone in the stratosphere. The third body may be oxygen or nitrogen.

23.1.1.2 Reaction of Nitrogen Oxides

The important oxides of nitrogen present in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). They undergo many reactions in the atmosphere both in the presence and absence of sunlight. Nitrous oxide is produced through the microbial activities while nitric oxide and nitrogen dioxide are produced from the combustion of coal, oil, natural gas and other human activities. The NO and NO_2, collectively designated as NO_x. Due to photochemical reactions, NO and NO_2 are converted to HNO_3. This nitric acid is removed from air as acid rains. On the other hand, the HNO_3 reacts with bases such as ammonia and particulate lime to produce particulate nitrates. The particulate nitrates comes down either by rain fall or as a dust.

23.1.1.3 Reaction of Sulphur Oxides

The oxides of sulphur present in the atmosphere are sulphur dioxide (SO_2) and sulphur trioxide (SO_3). These are colourless gases and have pungent odour. Some of

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the oxides of sulphur are originated from biological processes and from volcanoes (67%). The oxides of sulphur are also produced by burning of fuels like coal and petroleum.

$$S + O_2 \longrightarrow SO_2$$

The SO_2 is then oxidized to SO_3 in the atmosphere.

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3$$

The sulphur trioxide, in the presence of water vapours, is converted to sulphuric acid (H_2SO_4).

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The rate of photochemical oxidation of sulphur dioxide leading to the formation of H_2SO_4 aerosol is greatly accelerated in the presence of olefins and oxides of nitrogen which are present in photochemical smog.

23.1.1.4 Reaction of Organic Compounds

Generally, organic compounds such as hydrocarbons, aldehydes and ketones undergo redox and photochemical reactions. The reactions of organic compounds through a series of steps produce secondary pollutants in the atmosphere. The organic compounds in the lower atmosphere produce photochemical smog.

23.1.2 Air Pollutants (CO_x, NO_x, VOCs, SO_x, O_3, PANs) and their Harmful Effects

Pollutants can be defined as any substance in air that has harmful effect on living organism or their environment. Some of the important air pollutants are: (i) oxides of carbon (ii) oxides of nitrogen (iii) volatile organic compounds (VOCs) (iv) oxides of sulphur (v) ozone.

23.1.2.1 Oxides of Carbon (CO_x)

The oxides of carbon present in the atmosphere are carbon monoxide (CO) and carbon dioxide (CO_2).

Carbon Monoxide

Carbon monoxide is a colourless, odourless and tasteless gas. It is lighter than air and is insoluble in water. It is produced by:

(i) Incomplete combustion of fuel, namely coal, gas, charcoal, oil etc.

$$2\,C + O_2 \longrightarrow 2\,CO$$

(ii) It is also produced by forest fires and incineration of biomass (burning of forest debris, bushes, crop residue, weeds, and vegetation).

(iii) Industrial operations such as petroleum refining, paper industry, coal mining, electric and blast furnaces.

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Harmful Effects of CO

It is extremely toxic and causes suffocation if inhaled. Exposure of high concentration of CO causes headache, fatigue, unconsciousness and eventually death may occur if such exposure is experienced for a longer time.

Carbon Dioxide

It is a colourless gas. It is odourless at low concentrations and has a sharp and acidic odour at high concentrations. It is soluble in water. It is added to the atmosphere through human activities such as the burning of fossil fuels, biomass and the production of cement. It is added to the atmosphere naturally through respiration system of plants and animal cells, forest fires and eruption of volcanoes. The high rate of CO_2 emissions is because of the deforestation, increase of automobiles and high population growth, etc.

Harmful Effects of CO_2

It is usually considered nontoxic and harmless. But more than 65% of the anthropogenic greenhouse effect is attributed to CO_2 gas.

23.1.2.2 Oxides of Nitrogen (NO_x)

There are eight possible oxides of nitrogen. Out of these only three oxides namely, N_2O, NO and NO_2 are the important components of atmosphere. N_2O is high in concentration in atmosphere but it is not generally considered a pollutant. NO and NO_2 are more significant pollutants and they are usually represented together as NO_x. NO is a colourless, odourless gas, but NO_2 has a reddish-brown colour and pungent suffocation odour. The major man-made sources of oxides of nitrogen are combustion of coal, oil, natural gas, gasoline and other organic matter. The oxides of nitrogen can also be discharged by natural bacterial activity. The average residence time of NO is about 4 days and that of NO_2 is 3 days in the atmosphere.

Harmful Effects of NO_x

Nitric oxide (NO) and nitrogen dioxide (NO_2) both gases are toxic but NO is less toxic than NO_2. NO_x gases cause irritation in the airways and lungs. Long term exposure may cause asthma. These gases also contribute to the formation of fine particles and ground level ozone, both of which are associated with adverse health effects. Nitrogen dioxide, ozone and hydrocarbon in sunlight form peroxyacetyl nitrate (PAN) responsible for photochemical smog.

23.1.2.3 Volatile Organic Compounds

Volatile organic compounds (VOCs) include a variety of chemical gases emitted from certain liquids and solids. They are released from burning fuel, such as diesel, gasoline, wood, coal, or natural gas. They are also released from solvents,

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paints, glues, and other products that are used and stored at home and at work. They also found in paint thinners, varnishes, air fresheners, cosmetics, Tobacco smoke, flooring, carpet, wood preservatives, aerosol sprays and dry cleaning fluids. Some common examples of VOCs that are present in our daily lives are benzene, formaldehyde, toluene, xylene, styrene, tetrachloroethylene and ethylene glycol.

Harmful Effects of VOCs

Short-term exposure to high levels of some VOCs can cause headaches, dizziness, light-headedness, drowsiness, nausea, and eye and respiratory irritation. Long-term exposure to high levels of some VOCs has caused cancer and affected the liver, kidney and nervous system.

23.1.2.4 Oxides of Sulphur (SO_x)

Sulphur dioxide and small amounts of sulphur trioxide are formed during combustion of sulphur-containing materials such as fossil fuels. The most important and predominant form of sulphur oxides present in the lower atmosphere is SO_2. It is a colourless gas and has pungent odour. It is moderately soluble in water, forming weakly acidic sulphurous acid and tends to form aerosols. It is heavier than air. SO_3 is a colourless solid and has low melting and boiling points. It reacts quickly with water to form sulphuric acid tending to form aerosols. These acidic aerosols are eventually precipitated as acid rain, snow, sleet or fog but only when they encounter the right meteorological conditions.

Harmful Effects of Oxides of Sulphur

SO_2 causes irritation of the eyes, nose, and throat and premature mortality. Sulphur dioxide also causes damage to vegetation, including forests and agricultural crops.

23.1.2.5 Ozone (O_3)

Ozone is an allotrope of oxygen. It is a pale yellow gas and is fairly soluble in water. It is sweetish in taste. It occurs both in the earth's upper atmosphere and at ground level. Ozone affects life on earth in either good or bad ways, depending on where it is found. It acts as pollutant in the biosphere and as protector in the stratosphere.

Harmful Effects of Ozone

Ozone is a familiar component of photochemical smog. It causes various health problems. It cause eye irritation, throat irritation, coughing and asthma. It is harmful to plants. It reduces the durability and appearance of paint and fabrics.

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23.1.2.6 Peroxyacetyl Nitrate (PAN)

The peroxyacetyl nitrates (PANs) is a photochemical oxidant and is the major component of photochemical smog. PANs are both toxic and irritating, as they dissolve more readily in water than ozone.

Harmful Effects of PANs

At lower concentration, they cause eye irritation and at higher concentration, they cause extensive damage to vegetation.

23.1.3 Automobile Pollutants and the Catalytic Converter

The complete combustion in the petrol (or diesel) engine of automobile produce carbon dioxide and water vapours. The incomplete combustion leads to emissions of the poisonous carbon monoxide gas, and a wide range of various unburnt volatile organic compounds (VOCs), including hydrocarbons, aromatics and oxygenated species. Automobile also generate some oxides of nitrogen i.e. NO and NO_2. The nitric oxide is produced when atmospheric nitrogen and oxygen combine at the high temperatures present in an automobile engine. The NO released into the atmosphere further reacts with O_2 to form NO_2. The unburnt hydrocarbons produce photochemical smog and nitrogen dioxide form photochemical smog and acid rain.

The pollution that all the cars produced together can cause lung cancer, respiratory problems, urban smog and acid rain. In order to reduce air pollution, modern automobiles are equipped with a device called a catalytic converter that reduces emissions of harmful compounds such as CO, NO_2 and VOCs. These compounds are converted into less harmful compounds such as carbon dioxide, water, nitrogen, and oxygen before leaving the car's exhaust system. Catalytic converters can also be found in generators, buses, trucks, and trains; almost everything with an internal combustion engine has a form of catalytic converter attached to its exhaust system.

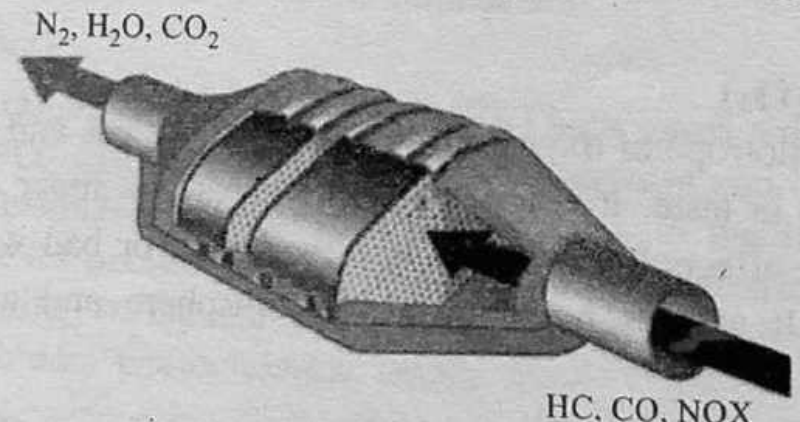


Figure 23.3: Catalytic Chamber

An efficient catalytic converter (three way catalytic converter), perform three functions: (i) it oxidizes CO and unburnt hydrocarbons to CO_2 and H_2O (ii) it reduces NO and NO_2 to N_2 and O_2 (iii) it oxidized hydrocarbons to carbon dioxide and water:

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$$2\,CO_{(g)} + O_{2(g)} \longrightarrow 2\,CO_{2(g)}$$

$$2\,NO_{(g)} \longrightarrow N_{2(g)} + O_{2(g)}$$

$$VOCs + O_{2(g)} \longrightarrow CO_{2(g)} + H_2O_{(g)}$$

Keep in Mind

Catalytic converters are effective at removing hydrocarbons, carbon monoxide, and nitrous oxides from car exhaust. But they do not reduce emission of carbon dioxide (CO_2), which is one of the most common greenhouse gases and contributes significantly to global warming.

Catalytic converters contain porous honeycomb structures made of ceramic materials that are coated with the catalysts. The catalyst used in a catalytic converter is a combination of platinum (Pt), palladium (Pd), and rhodium (Rh). Catalytic converter contains two different types of catalysts at work: (i) reduction catalyst (ii) oxidation catalyst. The reduction catalyst uses platinum and rhodium to reduce harmful pollutants such as nitrogen oxides in the exhaust whereas the oxidation catalyst uses platinum and palladium to reduce harmful pollutants like the carbon monoxide (CO) and VOCs in the exhaust of automobiles.

23.1.4 Industrial Smog

The word smog is a combination of smoke and fog. There are two types of smog: the industrial smog and the photochemical smog.

The industrial smog (sometimes known as London smog or gray smog) is created when SO_2 (from combustion of coal and oil) and particulate matter (larger solid particles such as metal oxides, soil particles, sea salts, fly ash, elemental carbon and small metal particles in the atmosphere) combine with the moisture in fog at suitable conditions. It produces a yellow-brown colour near ground level. It is a mixture of fly ash, soot, SO_2, smoke and some VOCs. One of the worst cases of industrial smog was the Great Smog of 1952 in London, where the smog was so thick it killed thousands of people (about 4000 people). This industrial smog is common in many cities in the world where heavy industry and power plants are found. Examples of such countries are India, China and European countries. This smog has serious negative effects on people, plants, and animals. Various human health problems such as emphysema, asthma, chronic bronchitis, lung infections, and cancers are caused by the effects of smog. It is formed in those cities where the weather is cold and wet. In many urban areas of developing countries, industrial smog is still a major problem.

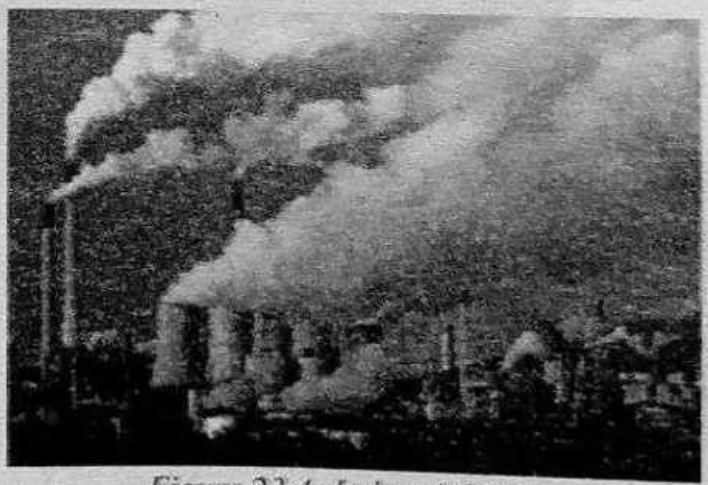


Figure 23.4: Industrial Smog

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23.1.5 Photochemical Smog

Photochemical smog (sometimes known as Los Angeles smog or brown smog) is created when oxides of nitrogen reacts with volatile organic compounds (VOCs) in the presence of sunlight. This reaction produces a mixture of hundreds of dangerous secondary pollutants, such as ozone, peroxyacetyl nitrate (PAN), aldehydes, and peroxybenzoyl nitrate (PBZN). It also appears to be yellow-brown haze. Photochemical smog is common in those cities that have a lot of automobiles along with a sunny, warm and dry climate. Examples of such cities are Los Angeles (California, USA), New York (USA), Sydney (Australia), Jakarta (Indonesia), Shanghai (China), Bangkok (Thailand), Rome (Italy) and Vancouver (Canada). Photochemical smog has serious negative effects on people, plants, and animals as well. It causes health hazards such as headache, eye irritation, asthma, lung tissue damage, bronchial infections and pulmonary edema (collection of fluids in lungs).

23.1.6 Greenhouse Effect and Global Warming

The greenhouse effect is the process during which radiation (thermal infrared radiation) from the sun is trapped by the gases such as carbon dioxide, water vapours, methane, nitrous oxide, and ozone and prevent the heat from escaping back into space. Although some of the energy passes back into space, most of it remains trapped in the atmosphere, which causes the earth to heat up. This natural process of maintaining the average temperature of our earth, and keeping it warm, is known as the greenhouse effect.

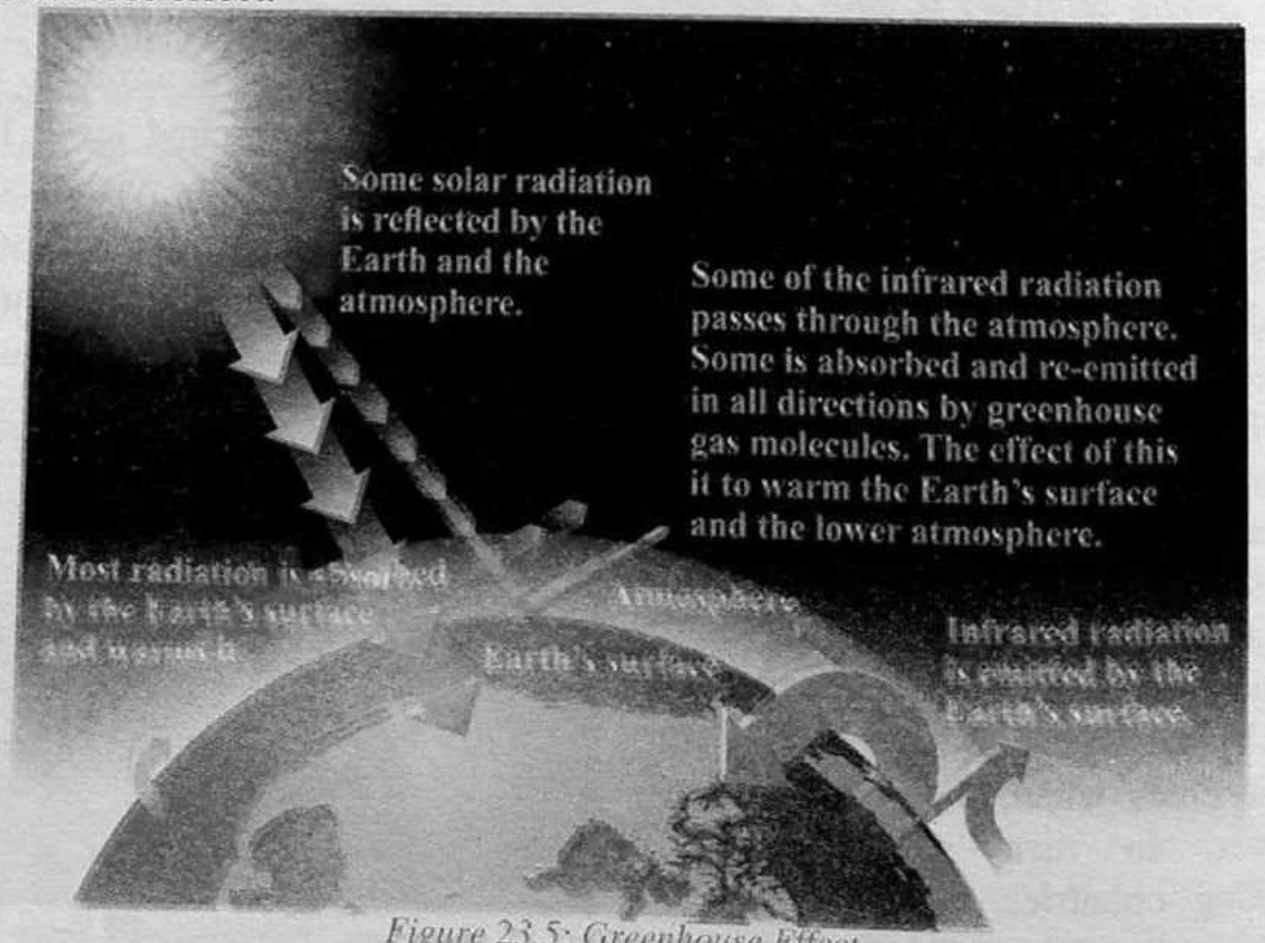


Figure 23.5: Greenhouse Effect

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Global warming (Scientists often use the term *climate change* instead of *global warming*) is the gradual increase in the overall temperature of the earth's atmosphere caused by gases that are collecting in the air around the earth and stopping heat escaping into space. The gases that are responsible for causing the greenhouse effect are known as greenhouse gases and they are carbon dioxide, water vapours, methane, nitrous oxide, and ozone. Average global temperatures are maintained at about 15°C due to natural greenhouse effect. Without this phenomenon, average global temperatures might have been around –17°C and at such low temperature life would not be able to exist. Actually, the greenhouse gases mainly carbon dioxide and water vapours are responsible for keeping the earth warm and thus sustaining life on it.

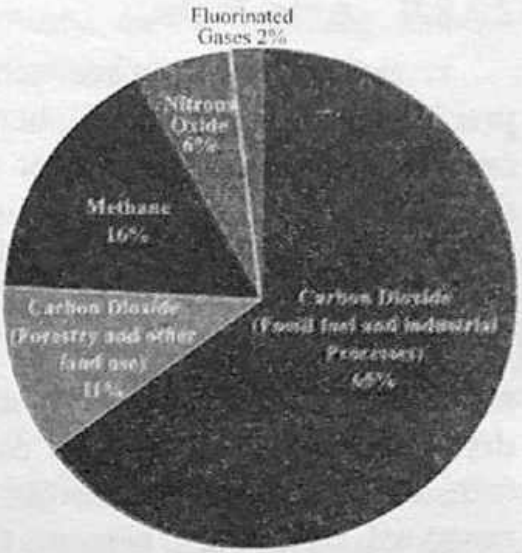


Figure 23.6: Global Greenhouse Gas Emissions

Consequences of Global Warming

If the amount of energy from the sun and the amount of greenhouse gases in the atmosphere remain the same, then the average temperature on earth will also be constant. If the greenhouse gases are very less or totally absent, the earth would be far colder and life on earth would not be possible. But, however, if the amounts of these gases exceed a certain limit, then the earth would be hotter. If global warming continues unchecked, by the turn of the century the temperature may rise by 5°C. Scientists believe that this rise in temperature will lead to deleterious changes in the environment and resulting in rise in sea levels, increasing ocean acidification, extreme weather events and other severe natural and societal impacts. Relative contribution of various greenhouse gases to total global warming is as:

- CO_2 contributes 76%
- CH_4 contributes 16%
- N_2O contributes 6%
- Fluorinated gases contributes 2%

The concentrations of methane and fluorinated gases are much lower than that of carbon dioxide, but they absorb heat much more effectively than carbon dioxide. Hence they make significant contributions to warming earth.

Carbon dioxide is the only greenhouse gas whose contribution is rising rapidly. It can be removed from the atmosphere when it is absorbed by plants. Removal of carbon dioxide from the atmosphere reduces the greenhouse effect and global warming.

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23.1.7 Acid Rain

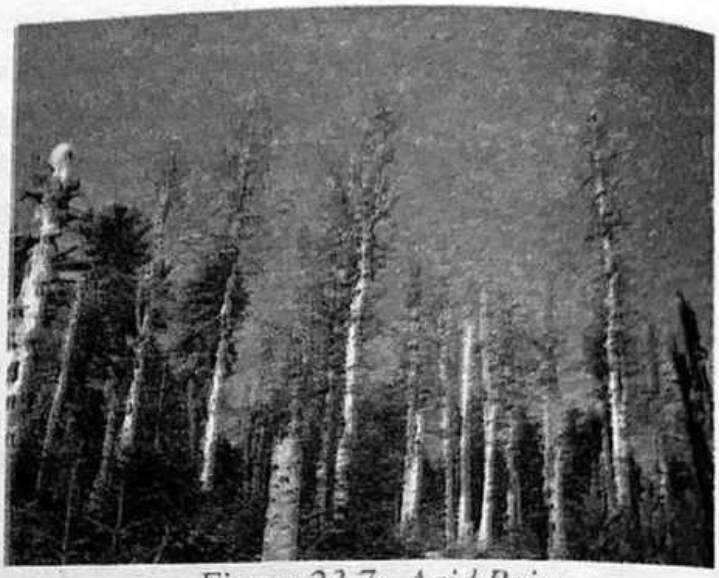


Figure 23.7: Acid Rain

Acid rain, or more accurately acid precipitation, is created when SO_2, NO_2 and CO_2 combines with water molecules in the atmosphere and result in producing mild solutions of sulphuric acid, H_2SO_4; nitric acid, HNO_3 and carbonic acid, H_2CO_3. It can also occur in the form of snow, sleet, fog, dew, hail and tiny bits of dry material that settle to earth. Normal rain water is slightly acidic with a pH range of 5.3 to 6.0, because CO_2 and H_2O present in the atmosphere combine together to produce carbonic acid, which is a weak acid. When the pH level of rain water drops below this range, it becomes acidic rain.

Harmful Effects of Acid Rain

Acid rain has negative effects on the environment and public health.

i) Acid rain can increase the acidity of rivers, dams, streams, lakes and oceans and significantly affect the aquatic life.

ii) Acid rain can increase the acidity of the soil, water and shallow groundwater that results in killing of plants and animals. Acidity may cause death of fish populations and other aquatic species including frogs, snails and crayfish.

iii) Acid rain makes water acidic, and causes them to absorb the aluminium that makes its way from soil into lakes and streams. This combination makes waters toxic to crayfish, clams, fish, and other aquatic animals.

iv) Acid rain affects trees. Acid rain can make them lose their leaves, damage their bark, and stunt their growth. Acid falling on a forest's soil is also harmful because it disrupts soil nutrients, kills microorganisms in the soil, and can sometimes cause a calcium deficiency.

v) Acid rain erodes buildings, monuments and stone statues. It corrodes steel structures such as bridges, towers etc. It also corrodes ceramics, textiles, plastics and paints.

vi) Acid rain adversely affects human health by creating particles in the air that can cause respiratory problems to humans and animals. Children and those who already have respiratory health conditions such as asthma are badly affected. Headaches and irritations of the nose, throat and eyes are some of the minor effects. Intensified levels of the acidic depositions are linked to risks of developing heart and lung problems such as asthma and bronchitis, and even cancer. When we drink tap water contaminated with acid rain, it can damage our brains.

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The harmful effects of acid rain may be minimized by minimizing the emissions of nitrogen oxides, sulphur oxides and other harmful gases from power plants, industries and automobile exhausts.

23.2 Chemistry of the Stratosphere

Stratosphere, is the region (second region) from 12 km to 50 km (approximately) above the earth's surface. It consists of nitrogen, oxygen and ozone. No weather takes place in the stratosphere. The stratosphere has over 15% of the total mass of the atmosphere, and is where the ozone layer is located. This layer is about 38 kilometres thick.

The ozone layer is present about 20–40 km above the earth's surface. Ozone (O_3) is a hazardous pollutant at low altitudes but is significantly important in the upper atmosphere because it helps protect us from hazardous ultraviolet radiation (UV) from the sun. The life on earth would not be possible without the protection of this layer. At earth's surface, it can cause various health problems such as skin cancer, effect immune system and may cause blindness.

Air temperature slowly increases with height in the stratosphere, in contrast with the troposphere where the temperature quickly decreases with height. This unusual temperature structure is caused by absorption of sunlight by ozone.

Production and Destruction of Ozone

Ozone is produced by photochemical reactions in the stratosphere when the rays of sun split oxygen molecules into single atoms. These atoms combine with nearby oxygen to form a tri-oxygen molecule, called **ozone**.

$$O_{2(g)} \xrightarrow{\text{UV (220nm)}} O_{(g)} + O_{(g)}$$

$$O_{2(g)} + O_{(g)} \longrightarrow O_{3(g)}$$

The ozone molecules, in turn absorb ultraviolet rays between 220 to 330 nm, and thus prevent these harmful radiations from entering the earth's atmosphere.

$$O_{3(g)} \xrightarrow{\text{UV (220 to 330 nm)}} O_{2(g)} + O_{(g)}$$

UV radiation at wavelength longer than 220 nm cannot be absorbed by O_2 and it cannot break the oxygen molecule into two oxygen atoms.

$$O_{2(g)} \xrightarrow{\text{UV (> 220 nm)}} \text{No Action}$$

Thus, the total amount of ozone is maintained by this continuous process of destruction, and regeneration.

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Ozone Depletion

The ozone layer protects the Earth from harmful ultraviolet radiation by absorbing these radiation. As the layer is reduced, the amount of harmful ultraviolet radiation that reaches the Earth increases. The ozone depletion (reduction) in the stratosphere is caused by ozone depleting chemicals. Examples of these chemicals are CFCs, halons, carbon tetrachloride, methyl bromide, hydrobromonfluorocarbons (HCFCs), and bromochloromethane (BCM).

Chlorofluorocarbons (CFCs) are anthropogenic compounds containing atoms of carbon, chlorine and fluorine. CFCs are also called Freons. They can be readily converted from a liquid to a gas and vice versa. Examples are trichlorofluoromethane and dichlorodifluoromethane.

Halons are also anthropogenic compounds containing atoms of carbon, bromine, chlorine and/or fluorine.

The CFCs and halons are very stable compounds. They are inert. The chlorofluorocarbons take 50 to 1700 years whereas halons take 65 years to breakdown. The CFCs are very important compounds and prepared on large scale in the world. These are non-toxic, non-flammable, and non-corrosive. CFCs are used as coolants in refrigerators and air-conditioners. They are also used as repellents in aerosol sprays. The halons also used as fire extinguishing agents.

CFCs contain chlorine atoms while halons contain bromine atoms. Chlorine and bromine atoms of these compounds cause chemical reactions that breakdown ozone molecules and in turn, reduce the ozone's ultraviolet radiation-absorbing capacity. Bromine is many times more effective at destroying ozone than chlorine. These compounds have been banned since 1996 in advanced countries.

Keep in Mind

The chemicals that are produced or influenced by human activities are known as anthropogenic (man-made) compounds. For example, chlorofluorocarbons are anthropogenic compounds in the atmosphere that are produced by aerosol propellants, refrigerator coolants and air conditioners. Many of the organic compounds that are produced by the human activities such as CO_2 and CH_4, also occur naturally, and in sufficient quantities. Some anthropogenic organic compounds such as DDT (insecticide) do not have a natural source. Anthropogenic compounds can have harmful effects on human health and the environment.

Substitutes of CFCs

Chlorofluorocarbons, halons and methyl bromide are ozone depleting substances (ODS). When these gases are carried to the stratosphere layer of atmosphere, where ultraviolet radiations from the sun break them to release chlorine (from CFCs) and bromine (from methyl bromide and halons). The chlorine and bromine react with the oxygen atoms in ozone and rips apart

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the ozone molecule. The ozone layer acts as a filter for highly hazardous ultraviolet radiation from the sun, protecting life on earth from its potentially harmful effects.

The protection of ozone layer is only possible by developing alternatives to ozone depleting chemicals. The scientists developed three primary substitutes for CFCs and these are: (i) HCFCs (ii) HFCs (iii) HCs.

Hydrochlorofluorocarbons (HCFCs)

They contain hydrogen, chlorine and fluorine atoms. They are just like CFCs, except hydrogen atoms have replaced some chlorine atoms. They were the first substances used as replacements for CFCs. HCFCs are less stable in the lower atmosphere, enabling them to break down before reaching the ozone layer. However, they still diffuse into the stratosphere and cause significant ozone destruction. They have shorter lifetime (2-25 years) in the lower atmosphere than CFCs (more than 100 years). But the problem is that they still contain chlorine that can attack the ozone layer. The HCFCs can contribute to global warming and are more expensive to make than CFCs.

Hydrofluorocarbons (HFCs)

They contain hydrogen and fluorine atoms. They are chlorine free. They are like CFCs, except hydrogen atoms have replaced the chlorine atoms. Due to absence of chlorine, they have no ozone depletion potential. They are now widely used as replacements for CFCs. They have shorter lifetime (2-25 years) in the lower atmosphere than CFCs (more than 100 years). But the problem is that the HFCs can contribute to global warming and are more expensive to make than CFCs.

The HCFCs and HFCs substitutes are six to fifteen times more expensive than CFCs. It is better to use HFCs as compared to HCFCs because HFCs have no ozone depletion potential.

Hydrocarbons (HCs)

They contain hydrogen and carbon atoms. They are free from halogens. They (a propane/isobutane blend) replaced CFCs and are extensively used in mobile air conditioning systems as refrigerants in many countries. They are also used in domestic and commercial refrigeration applications worldwide. They are used as propellants in spray cans.

23.3 Water Pollution and Water Treatment

Any physical, chemical and biological change in the quality of water by the addition of other substances that badly affect the living organisms is called water pollution. Water is essential for life on earth. We use water for drinking, washing, cooking, agriculture, industry, transport and recreation. Marine life is also impossible without water. Hence it must free from deadly chemicals and bacteria in order to be drinkable.

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The method in which raw water is made fit for drinking and other domestic purposes by removing foreign materials is called water treatment. The goal of water treatment is to remove contaminants and organisms through a combination of biological, chemical, and physical processes to make it safe for drinking. Contaminated water is the main source of infectious diseases such as amoebiasis, dysentery, cholera, typhoid, jaundice, malaria and paratyphoid fever.

23.3.1 Types of Water Pollutants

There are three major types of water pollutants: (i) Suspended Solids and Sediments, (ii) Dissolved Solids (iii) Thermal Pollution.

23.3.1.1 Suspended Solids and Sediments

The small solid particles that remain suspended in water and act as collide are known as suspended solids. They include silt, coal dust, plankton and industrial wastes. The loose sand, clay, silt and other soil particles that settle to the bottom of liquid are called sediments.

The process of natural erosion of soil and the decomposition of plants and animals gives rise to sediments and suspended solids in water. Sediment is subsequently transported by the action of winds, water or ice. Sediment is the most common pollutant in rivers, lakes, streams and other water reservoirs. The suspended particles and sediments produce turbidity in water and consequently reduce the amount of sunlight available to the aquatic life, which is required for the photosynthesis by bottom vegetation. They reduce the storage capacities of reserves.

23.3.1.2 Dissolved Solids

Dissolved solids are a mixture of different organic and inorganic compounds contained in a water. These solids are mostly minerals, salts, organic matter, metals, cations or anions dissolved in water. The major components of dissolved solids are the cations such as calcium, magnesium, sodium and potassium, and the anions such as bicarbonate, carbonate, sulphate and chloride. Dissolved solids may come from organic sources such as leaves, silt, plankton and industrial waste and sewage. Other sources come from runoff from urban areas, road salts and/or fertilizers and pesticides. Dissolved solids may come from runoff rain water and inorganic materials such as rocks. A constant level of minerals is essential for aquatic life in the water. Changes in the quantities of dissolved solids can be damaging. The amounts of dissolved solids, which are too low or too high limit the growth and lead to the death of aquatic life.

23.3.1.3 Thermal Pollution

Thermal pollution is the increase or decrease in the temperature of a natural body of water caused by human influence. The rates of biological and chemical processes depend on temperature. Thermal power plants, nuclear power plants and industries use large amounts of water for cooling purposes. They used coolant water,

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which is hot, is usually discharged directly into water bodies. As a result of this hot water discharge, the temperature of water body increases, which reduces the dissolved content of the water and adversely affects the aquatic life.

Various Parameters of Water Analysis

There are six major categories of parameters of water analysis:

i) Physical Tests

Colour, turbidity, total solids, dissolved solids, suspended solids, odour and taste are estimated.

ii) Chemical Tests

The pH, hardness, presence of a selected group of chemical parameters, biocides, highly toxic chemicals, and BOD are estimated.

iii) Toxic Element Tests

Toxic elements such as iron, calcium, copper, chromium, manganese, magnesium, mercury, cadmium, molybdenum, selenium, arsenic, lead, zinc, aluminium, nickel, boron, etc. are estimated.

iv) Bacteriological Tests

In these tests, the presence of harmful bacteria such as *E.coli* bacteria and Total coliform bacteria are checked.

v) Pesticides Tests

Here the pesticides such as alachlor, atrazine, aldrin/dieldrin, alpha HCH, beta HCH, butachlor, chlorpyrifos, delta HCH, DDT, endosulfan, etc. are estimated.

vi) Volatile Organic Compounds (VOCs) Tests

Benzene, toluene, xylenes, bromobenzene, butylbenzense, chlorotoluenes, dichlorobenzenes, phenolic compounds, polyaromatic hydrocarbons etc. are estimated.

The physical, biological, and chemical properties of drinking water have great importance because a minor variation in these parameters affects the human health. The defined standards of drinking water in Pakistan have been developed by the Pakistan Standards Quality Control Authority. The permissible limits, as laid down by the World Health Organisation (WHO) and Pakistan Standards Quality Control Authority (PSQCA) are listed for comparison. A parametric value may be a count such as 500 E. coli per litre or a statistical value such as the average concentration of copper is 2 mg/l.

Keep in Mind

Biological oxygen demand (BOD) also known as biochemical oxygen demand is a measure of the amount of dissolved oxygen (DO) used by microorganisms (e.g., aerobic bacteria) in the oxidation of organic matter when dissolved into a body of water. BOD is measured experimentally by calculating the amount of oxygen at the beginning and at the end of five days period at 20°C.

A small amount of oxygen up to 10 ppm is actually dissolved in water. This dissolved oxygen is required by fish and other aquatic life to survive. Dissolved oxygen is also important for us because it is an important indicator of quality of water. If water has 4ppm or less dissolved oxygen, some fish and other organisms may not be able to survive. Dissolved oxygen is used by bacteria when large amounts of organic matter are present in the water.

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Table 23.2:Parameters and National Standards for Water Quality

Parameters	WHO Standards	PSQCA Standards
Colour	≤15 TCU (true colour units)	≤15 TCU
Odour	Odourless	---
Taste	Tasteless	---
Turbidity	<5 NTU (Nephelometric Turbidity Unit)	<5
Hardness as $CaCO_3$	—	<500mg/L
Total Dissolved Solids	<1000 mg/L	<1000 mg/L
pH	6.5–8.5	6.5–8.5
	mg/L	mg/L
Aluminium	0.2	<0.2
Antimony	0.02	≤0.005
Arsenic	0.01	≤0.05
Barium	0.7	0.7
Boron	0.3	0.3
Cadmium	0.003	0.01
Chloride	250	<250
Chromium	0.05	≤0.05
Copper	2	2
Cyanide	0.07	≤0.05
Fluoride	1.5	≤1.5
Lead	0.01	≤0.05
Manganese	0.5	≤0.5
Mercury	0.001	≤0.001
Nickel	0.02	≤0.02
Nitrate	50	≤50
Nitrite	3	≤3
Selenium	0.01	≤0.01
Zinc	3	5
Phenols	≤0.002	—
PAH (Polyaromatic hydrocarbons)	2	—

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23.3.2 Waste Water Treatment (or Sewage Treatment)

Waste water (or sewage) is the mixture of wastes from the human body and used water. It includes domestic waste water (or domestic sewage), industrial waste water (or industrial sewage) and storm waste water (or storm sewage). The waste water come from sinks, showers, bathtubs, toilets, washing machines, kitchen, and bathrooms is called domestic waste water. It is also called sanitary sewage. Industrial waste water is produced from industrial activities such as manufacturing or chemical processes. Storm waste water is rainfall runoff and other drainage that is collected in a system of pipes or open channels. The sewage that is carried away from buildings by pipes under the ground called a sewerage system. Waste water treatment (or Sewage treatment) is the process of removing contaminants from wastewater. The major aim of wastewater treatment is to remove the contaminants to acceptable levels to make the water safe for discharge back into the environment. The wastewater that flows into a treatment plant, basin, or reservoir is called influent.

Waste water treatment consists mainly of three steps: primary, secondary and tertiary treatments. Primary treatment removes around 40–60% and secondary treatment removes around 90% of suspended solids.

Primary Treatment

Primary treatment is also called physical treatment because it is a mechanical process by which large suspended and floating material such as sand, silt and large lump of organic matter are removed. Primary treatment removes around 40–60% suspended solids and about 35% BOD (biochemical oxygen demand or biological oxygen demand). We are unable to remove water dissolved substances and pathogens by this process.

Secondary Treatment

Secondary treatment is also known as biological treatment because it involves the use of bacteria and other microbes. These process may be aerobic or anaerobic. **Aerobic wastewater treatment** is a process where bacteria utilize oxygen to degrade organic matter (generally quantified as BOD) and other pollutants involved in various production systems. **Anaerobic treatment** is a process where wastewater or material is broken down by microorganisms without the aid of dissolved oxygen. However, anaerobic bacteria can and will use oxygen that is found in the oxides introduced into the system or they can obtain it from organic material within the wastewater. Anaerobic systems are used in many industrial systems including food production and municipal sewage treatment systems. The sludge left after decomposition of sewer by aerobic and anaerobic bacteria is rich in phosphorus, nitrogen and minerals. After drying, it is used as manure.

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Secondary treatment may require a separation process to remove the microorganisms from the treated water prior to discharge or tertiary treatment. Secondary treatment removes around more than 85% of suspended solids and BOD.

Tertiary Treatment

This is the third and last step of waste water treatment. Tertiary treatment consists of advanced physical, chemical and biological processes. Tertiary wastewater treatment is used when particular wastewater components which cannot be removed by secondary treatment must be removed. The major objectives of tertiary treatment are the removal of bacteria, dissolved inorganic solids, fine suspended solids and final traces of organic compounds if needed.

The water at this stage is almost free from harmful substances and chemicals. The water is allowed to flow over a wall where it is filtered through a bed of sand to remove any additional particles. The filtered water is then used for the irrigation of a golf course, green way or park, or released into the stream, river, bay, lagoon or wetland.

Disinfection

There are still some microorganisms and pathogen contaminants in the remaining treated wastewater. To kill them, the wastewater must be disinfected for at least 20-25 minutes in tanks that contain a mixture of chlorine and sodium hypochlorite. Chlorination is done during tertiary treatment.

23.4 Green Chemistry

Green chemistry, also called sustainable chemistry, is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green Chemistry is based on a set of twelve principles that can be used to design or re-design molecules, materials and chemical transformations to be safer for human health and the environment.

Goal of Green Chemistry

The goal of green chemistry is:

i) To choose the most efficient ways to synthesize the chemicals.

ii) To make safe, sustainable and non-polluting chemicals that consumes minimum amount of materials and energy while generating little or no waste material.

iii) To prevent and minimize the production and use of hazardous chemicals.

Principles of Green Chemistry

In 1998, two US chemists, Paul Anastas and John Warner sketched Twelve Principles of Green Chemistry and these are:

i) **Prevention:** It is better to prevent the generation of waste than to treat or clean up waste after it has been produced.

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ii) **Atom Economy:** Synthetic methods should be planned to maximize the incorporation of all materials used in the synthesis into the desired product.

iii) **Design less Hazardous Chemical Syntheses:** Synthetic methods should be designed to use and generate substances with little or no toxicity to either humans or the environment.

iv) **Designing Safer Chemicals:** Chemical products should be developed to affect their desired function while considerably reducing their toxicity.

v) **Safer Solvents and Auxiliaries:** The use of auxiliary substances such as solvents, separation agents, and others, should be avoided wherever possible. If you must use these chemicals, use harmless auxiliaries.

vi) **Design for Energy Efficiency:** Chemical synthesis should be performed at ambient temperature and pressure, if possible.

vii) **Use Renewable Feedstocks:** A raw material or feedstock should be renewable rather than depleting whenever feasible in technological and economic terms.

viii) **Reduce Chemical Derivatives:** Minimize or avoid unnecessary derivatization, e.g. protection / deprotection, use of blocking groups, temporary modification of physical/chemical processes) if possible, because such steps require additional reagents and can generate waste.

ix) **Use Catalysts:** Catalytic reagents are superior to stoichiometric reagents. Catalysts are effective in small amounts and can carry out a single reaction many times. Hence, minimize waste by using catalytic reactions.

x) **Design for Degradation:** Chemical products should be designed so that at the end of their function they break down into harmless degradation products and do not persist in the biosphere.

xi) **Real-time analysis for Pollution Prevention:** Advanced analytical methods have to be developed to allow for real-time, in-line process monitoring and control prior to the generation of hazardous substances.

xii) **Accident Prevention:** Reagents and solvents used in a chemical process should be chosen to minimize the risk for chemical accidents, including explosions, fires and releases.

Summary of Facts and Concepts

- Environmental chemistry is the branch of chemistry in which study about the sources, reactions, transportations and effects of the pollutants on the environment.
- The environment consists of four components: (i) atmosphere (ii) hydrosphere (iii) lithosphere (iv) biosphere.
- The layers of gases surrounding the earth is called atmosphere. It consists of nitrogen, oxygen, carbon dioxide and trace amounts of hydrogen, ozone, methane, carbon monoxide, helium, neon, krypton, xenon, and water vapours.

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- The water containing parts of our earth is called hydrospheres. It includes all water resources like oceans, rivers, streams, lakes, polar ice caps.
- Biospheres consists of the region of earth where all living species exist above as well as below sea level.
- Lithosphere is the upper rigid and rocky layer of earth's crust. It includes soil, earth, rocks and mountains.
- Troposphere is the nearest to the earth's surface extending up to 11 km. It accounts for about 70% of the atmospheric mass.
- The substance in the environment that has adverse effects on human health, quality of life and natural functioning of ecosystem is called environmental pollutant.
- Global warming is the gradual increase in the overall temperature of the earth's atmosphere caused by gases that are collecting in the air around the earth and stopping heat escaping into space.
- The rain having pH value less than 5.3 is termed as acid rain. It is due to presence of carbon dioxide, sulphur dioxide and NO_2 which get mixed with rain water in the presence of pollutants to form carbonic acid, nitric acid and sulphuric acid.
- Ozone is the protective layer in the atmosphere which absorbs harmful ultraviolet radiations and cosmic rays of the sun and thus blocks them to reach on the earth.
- The addition of any harmful substance in water is called water pollution. Water is essential for all the living beings on the earth. The process of removing contaminants from wastewater is called Waste water treatment. Waste water (or sewage) is the mixture of wastes from the human body and used water.

Multiple Choice Questions

Q. Select one answer from the given choices for each question:

i) The segments of environments are
   (a) One
   (b) Two
   (c) Three
   (d) Four

i) Polar ice caps, glaciers, rivers, rocks, mountains, soils are the parts of
   (a) Lithosphere
   (b) Hydrosphere
   (c) biosphere
   (d) Geosphere

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iii) Most of mass of atmosphere is present in:
(a) Troposphere
(b) Stratosphere
(c) Mesosphere
(d) Thermosphere

iv) Rust is:
(a) Iron (III) oxide
(b) Iron (II) oxide
(c) Hydrated Iron (III) oxide
(d) Hydrated Iron (II) oxide

v) Acid rain is mainly caused in the atmosphere by the emission of:
(a) NO_X and KNO_3
(b) SO_X and charcoal
(c) CO_X and sulphur
(d) SO_X and NO_X

vi) Smog is derived from:
(a) Smoke and water droplet
(b) Fog and water droplet
(c) Fog and smoke
(d) Mist and water droplet

vii) London smog or gray smog is caused by
(a) SO_2 + particulates + moisture of fog
(b) NO_2 + particulates + moisture of fog
(c) CO_2 + particulates + moisture of fog
(d) PAN + particulates + moisture of fog

viii) Brown smog results from the mixing of:
(a) NO_2 + particulates + sun light
(b) NO_2 + VOCS + sun light
(c) CO_2 + VOCS + sun light
(d) PAN + particulates + sun light

ix) Which two gases of the following are the major contributors to global warming:
(a) Carbon dioxide and nitrous oxide
(b) Methane and nitrous oxide
(c) Carbon dioxide and methane
(d) Methane and water vapours

x) The ozone layer lies in which of the following layers of the atmosphere?
(a) Troposphere
(b) Mesosphere
(c) Exosphere
(d) Stratosphere

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Short Answer Questions

Q.1. Why Environmental Chemistry is important?
Q.2. Why it is important to protect the environment?
Q.3. Why is the environment important to us?
Q.4. How do human activities affect the environment?
Q.5. What are the effects of pollution in our environment?
Q.6. Earth is called blue planet, why?
Q.7. How does the hydrosphere affect us?
Q.8. What is the importance of the hydrosphere?
Q.9. How atmosphere is important for us?
Q.10. What is the Earth's atmosphere made up of?
Q.11. What are the main pollutants in the air?
Q.12. How much do automobiles contribute to air pollution?
Q.13. What is the role of the catalytic converter?
Q.14. What is the importance of catalytic converter?
Q.15. How is smog caused?
Q.16. How is smog harmful to the environment?
Q.17. What is the main cause of greenhouse gases?
Q.18. How are greenhouse gases produced by humans?
Q.19. How does acid rain affect humans?
Q.20. Why is chlorine added to remaining treated waste water?

Long Answer Questions

Q.1. What is environmental chemistry? Briefly describe the segments of the environment.
Q.2. Explain the chemical reactions of nitrogen oxides and sulphur oxides in the atmosphere.
Q.3. Discuss the chemical reactions of oxygen in atmosphere.
Q.4. How do the chemical reactions of organic compounds carried out in the atmosphere?
Q.5. Define air pollutants. Describe the sources and harmful effects of oxides of carbon, nitrogen and Sulphur.
Q.6. What are the sources of volatile organic compounds in the atmosphere? What are the adverse effects indicated by them?
Q.7. Discuss the characteristic and undesirable effects of ozone and peroxyacetyl nitrate (PAN).

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Q.8. What do you know about automobile pollutants? What are the importance and role of catalytic converters?

Q.9. Define smog and explain industrial and photochemical smog.

Q.10. What is the effect of smog on the health of peoples? How to prevent smog?

Q.11. How does car exhaust produce the smog that hangs over our cities?

Q.12. What is greenhouse effect? What are greenhouse gases? Discuss their contribution to global warming? What are the consequences of global warming?

Q.13. What is the acid rain? Discuss briefly. What are bad effects of acid rain on the environment and public health? How can we minimize its bad effects?

Q.14. Define water pollution and water pollutants? What are the different types of water pollutants and how they are produced? What are their effects?

Q.15. Explain the various parameters of water analysis.

Q.16. Define waste water and write an informative note on waste water treatment. What are the steps involved in waste water treatment?

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Chapter 24

Analytical Chemistry

Major Concepts

24.1 Classical Method of Analysis
24.2 Modern Methods

Learning Outcomes:

Students will be able to:

- Compare the classical method of analysis with modern methods. **(Understanding)**
- Discuss the procedure of combustion analysis. **(Understanding)**
- Define spectroscopy and discuss its applications in analytical Chemistry. **(Applying)**
- State the regions of electromagnetic spectrum used in IR and UV/Vis spectroscopy. **(Applying)**
- Explain the origin of IR absorption of simple molecules. **(Analyzing)**
- Predict whether a given molecule will absorb in the UV/Vis region. **(Analyzing)**
- Predict the colour of a transition metal complex from its UV/Vis spectrum. **(Analyzing)**
- Outline in simple terms the principles of proton NMR spectroscopy. **(Applying)**
- Explain how chemical environment of a Proton affects the magnetic field it experiences and hence the absorption of energy at resonance frequency. **(Applying)**
- Describe standard scales used in proton NMR. **(Applying)**
- Explain instrumentation and working of MS. **(Applying)**
- Outline the use of MS in determination of relative isotopic masses and isotopic abundance. **(Applying)**
- Define and explain atomic emission and atomic absorption spectrum. **(Understanding)**

Introduction

Analytical chemistry can be considered as one of the essential branches of chemistry. It can be defined as the branch of chemistry in which we study about the separation, identification and quantification of components of samples of matter. Analytical chemist uses instruments and methods to separate, identify, and quantify matter. Analytical chemistry plays an important role not only in the fields of chemistry such as organic, inorganic, physical, nuclear and environmental, but also in the other fields of science such as physics, biology, archaeology, agriculture and industries. Because all these fields require analysis of materials.

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Classification of Chemical Analysis

The process of estimation or determination of the components present in given sample is known chemical analysis. Chemical analysis procedures are usually classified in two ways:

i) In terms of the goal of analysis.
ii) In terms of the nature of analysis.

Classification in terms of Goal of Analysis

The chemical analysis can be classified into qualitative and quantitative analyses in terms of the goal of analysis.

Qualitative analysis

Qualitative analysis means what constituents are present in the sample. It is the determination of the chemical composition of a sample of matter. It can tell you whether an atom, ion, functional group, or compound is present or absent in a sample, but it does not provide information about its quantity.

There are two main types of qualitative analysis: organic compounds analysis and inorganic compounds analysis.

Organic compounds analysis involves the determination of atoms or functional groups in the sample. Examples include: (i) combustion analysis (ii) detection of elements in an organic compound (iii) identification of functional groups in an organic compound and (iv) identification of organic pollutants in the air.

Inorganic compounds analysis finds elemental composition of inorganic compounds. It is used to identify and separate cations and anions in a sample. Example for inorganic compounds analysis is salt analysis. The common qualitative test, used in inorganic chemical analysis, is the flame test. Flame tests can be used to identify the presence of a particular metal. Different metals give different colours to the flame.

Quantitative Analysis

Quantitative analysis means how much constituents is present in the sample. It is carried out when the identity of the components already known and when it is necessary to also know the amounts of these components. It is the determination of the amounts or concentrations of one or more components present in a sample. It is done by either a classical or modern (instrumental) procedure. For quantitative analyses, the amount of analyte (the material being analyzed) is determined by gravimetric or by titrimetric measurement.

In **gravimetric analysis**, the substance being determined is converted into an insoluble precipitate which is collected and weighed.

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In **titrimetric analysis** (also known as volumetric analysis) the substance to be determined is allowed to react with suitable reagent added as a standard solution and the volume of solution needed for whole reaction is determined. The common titrimetric reactions are acid-base reactions, precipitation reactions and oxidation-reduction reactions.

Classification in terms of the Method of Analysis Used

The chemical analysis can also be classified into classical and instrumental methods in terms of the nature of method used.

24.1 Classical Method of Analysis

Classical methods are also known as wet chemical methods or earliest methods of chemical analysis. They are the traditional methods of chemical analysis which are still being used by chemists. The classical methods that were used to separate the components of interest in a sample were distillation, crystallization, extraction or precipitation. These methods usually involve the chemical reactions and/or classical reaction stoichiometry, but no electronic instruments are used other than an analytical balance or volumetric apparatuses such as pipette, burette etc. The instruments of classical methods are not highly specialized.

Classical methods are cheaper and easily available for labs of schools, colleges and industries. The classical methods consume more time than instrumental methods of analysis. Classical methods are more useful for accurate and precise measurements of analyte concentrations (at the 0.1% level or higher).

The Combustion Analysis

Combustion analysis is one the most widely used method for determining percentage composition and empirical formula of an unknown compound in the laboratory. This method is commonly used for compounds containing carbon and hydrogen.

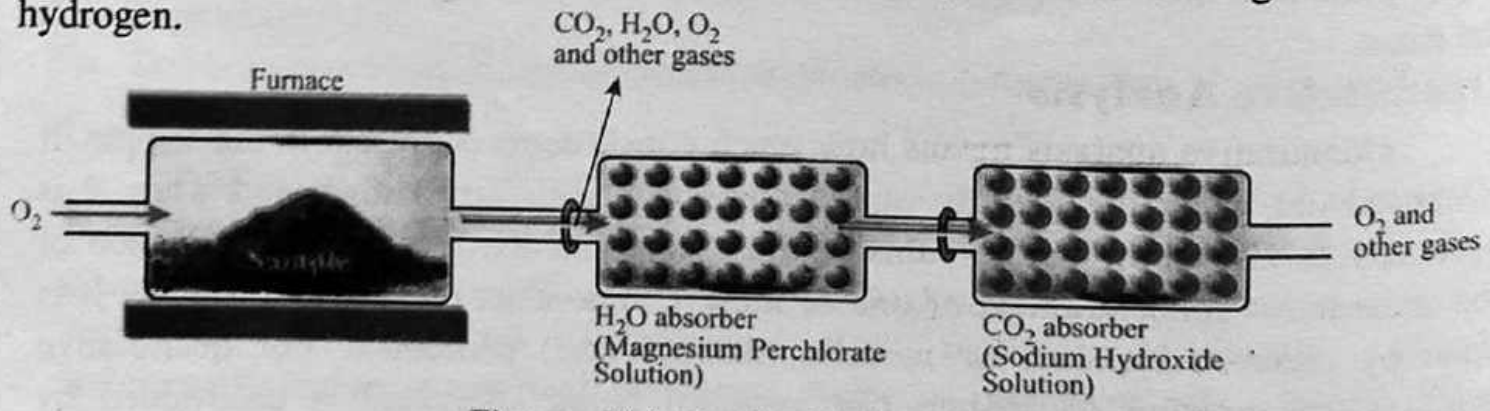


Figure: 24.1: Combustion Apparatus

In this method, a known mass of compound is burnt in stream of oxygen gas. Here each element in the compound combines with oxygen to produce volatile

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combustion products (CO_2 and H_2O). The carbon is converted to carbon dioxide and the hydrogen is converted to water vapours. Water vapours are absorbed in magnesium perchlorate, $Mg(ClO_4)_2$ whereas carbon dioxide is absorbed in 50% potassium hydroxide, KOH solution. The masses of CO_2 and H_2O are determined by measuring the mass increase in the CO_2 and H_2O absorbers. From the masses of CO_2 and H_2O we can calculate the percentage of carbon and hydrogen with the help of following equations:

$$\% \text{ age of carbon in compound} = \text{Mass of } CO_2 \times \frac{12}{44} \times \frac{100}{\text{Mass of compound}}$$

$$\% \text{ age of hydrogen in compound} = \text{Mass of } H_2O \times \frac{2}{18} \times \frac{100}{\text{Mass of compound}}$$

If third element such as oxygen is present in the compound, its percentage can be calculated by subtracting the percentages of carbon and hydrogen as:

$$\% \text{ age of oxygen in compound} = 100 - (\% \text{ age of carbon} + \% \text{ age of hydrogen})$$

Combustion analysis can be used to determine the empirical formula of an unknown organic compound.

Example 24.1:

Combustion of 1.125 g of an organic compound produces 3.447g of CO_2 and 1.647 g of H_2O. Calculate the % age of carbon and hydrogen.

Data:

Mass of organic compound	= 1.125g
Mass of CO_2	= 3.447g
Mass of H_2O	= 1.647g
%age of carbon	= ?
%age of hydrogen	= ?

Solution:

% age of carbon in organic compound

$$= \text{Mass of } CO_2 \times \frac{12}{44} \times \frac{100}{\text{Mass of compound}}$$

$$= 3.447\text{g} \times \frac{12}{44} \times \frac{100}{1.125\text{g}}$$

$$= 83.6\ \%$$

% age of hydrogen in organic compound

$$= \text{Mass of } H_2O \times \frac{2}{18} \times \frac{100}{\text{Mass of compound}}$$

$$= 1.647\text{g} \times \frac{2}{18} \times \frac{100}{1.125\text{g}}$$

$$= 16.3\ \%$$

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Determination of Empirical Formula

The following steps are used to determine the empirical formula:

i) Divide the % by the atomic mass of each element to calculate the mole ratios.

$$\text{Mole ratio} = \frac{\%\text{age of an element}}{\text{Atomic mass}}$$

ii) Determine simple atomic ratio by dividing number of mole ratio of each element by the smallest one.

iii) If atomic ratios are in fractions, change them into whole numbers by multiplying with a suitable number.

iv) Write atomic ratios as subscript with each element to get empirical formula.

Example 24.2:

Caffeine, central nervous system stimulant, is found is tea and coffee, and has 49.48% carbon, 5.19% hydrogen, 16.48% oxygen and 28.85% nitrogen. Calculate its empirical formula.

Data:

%age of carbon = 49.48%
%age of hydrogen = 5.19%
%age of oxygen = 16.48%
%age of nitrogen = 28.85%
Empirical formula of caffeine = ?

Solution:

i) Calculate mole ratio of each element.

$$\text{Mole ratio of carbon} = \frac{49.48\%}{12.01\,\text{amu}} = 4$$

$$\text{Mole ratio of hydrogen} = \frac{5.19\%}{1.01\,\text{amu}} = 5$$

$$\text{Mole ratio of oxygen} = \frac{16.48\%}{16.00\,\text{amu}} = 1$$

$$\text{Mole ratio of nitrogen} = \frac{28.85\%}{14.01\,\text{amu}} = 2$$

ii) Determine simple atomic ratio

$$\text{Atomic ratioof carbon} = \frac{4}{1} = 4$$

$$\text{Atomic ratio of hydrogen} = \frac{5}{1} = 5$$

$$\text{Atomic ratio of oxygen} = \frac{1}{1} = 1$$

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Atomic ratio of nitrogen $= \frac{2}{1} = 2$

iii) The empirical formula of caffeine is $C_4H_5ON_2$

Determination of Molecular Formula

Following steps are used to calculate molecular formula:

i) Divide the molecular formula mass by empirical formula mass to get value of n.

$$\text{Value of n} = \frac{\text{Molecular Formula Mass}}{\text{Empirical Formula Mass}}$$

ii) Multiply number of atoms of each element with value of 'n' to get molecular formula.

Example 24.3: The empirical formula of benzene is CH. It molecular mass is 78 amu. Determine its molecular formula.

Data:

Empirical formula of benzene	= CH
Empirical formula mass of benzene	= 13 amu
Molecular formula of benzene	= ?
Molecular formula mass of benzene	= 78 amu

Solution:

i) Value of $n = \frac{78\,amu}{13\,amu} = 6$

ii) Molecular formula of benzene = 6 (CH) = C_6H_6

24.2 Modern Methods of Analysis

These are the newer methods of chemical analysis. These methods use modern or highly specialized instruments to measure physical quantities of the analyte such as light absorption or emission, fluorescence, mass-to-charge ratio, or conductivity. Highly efficient chromatographic and electrophoretic techniques are used to replace the classical methods (distillation, extraction and precipitation) for the separation of components of complex mixtures. Examples of modern methods are spectroscopy, chromatography, microscopy, etc.

Modern methods are expensive because of the use of high specialized machines for chemical analyses. Modern methods have certain advantages over classical methods, which include the speed (they are fast), high sensitivity (they can detect very small amounts of a substance in a small amount of sample), versatility (simultaneous detection capabilities), multi-element analysis and automated operation of modern instruments.

In the early years of chemistry, the unsaturation in a compound was determined by the amount of hydrogen or halogen consumed. The presence of functional groups

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in organic compounds was determined by chemical tests. The halogens or sulphur in organic compounds were detected by chemical tests (sodium fusion tests). The aromaticity was determined by flame test. The molecular masses of compounds were determined by using the colligative properties.

Today's scientists have developed sophisticated instruments that enable chemists to:

i) Determine the unsaturation in a compound by UV spectroscopy.
ii) Determine the presence of functional groups in organic compounds by IR spectroscopy.
iii) Detect the halogens or sulphur in organic compounds by mass spectroscopy.
iv) Measure the aromaticity by NMR spectroscopy.
v) Determine molecular masses by mass spectroscopy.

Organic chemistry has been revolutionized by the invention of spectroscopic methods. Spectroscopic methods are used for analysis and structure determination.

The spectrometric methods use electromagnetic radiations as the basic tool. It is therefore necessary to understand the nature of electromagnetic radiations.

Electromagnetic Radiations

Electromagnetic radiation (EMR) is a form of energy and consists of both electric and magnetic fields. These fields are at right angles to each other and to the direction in which the wave is moving. Electromagnetic radiation carries energy through space, it is also called radiant energy.

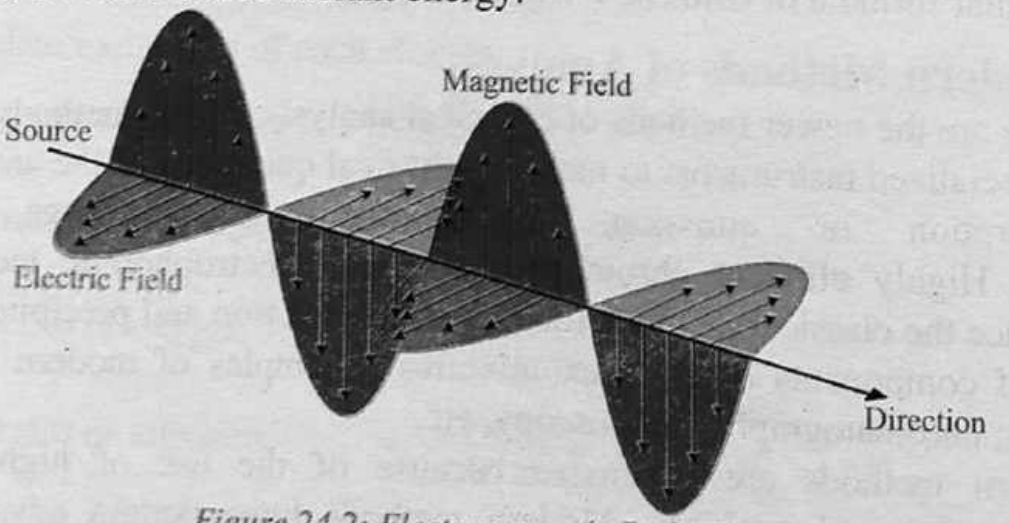


Figure 24.2: Electromagnetic Radiations

Electromagnetic radiations are all around us and take many forms. The heat (infrared radiations) from a burning fire, the light that is emitted from the bulb, sun or television, the X-rays used by doctors, the energy used to cook food in a microwave and the radio waves that carry music to our radios are all forms of electromagnetic radiation. Electromagnetic radiation includes gamma ray, X-ray, ultra-violet (UV), visible, infra-red (IR), microwave and radio wave. They seem very different from one

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another, but they all show wavelike properties. Their waves are similar to those waves that move through water. All types of electromagnetic radiations move through a vacuum with the velocity of light (2.998×10^8 m/s). All electromagnetic radiations travel in straight lines. They are not affected by electric or magnetic fields. All electromagnetic waves can be reflected, refracted and diffracted just like light waves. Visible light (the light we see with our eyes) is only a small portion of the EM spectrum, which contains a broad range of electromagnetic wavelengths.

Wavelength, Frequency and Energy

All electromagnetic radiations can be characterized by their wavelengths, energy and frequency. The energy of radiation increases with increasing frequency and decreases with increasing wavelength.

$$E = h\nu = hc/\lambda$$

Where, E is energy, h is Planck's constant, ν (nu) is frequency, c is velocity of light and λ (lambda) is wave length of radiations.

Keep in Mind

Wavelength
The distance between two adjacent crests or troughs of wave is called wavelength. It is shown by λ (lambda). Its units are m, nm or A°.

Frequency
The number of waves passing through a point in one second is called frequency. It is shown by 'ν'. Its units are hertz or cycles/sec.

$$\nu = {}^{c}/_{\lambda}$$

Frequency (ν) is inversely proportional to wavelength (λ).

Wavenumber
The number of waves present in one centimetre distance is called wave number. It is the inverse of wavelength. It is shown by $\bar{\nu}$ (nu bar). The unit of wavenumber is cm^{-1}.

Electromagnetic Spectrum

In addition to visible region, there are seven other regions of the spectrum. The ultraviolet, X-rays and γ-rays are towards the lower wavelength end and infrared, microwave and radio waves are towards higher wavelength end. Visible light falls in the range of the electromagnetic spectrum between infrared (IR) and ultraviolet (UV). It has wavelengths of about 400 nanometers (nm) to 800 nm. When the different types of electromagnetic radiations are arranged in order of their increasing wavelengths or decreasing frequencies, the complete arrangement is called electromagnetic spectrum. Although almost all parts of the electromagnetic spectrum are used for studying matter but in organic chemistry we are mainly concerned with three or four regions that are ultraviolet-visible, infrared, microwave and radio wave.

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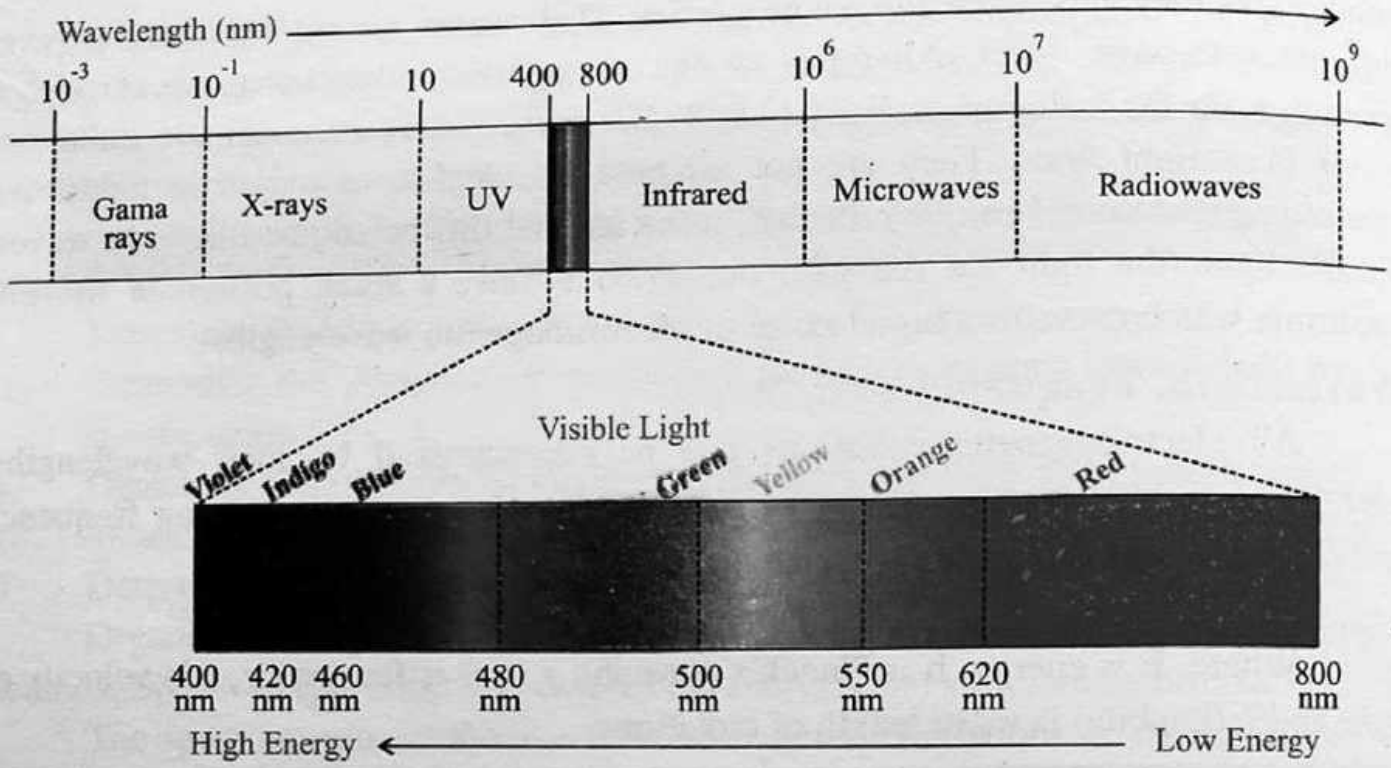


Fig. 24.3: Spectrum of Electromagnetic Radiations

The regions in increasing order of wavelength are:

Gamma Rays: the energy change involves the nuclear excitation.

X-rays: the energy changes involve the inner electrons of an atom or molecule.

UV-Visible: the energy changes involve valence electrons of molecules.

Infrared: the energy changes involve transitions between the vibrational levels of molecules.

Microwave: the energy changes involve transitions to higher energy rotational levels of molecules.

Radio wave: the energy changes involve the reversal of spin of a nucleus or electron.

Table 24.1: Electromagnetic Radiations and their Sources

Electromagnetic Radiations	Wavelength range (nm)	Sources	Uses
Gamma rays	10^{-3} —10^{-1}	Sun, star, Unstable atomic nuclei	Used to kill cancer cells and may used for imaging.
X-rays	10^{-1} — 10^{1}	Heavy metal anode	Used to image internal bones and organs
UV-light	10 — 400	Sun light	Used to sterilize food, medicine and surgical equipments and cause the body to produce vitamin D.

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Electromagnetic Radiations	Wavelength range (nm)	Sources	Uses
Visible light	400 — 800	Sun, light bulb	Enable us to see
IR light	800 — 10^6	Hot objects	Warm objects and used in night vision technology to "see" in the dark
Microwave	10^6 — 10^7	Oven, radar	Used for radar and in microwave oven to warm food
Radio wave	10^7 — 10^9	Radio, TV	AM and FM radio, TV, mobile phone

24.2.1 Spectroscopy

Spectroscopy is the branch of science which deals with the study of interaction of electromagnetic radiation with matter. It is one of the important experimental techniques used to determine the electronic structure of atoms and molecules. It is used to determine the structure and functional groups in organic compounds and is useful for studying the properties of molecules. It is used to monitor the progress of chemical processes. It can also be used to measure the purity of products. Spectroscopy is also used to determine the chemical composition and physical properties of astronomical objects (such as their temperature and velocity).

24.2.2 Spectroscopic Methods

The spectroscopic methods most often used by organic chemists are: ultraviolet (UV) and visible, infrared (IR), nuclear magnetic resonance (NMR) and mass spectroscopy (MS).

24.2.2.1 Ultraviolet-visible Spectroscopy

The spectroscopy which deals with the study of interaction of electromagnetic radiation with matter in the ultraviolet region (200-400nm) and visible region (400-800nm) is called ultraviolet-visible (UV/Vis) spectroscopy. The amount of energy available in this radiation is sufficient to cause the promotion of loosely held electrons (non-bonding electrons or the electrons involved in a π-bond) to higher energy levels. As UV/Vis spectroscopy involves electronic transitions, hence it is also known as electronic spectroscopy. Keep in mind that the energy levels of an atom are quantized, only light with specific amount of energy can cause transitions from one level to another.

Principle of UV Spectroscopy

Molecules containing π-electrons or non-bonding electrons can absorb energy in the form of UV-Visible light to stimulate these electrons to higher anti-bonding

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molecular orbitals. The more easily excited the electrons from lower energy level to higher energy level, the longer the wavelength of light it can absorb. The greater is the number of the molecules that are capable of absorbing light at a certain wavelength, the greater is the extent of the absorption of light.

Types of Electrons Present in Compounds

In UV/Vis spectroscopy, three types of electrons are involved in transitions:

i) Sigma electrons (σ-electrons): these electrons are present in sigma orbitals. σ-Bonds are strong so that high energy is required for the promotion of these electrons. These types of electrons are found in alkanes.

ii) Pi-electrons (π-electrons): these electrons are present in π-orbitals. These electrons are found in those molecules which have double or triple bonds. Examples are alkenes, alkynes, aromatic compounds, etc.

iii) Non-bonding electrons (n-electrons): these electrons are not involved in bonding. Non-bonding electrons are found in those compounds, which have heteroatoms (N, O, S, etc.).

Types of Electronic Transitions

Four types of electronic transitions are possible:

(i) $\sigma \rightarrow \sigma^*$ (ii) $\pi \rightarrow \pi^*$ (iii) $n \rightarrow \sigma^*$ (iv) $n \rightarrow \pi^*$

(i) • $\sigma \rightarrow \sigma^*$ Transition

(ii) • $\pi \rightarrow \pi^*$ Transition

(iii) • $n \rightarrow \sigma^*$ Transition

(iv) • $n \rightarrow \pi^*$ Transition

The $\sigma \rightarrow \pi^*$ transition is not allowed by selection rules. The order of energy for different transitions is as: $n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* << \sigma \rightarrow \sigma^*$

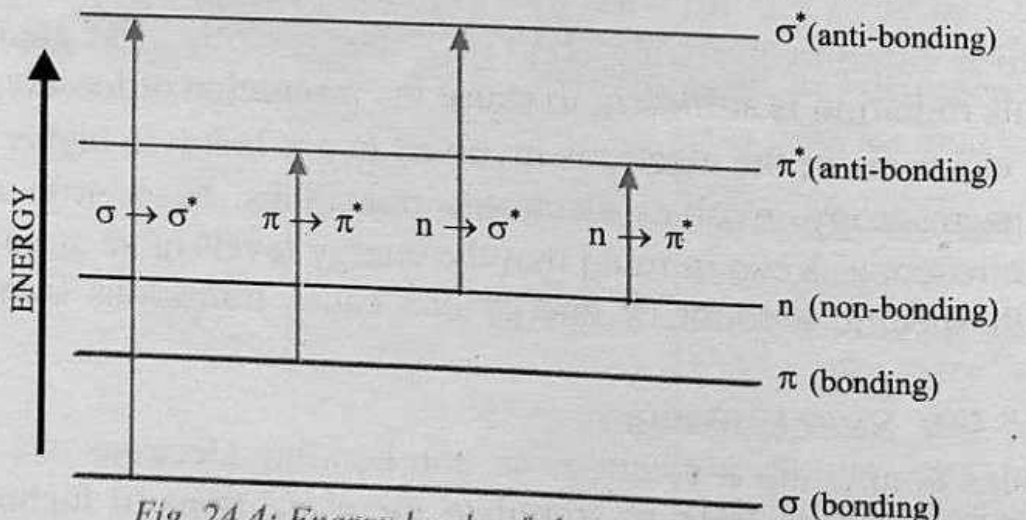


Fig. 24.4: Energy levels of electronic transitions

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i) Sigma to Sigma Star ($\sigma \rightarrow \sigma^*$) Transitions

The promotion of electron from bonding sigma orbital to associated high energy antibonding sigma orbital ($\sigma \rightarrow \sigma^*$) require higher amounts of energy and usually involve absorption of ultraviolet radiation below 150nm. This is due to stronger sigma bonds. This is the only transition available in alkanes. For example, methane has carbon-hydrogen bonds only and shows absorbance maximum at 125nm. These transitions are not available in normal UV-Visible regions (200-800nm).

ii) Pi to Pi Star ($\pi \rightarrow \pi^*$) Transitions

The promotion of electron from bonding pi orbital to associated high energy antibonding pi orbital ($\pi \rightarrow \pi^*$) require lesser amounts of energy than $n \rightarrow \sigma^*$, $\sigma \rightarrow \sigma^*$ transitions. The transitions in unconjugated alkenes usually involve absorption of ultraviolet radiation around 170-190 nm and the non-conjugated carbonyl compounds involve the absorption of visible radiation around 200-300nm. This transition is available in conjugated alkenes, alkynes, carbonyls, nitriles, aromatic compounds, etc.

iii) n to Sigma Star ($n \rightarrow \sigma^*$) Transitions

The promotion of electron from non-bonding orbital to high energy antibonding sigma orbital ($n \rightarrow \sigma^*$) require lesser amounts of energy than $\sigma \rightarrow \sigma^*$ transitions and usually involve absorption of 150-250nm. This type of transition is shown by saturated compounds containing atoms with lone pairs of electrons like N, O, S and halogens. For example, the maximum absorption for hydrogen monoxide (H_2O) is 167nm and that of methyl alcohol (CH_3OH) is 183nm.

iv) n to Pi Star ($n \rightarrow \pi^*$) Transitions

The promotion of electron from non-bonding orbital to high energy antibonding pi orbital ($n \rightarrow \pi^*$) require the least amounts of energy than all other transitions and usually involve absorption at longer wavelengths around 300nm. This kind of transition is shown by unsaturated molecules containing heteroatoms such as N, O and S. Saturated aliphatic ketones show absorption around 280nm. For example, acetone shows absorption maximum at 279 nm.

Instrumentation and Working of UV/Visible Spectroscopy

The modern UV spectrometers (double beam spectrophotometer) consist of the following parts:

i) Light source
ii) Monochromator
iii) Beam Chopper
iv) Sample and reference cells
v) Detectors
vi) Amplifier
vii) Recording device

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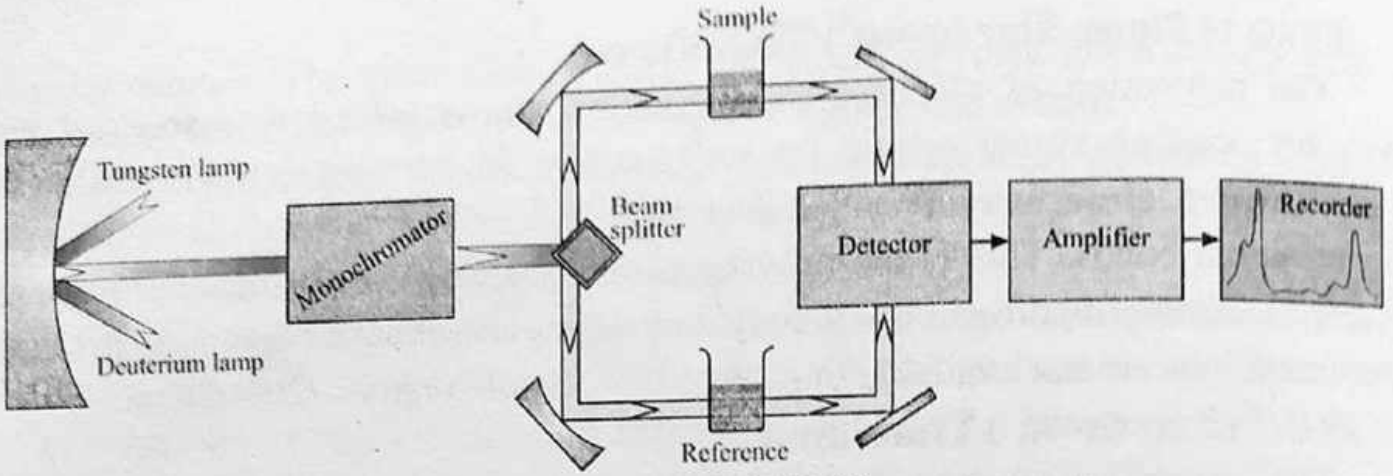


Fig. 24.5: Instrumentation of UV/Visible spectroscopy

Light Source

Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used.

Monochromator

Electromagnetic radiation from the source of light enters the monochromator through entrance slit. The monochromator is used to disperse the radiation into different wavelengths. Monochromators (also known as wavelength selector) generally composed of prisms and slits.

Beam Chopper (Beam Splitter)

Chopper is device consisting of circular disc. It splits the monochromatic beam of light into two beams of equal intensities.

Sample and reference cells

These cells are made of either silica or quartz. Sample under measurement and the reference solution are placed in the cells. One of the two divided beams is passed through the sample solution and second beam is passed through the reference solution.

Detectors

Detectors have photocells. One of the detector receives the beam from sample cell and second detector receives the beam from the reference. Both the detectors generate voltage proportional to the radiation energy that strikes them.

Amplifier

The voltage generated in the photocells is transferred to the amplifier. Generally voltage generated in the cells is of very low intensity, the main function of amplifier is to amplify the signals many times to generate clear and recordable signals.

Recording device

Recording device is generally computer system. It automatically stores and records all the data and generate the spectrum of sample under investigation as a plot of wavelengths of absorbed radiations against absorbance.

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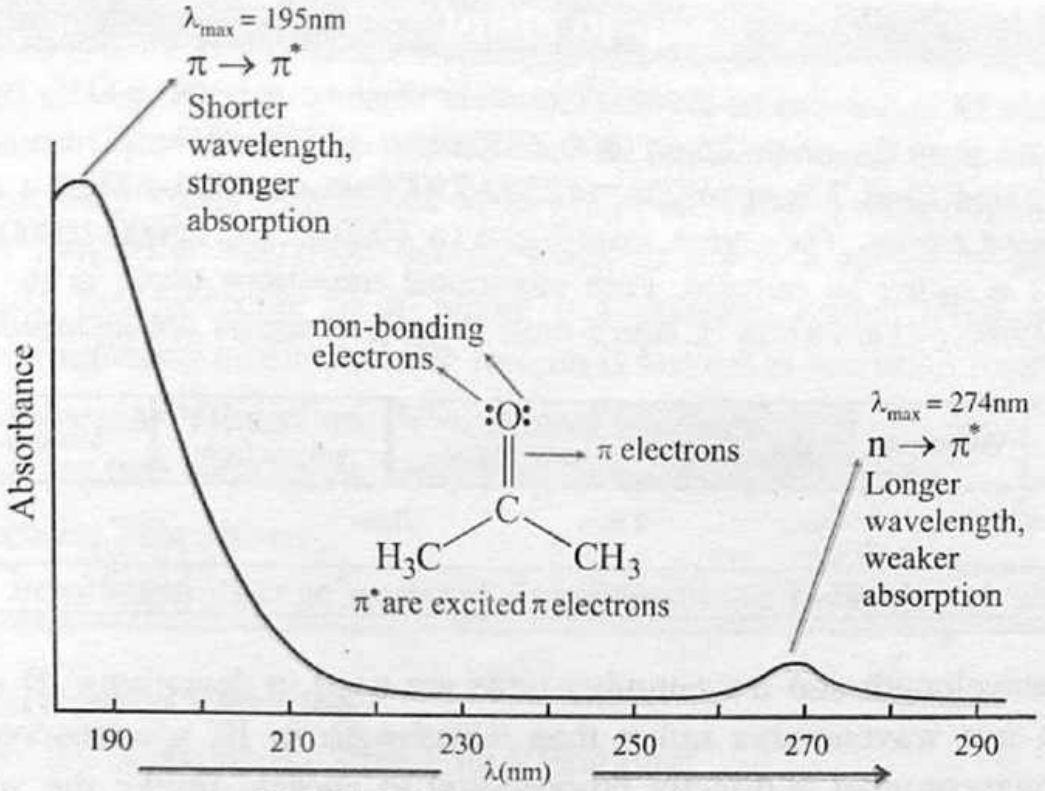


Fig. 24.6: UV/Vis Spectrum of Acetone

Applications of UV-Visible Spectroscopy

UV-Visible spectroscopy is one of the most useful tools and is usually used in analytical chemistry for qualitative and quantitative analyses. Some of the applications of UV-Visible spectroscopy are:

i) It is used for the determination of equilibrium and dissociation constants.

ii) It is useful for the determination of rate of chemical reaction.

iii) It is also useful to detect the structure of organic compounds, the presence or absence of unsaturation, the presence of heteroatoms and the impurities in the samples of organic compounds.

24.2.2.2 Infrared Spectroscopy

The spectroscopy which deals with the study of interaction of electromagnetic radiation with matter in the infrared region from 0.8μm to 1000μm (or 800-1000000nm) is called infrared (IR) spectroscopy. IR spectroscopy is concerned with the study of absorption of infrared radiation, which causes vibrational transition in the molecule. Hence, IR spectroscopy is also known as vibrational spectroscopy. Not all the molecules can absorb IR radiation. Molecules absorb radiation when a bond in the molecule vibrates at the same frequency as the incident radiant energy. After absorbing energy, the molecules have more energy and vibrate at increased amplitude.

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Keep in Mind

The entire IR region can be divided into three regions: near IR, middle IR and far IR. The region from 0.8μm to 2.5μm (800-2500nm or 12500-4000cm^{-1}) is called near infrared and that from 2.5μm to 25μm (2500-25000nm or 4000-400cm^{-1}) is called middle infrared region. The region from 25μm to 1000μm (or 25000-1000000nm or 400-10cm^{-1}) is called far infrared. Pure vibrational transitions occur in the infrared region 2.5-15μm (4000-667cm^{-1}), hence most organic chemists are interested in this region.

	Visible Light	Near Infrared Light	Middle Infrared Light	Far Infrared Light	Microwaves	
Wavelength	400nm	800nm (0.8μm)	2.5μm	25μm	1mm (10^6nm)	10^7nm
Wavenumber		12500cm^{-1}	4000cm^{-1}	400cm^{-1}	10cm^{-1}	

Both wavelength and wavenumber units are used in describing IR spectra but most chemist use wavenumber rather than wavelength in IR spectroscopy. This is because the wavenumber is directly proportional to energy, unlike the wavelength, which is inversely proportional to energy. Thus, the wavenumber is more comparable to frequency as compared to wavelength.

Keep in Mind

When we sit in the sun or close to a heater or fire, we are irradiated by infrared radiations (also called heat waves) of the spectrum. The energy provided by this type is enough to vibrate our skin molecules, this vibration increases the kinetic energy of our skin molecule, so we feel warmth.

Principle of IR Spectroscopy

Molecules are made up of atoms linked by chemical bonds. The movement of atoms and the chemical bonds is like spring and balls (vibration).This characteristic vibration is called natural frequency vibration.If the bond is stretched or compressed and then released, the atoms vibrate.

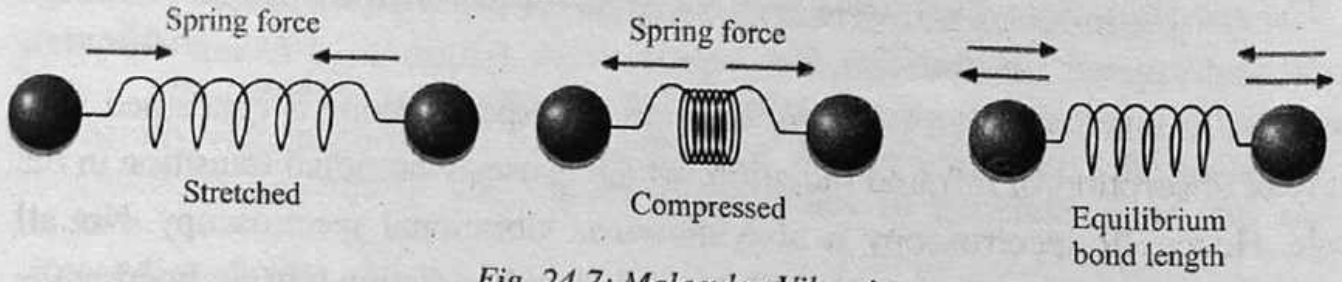


Fig. 24.7: Molecular Vibrations

When energy in the form of IR radiation is applied then it causes the vibration between the atoms of the molecules. As a result the absorption of IR radiation takes place and a peak is observed.

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Molecular Vibrations (Vibrational Modes) of IR Spectroscopy

Atoms in a molecule do not remain at fixed positions with respect to each other, but actually vibrate back and forth about an average value of the interatomic distance. A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. The frequency of the periodic motion is known as vibration frequency.

Types of Molecular Vibrations (Vibrational Modes)

There are two main types: stretching and bending vibrations.

i) Stretching Vibrations

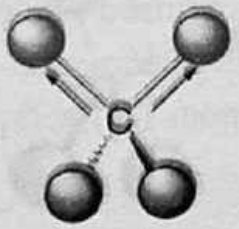
Stretching involves a change in bond lengthsresulting in a change in interatomic distance.

Types of Stretching Vibration

There are two types of Stretching Vibrations:

Symmetric stretching:

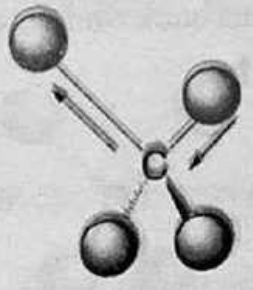
In symmetric stretching vibration, two or more bonds vibrate in and out together.



Symmetric Stretching

Asymmetric stretching:

In asymmetric stretching, some bonds are getting shorter and the others are getting longer at the same time with respect to the central atom.



Asymmetric Stretching

ii) Bending vibrations

Bending vibrations involve the change in bond angles or change in the position of a group of atoms with respect to the rest of the molecule. The bond lengths, in bending vibrations, remain constant.

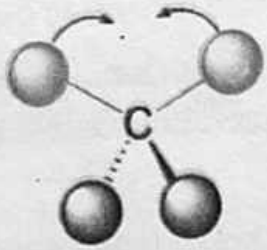
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Types of Bending Vibrations

There are four types of bending vibrations:

Scissoring

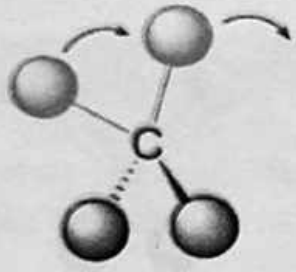
Scissoring is the movement of two atoms toward and away from each other like the movement of scissors.



Scissoring

Rocking

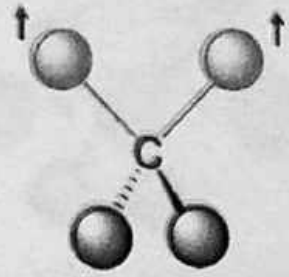
Rocking is the movement of atoms in the same direction within a plane. It is like the motion of pendulum on a clock, here an atom is a pendulum and there are two instead of one.



Rocking

Wagging

Wagging is the simultaneous motion of two atoms that move up and down the plane with respect to the central atom. It is like the motion in which you make a "V" sign with your fingers and bend them back and forth from your wrist.

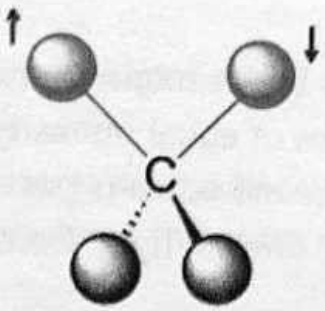


Wagging Vibrations

Twisting

Twisting involves when one atom moves up the plane and the other atom moves down the plane with respect to the central atom.

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Twisting Vibrations

Factors Affecting Vibrational Frequency

The frequency absorbed depends on:

(i) the masses of atoms in the bond (ii) the strength of the bond (iii) the geometry of the molecule (iv) and several other factors.

Keep in mind that heavier the atoms, lower is the vibration frequency of the bond between them. Stronger the bond, higher is the vibration frequency.

Instrumentation of IR Spectroscopy

Instrument that is used to determine the absorption spectrum of compound is called infrared spectrometer or, more accurately, infrared spectrophotometer. The most common spectrophotometer is double beam spectrophotometer. It is similar to that of UV spectrophotometer. Its main components are:

(i) radiation Source (ii) Fore optics (iii) monochromator (iv) sample cell (v) detector (vi) recorder

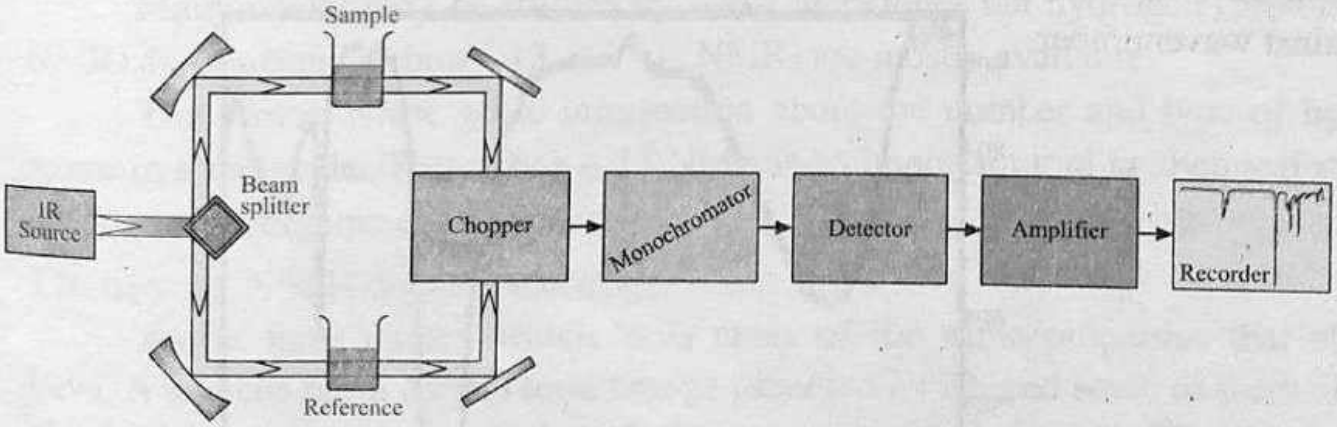


Fig. 24.8: IR Spectrophotometer

i) Radiation Source

The commonly used sources are Nernst glower and globar.

Nernst glower is ahollow rod of rare earth oxides (zirconium, thorium and cerium).

Globar is a silicon carbide rod.

Nernst glower is used for shorter wavelengths and globar filament is used for longer wavelengths.

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ii) Optics

Optics consists of mirrors and a rotating mirror. Mirrors divide the light from the infrared source into two beams of equal intensity. One of the two divided beams is passed through the sample and second beam is passed through the reference (solvent). The rotating mirrors alternately allows light from each of the beams to enter the monochromator.

iii) Chopper

Chopper recombines the light before entering into monochromator. It passes the two beams alternately to a prism (or diffraction grating).

iv) Monochromator

Prisms and grating can be used as monochromator. Monochromator produces single wavelength radiations.

v) Detector

Detectors convert thermal energy into electrical energy.

vi) Amplifier

The signals obtained in the detector are amplified many times to generate clear and recordable signals.

vii) Recorders

Recorder automatically records all the data on a computer and plots the IR spectrum of the sample on a graph. It usually plots the transmittance or absorbance against wavenumber.

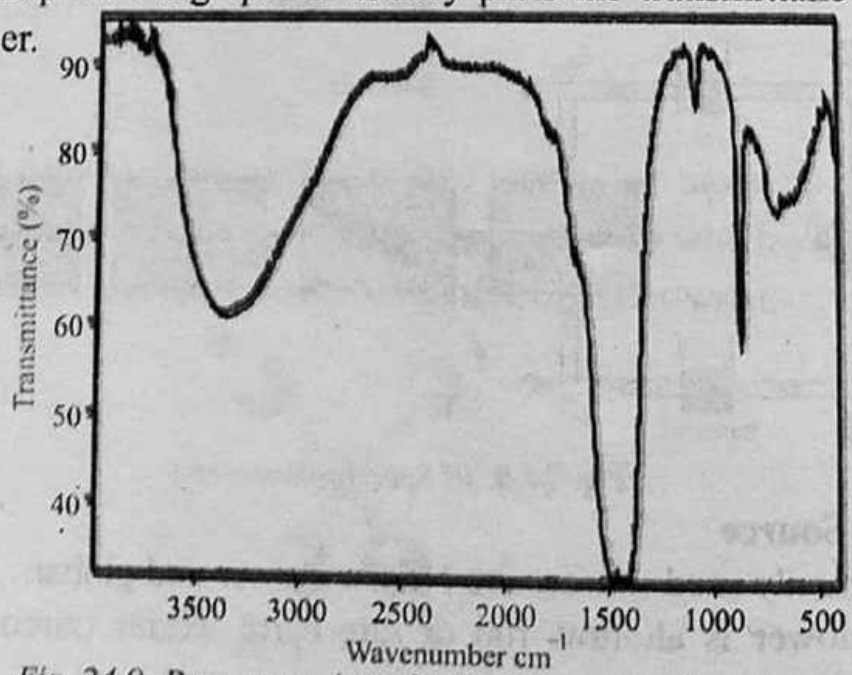


Fig. 24.9: Representation of IR Spectrum of a Sample

Keep in Mind

The frequency is usually plotted as transmitted light, nor light absorbed.

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Applications of IR Spectroscopy

It is widely used in both organic and inorganic chemistry. Some of the applications of IR spectroscopy are:

i) It is mainly used for structural determination of organic compounds.

ii) It is used to detect the presence or absence of a particular functional group in the compound.

iii) It is being used to help identify the structure of complex molecules in space.

iv) It is very effective for the detection and measurement of even minute quantities of the chemical compounds; hence it is widely applied in environment analysis, forensic analysis, industries and research.

v) It has also been successfully utilized in the field of semiconductor microelectronics: for example, infrared spectroscopy can be applied to semiconductors such as silicon, gallium arsenide, gallium nitride, zinc selenide, amorphous silicon, silicon nitride, etc.

24.2.2.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

The spectroscopy which deals with the study of interaction of electromagnetic radiation with matter in the radiofrequency region is called nuclear magnetic resonance (NMR) spectroscopy.

The range of NMR region is from 7.5×10^{10} nm to 4.0×10^{8} nm (75m to 0.4m or 4 MHz to 750 MHz).

Many nuclei may be studied by NMR techniques but hydrogen (proton i.e. ^{1}H NMR) and carbon (carbon – 13 i.e. ^{13}C NMR) are mostly available.

The proton NMR gives information about the number and type of hydrogen atoms in a molecule. The carbon – 13 NMR is an important tool in chemical structure elucidation in organic chemistry.

Theory of NMR Spectroscopy

Atoms have nuclei, which have many of the same properties that electrons have. A nucleus has a certain total charge (denoted by Z), and some of them also spin about their axes in a manner that electrons spin about their axes. The spin quantum number (spin) of a nucleus is denoted by ℓ . The spin quantum number of a nucleus is determined by the number and pairing of the individual particles. The rules for determining the net spin of a nucleus are as:

i) The nucleus has **NO** spin when the number of protons and the number of neutrons are both even.

ii) The nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2) when the sum of the number of protons and neutrons is odd.

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iii) The nucleus has an integer spin (i.e. 1, 2, 3) when the sum of the number of protons and neutrons is even. The number of protons and the number of neutrons are both odd in this case.

Table 24.2: The Spin Quantum Number of Some Atoms

No. of Protons (Atomic Number)	No. of Neutrons	Mass Number	Spin Quantum Number	Examples
Even	Even	Even	Zero	$^{4}_{2}He(0)$, $^{12}_{6}C(0)$, $^{16}_{8}O(0)$
Even or odd	Even or odd	odd	Half-integer	$^{1}_{1}H(1/2)$, $^{7}_{3}Li(3/2)$, $^{13}_{6}C(1/2)$, $^{17}_{8}O(5/2)$
Odd	Odd	Even	Integer	$^{2}_{1}H(1)$, $^{6}_{3}Li(1)$, $^{10}_{5}B(3)$ $^{14}_{7}N(1)$

The table shows that the nuclei with an odd mass number or odd atomic number have nuclear spins. The nuclei that have nuclear spins such as ^{1}H or ^{13}C are said to be NMR active nuclei i.e. they have magnetic fields. When the nuclei have an even number of protons and neutrons such as ^{12}C and ^{16}O, their magnetic fields cancel out and they have no overall magnetic fields. These nuclei are NMR inactive.

Principles of NMR Spectroscopy

All nuclei with non-zero spins have magnetic moments (μ). Thus the nucleus can be considered to be a tiny bar magnet. The magnetic moment is generated by charge and spin of nuclei.

Without an external applied magnetic field, the nuclear spins are random in directions. But when an external magnetic field is applied, the nuclei align themselves either with or against the field of the external magnet.

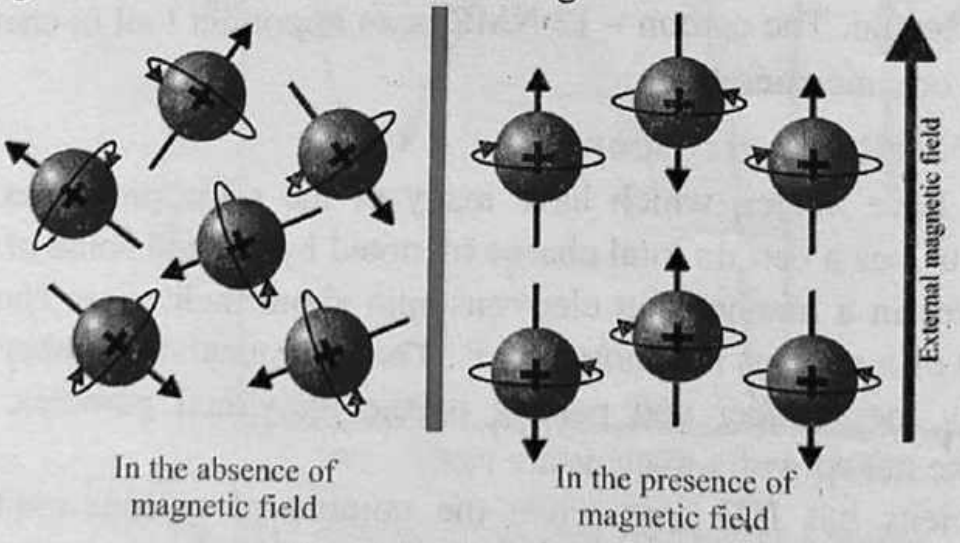


Fig. 24.10: Nuclear Spin

It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy

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between the energy levels.This is very important to know that the lower energy level will contain slightly more nuclei than the higher level.

In the presence of an external magnetic field, two spin states exist, +1/2 and −1/2.

The magnetic moment of the lower energy +1/2 state is aligned with the external field, but that of the higher energy −1/2 spin state is opposed to the external field.

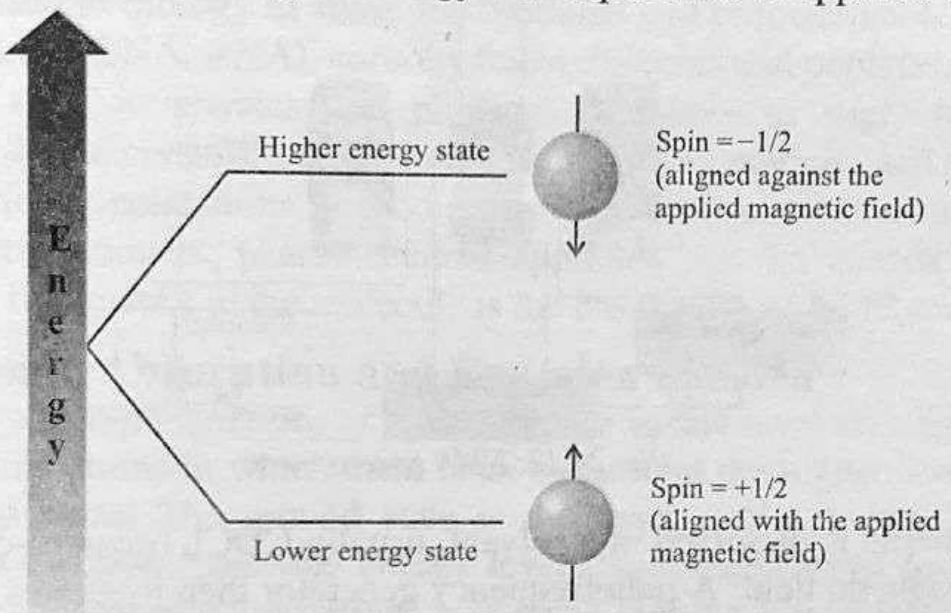


Fig. 24.11: Energy Level for a Nucleus

The stronger the magnetic field, the larger the energy difference between two nuclear spin states and higher the energy (frequency, ν) needed for the resonance.

The amount of energy absorbed is recorded as NMR Spectrum. In practice either the magnetic field can be held constant and the radio frequency varied or more commonly the radio frequency can be held constant and the magnetic field varied. The main purpose of NMR is not to detect the presence of proton in a molecule. It can be distinguish between protons in different chemical environments with in the molecule. The number of signals recorded on the NMR chart paper indicates the number of different types of protons in molecules. The position of the peak can give information about the molecule structure in the vicinity of the proton. Protons are of two types' equivalent and non-equivalent protons. Equivalent protons are those in the molecule that are chemically indistinguishable while non-equivalent protons are chemically distinguishable.



a = Equivalent Protons
b = Non-equivalent Protons

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Instrumentation and Working of NMR Spectrometer

Instruments that are used to get NMR spectra are usually named NMR spectrometer. It contains a complex collection of electronic equipment. NMR spectrometers use very powerful magnets to create a small but measurable energy difference between two possible spin states.

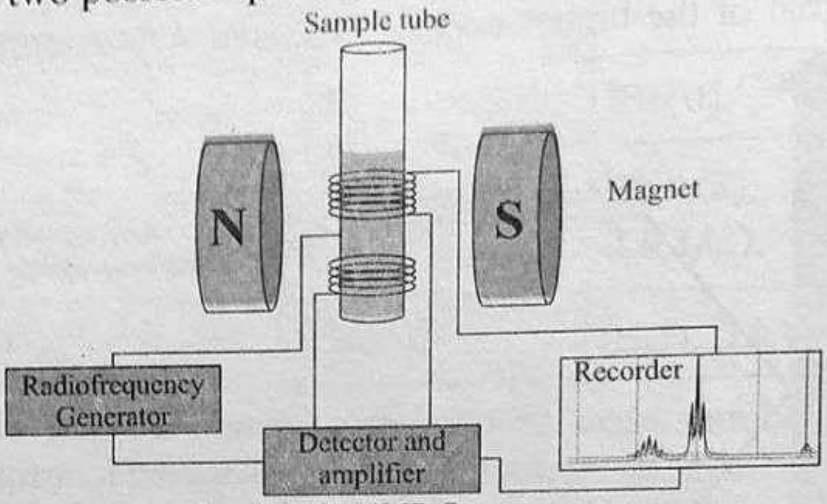


Fig. 24.12: NMR Spectrometer

Working

The sample is dissolved in a solvent, usually $CDCl_3$ (deutero-chloroform), and placed in a magnetic field. A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance. When the nuclei fall back to their lower energy state, the detector measures the energy released and a spectrum is recorded.

NMR Spectrum

The NMR spectrum is a plot of intensity of NMR signals versus magnetic field (frequency) in reference to TMS (tetramethylsilane). NMR signal is plotted on the y-axis and frequency on the x-axis. The value of frequency increases from right to left rather than left to right. In NMR spectrum we do not use unit Hertz (cycles per second) but rather we use parts per million (ppm).

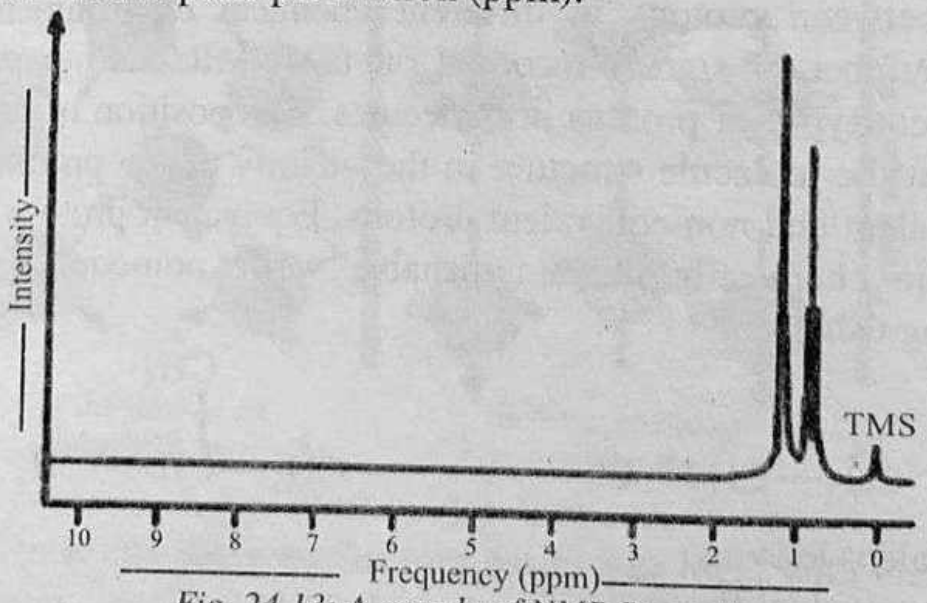


Fig. 24.13: A sample of NMR Spectrum

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Applications of NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful and widely used techniques in chemical research for investigating structure and dynamics of molecules. Some of the applications of NMR spectroscopy are:

i) Advanced methods can even be utilized for structure determinations of biopolymers, for example proteins or nucleic acids. NMR is also used in medicine for magnetic resonance imaging (MRI).

ii) NMR is used in biology to study the biofluids and biomacromolecules such as Nucleic acids (DNA, RNA), carbohydrates, Proteins and peptides.

iii) NMR is used in physics and physical chemistry to study high pressure diffusion, liquid crystals, liquid crystal solutions, membranes and rigid solids.

iv) It has various applications in food industries, food science, chemical analysis of different products, pharmaceutical approach etc. To analyse the carbon-hydrogen framework in the molecule is the basic work of NMR technique.

24.2.2.4 Atomic Absorption and Emission Spectra

Atoms in which no electrons are in the higher vacant level are said to be in the **ground state** while atoms in which there is an electron in the higher level are said to be in an **excited state**. The ground state is the most stable electronic state. The movement of an electron from one energy level to another energy level within an atom is known as **electronic transition**. It is noted that the light coming is must be exactly equal to the energy difference between the two electronic energy levels, otherwise the atom will not absorb it.

Atomic Absorption Spectrum

The absorption spectrum of an atom is the spectrum of wavelengths or frequencies of photons that are absorbed by the atoms due to jumping of electron from lower energy level to higher energy level. The wavelengths or frequencies that are absorbed will appear as dark lines on a bright background. Absorption occurs upon supplying radiation. The absorption spectrum of sodium gives two dark lines of wavelength 589.0 nm and 589.6 nm and that of hydrogen gives four different dark lines of wavelength 410 nm, 434 nm, 486 nm, and 656 nm.

Atomic Emission Spectrum

The emission spectrum of an atom is the spectrum of wavelengths or frequencies of photons that are emitted by the atom due to falling of electron from higher energy level to lower energy level. The wavelengths or frequencies that are emitted will appear as bright lines on a dark background. Emission occurs even in the absence of a radiation source. It is interesting to know that, the positions of bright lines in emission spectrum is exactly same as the position of dark lines in absorption spectrum, that is the energy of radiations emitted by excited hydrogen are exactly the

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same as energies absorbed by cold hydrogen. The emission spectrum of sodium gives two bright lines (golden yellow lines) of wavelength 589.0 nm and 589.6 nm and that of hydrogen gives four different bright lines of wavelength 410 nm (violet), 434 nm (blue), 486 nm (bluish-green), and 656 nm (red).

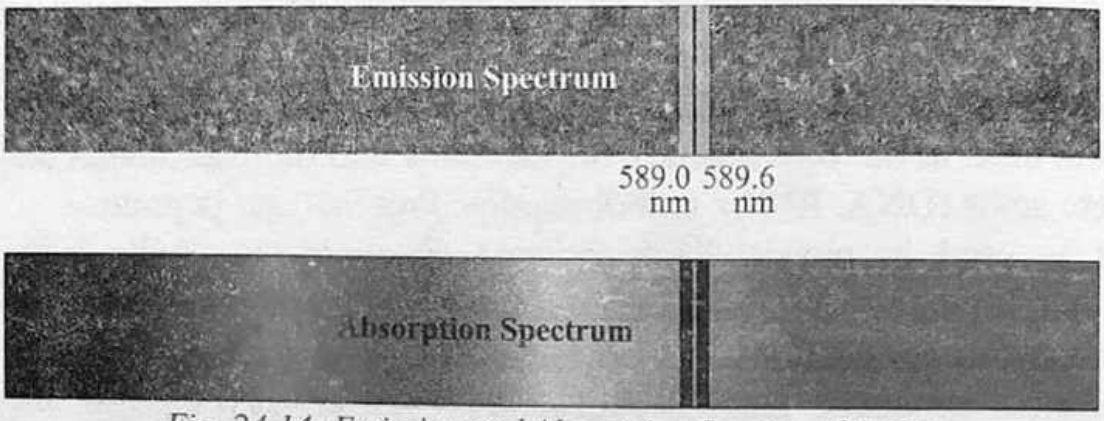


Fig. 24.14: Emission and Absorption Spectra of Sodium

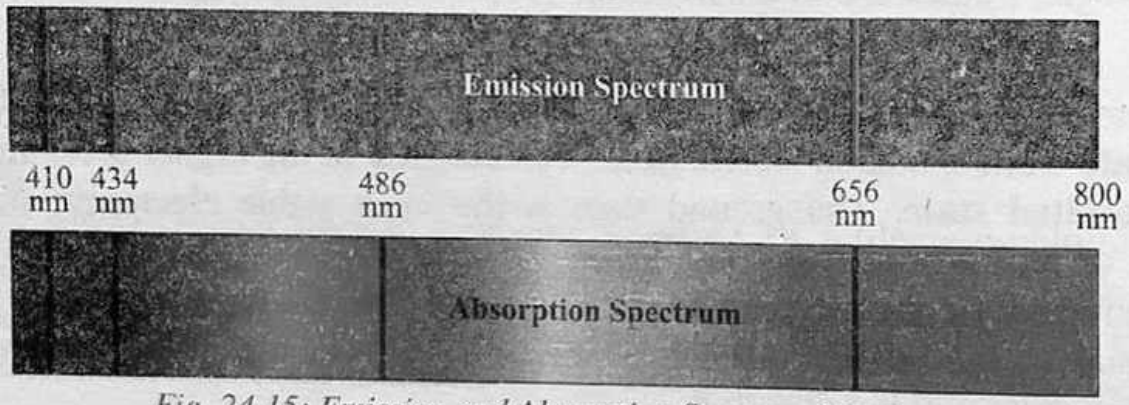


Fig. 24.15: Emission and Absorption Spectra of Hydrogen

Interesting Information

Strontium gives red, barium gives green, potassium gives violet and copper gives blue coloured lines on heating. These are the colours of the flame test of these elements. In the discharge tube, the helium gas glows with pink colour while neon glows with an orange red colour.

Elements can be identified by their spectral lines because the spectral lines are different for every element.

Table 24.3: Difference between Emission and Absorption Spectra

S.No.	Emission Spectrum	Absorption Spectrum
1	It is formed at high temperature.	It is formed at low temperature.
2	It is formed when the substance is in the gaseous state (vapours).	It is formed when the substance is even in the liquid or solution state.
3	In this spectrum, bright (coloured) lines are present on dark background.	In this spectrum, dark lines are present on bright background.

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S.No.	Emission Spectrum	Absorption Spectrum
4	It has bright (definite colour) lines.	It has dark black lines.
5	It is formed when an electron jumps from higher energy level to lower energy level.	It is formed when an electron jumps from lower energy level to higher energy level.
6	Energy is released.	Energy is absorbed.

24.2.2.5 Mass Spectrometry (MS)

Mass spectroscopy is a technique that is used to measure molecular masses, to analyze the composition of sample and to elucidate the structures of molecules and other compounds by means of the separation of gaseous ions according to their mass-to-charge ratio (m/z). Mass spectroscopy is also known as mass spectrometry.

Mass spectroscopy is not a true spectroscopic technique because absorption of electromagnetic radiation is not involved at all. Mass spectroscopy has very high sensitivity, low detection limits and the possibility of ionizing very small sample volumes.

Principle of Mass Spectrometry

Mass spectrometry does not directly determine mass; it determined the mass-to-charge ratio. Mass spectrometry carry out three main functions that is: (i) the ionization of molecules, (ii) the separation of these molecules according to their mass-to-charge (m/z) ratio (iii) the determination of the respective abundance of each ion produced.

Instrumentation and Working of Mass Spectrometry

The simplest form of mass spectrometer has following components:

i) Sample inlet system (vapourizer)
ii) Ion source (ionization chamber)
iii) Accelerating plates and slits
iv) Analyzer (ion separation system)
v) Detector (ion collector)
vi) Amplifier
vii) Recorder

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These basic parts are well shown in the following schematic diagram.

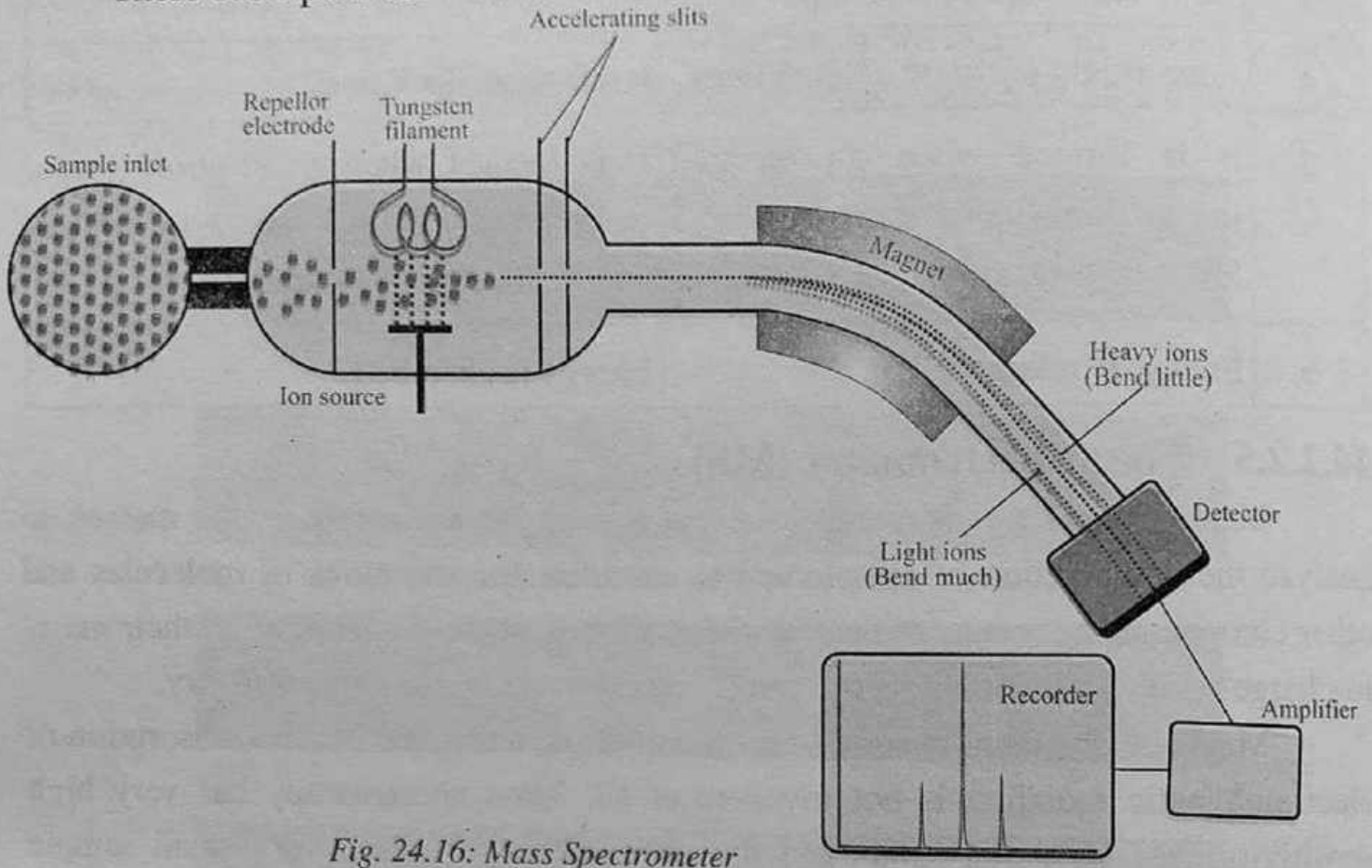


Fig. 24.16: Mass Spectrometer

The sample (material to be analysed) is introduced into an inlet chamber and converted into vapours state. These vapours are allowed to enter into ionization chamber.

The ion source is an essential component of all the mass spectrometers where the sample molecules pass through a beam of very high energy electrons emitted from electrically heated filament (usually tungsten filament). The electron-molecule collision gives considerable energy to the sample molecules that in turn emit electrons and produce positively charged ions. These positively charged ions have different masses depending upon the nature of isotopes of the element present in them.

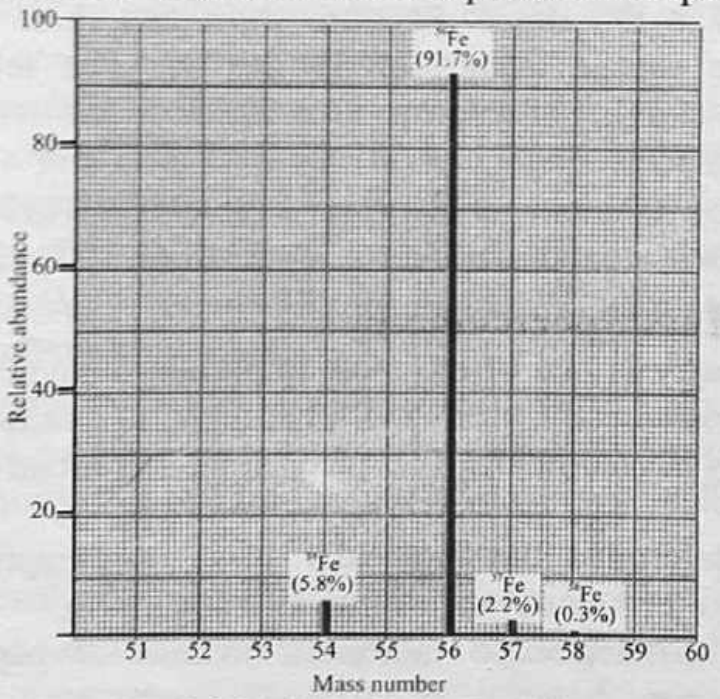
One essential component of all mass spectrometers is the vacuum system. It produces the required vacuum conditions for ion generation and for separation and detection of ions. The pressure of the system is kept at very low so the ions move freely without any resistance from air molecules.

A repeller plate, which carries a positive electrical potential, directs these newly created positive ions toward a series of accelerating plates. A large potential difference of 1 to 10 kilovolts (kV) is applied across the accelerating plates to produce a beam of fast moving positive ions. The positive ions pass through one or more focusing slits to produce a uniform beam.

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Analyser (the ion separation system) separates the fast moving ions with respect to their mass-to-charge (m/z) ratios. If all ions have single positive charge and have the same velocity, then the amount of deflection is inversely proportional to the mass of each ion. The lighter ions are deflected more than the heavier ions.

The ions ultimately reach an ion collector, where they are detected. An electronic signal is generated by the collector and is amplified before it is recorded. Frequently the data go directly into an on-line computer which generates the mass spectrum in digital or bar graph form. The mass spectrum is the 2D representation of ion intensity (relative abundance) against the mass-to-charge (m/z) ratio. In mass spectrum, the highest peak, called the base peak, is the standard against which the other peaks are measured. The base peak is arbitrary assigned a relative intensity value of 100. The spectrum helps us in determining the relative atomic masses as well as relative abundance (ion intensity) of isotopes of elements. In mass spectrum, the position of peaks shows relative atomic mass and the length of peaks shows the relative abundance of the ion. Consider the example of mass spectrum of iron.



Graph 24.1: Mass Spectrum of Iron

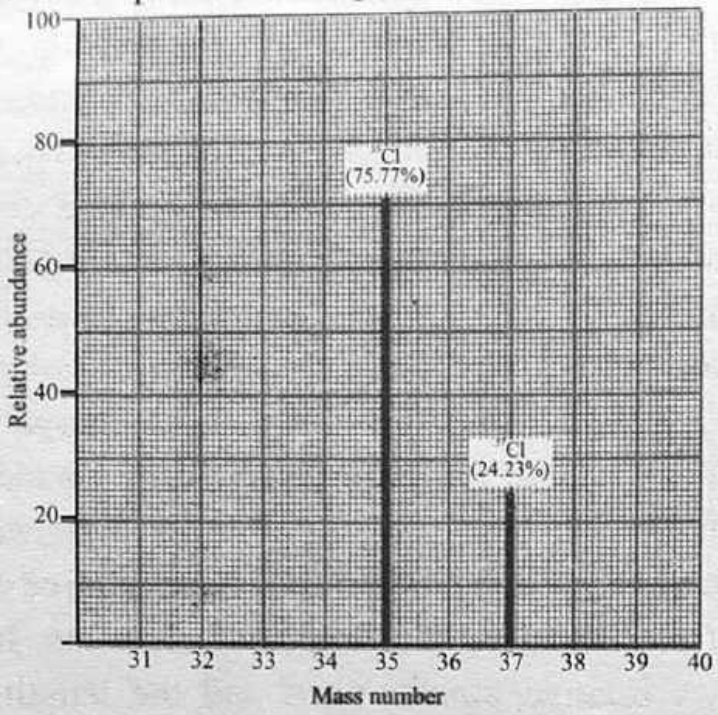
Here the horizontal axis shows the mass of each detected ion. The relative abundance of each ion can be found from the height of each peak. It is seen that there exist four isotopes of Iron, i.e. ^{54}Fe, ^{56}Fe, ^{57}Fe and ^{58}Fe, each with a relative abundance 5.8%, 91.7%, 2.2% and 0.3% respectively. Thus ^{56}Fe is much more abundant in nature than the other isotopes. From this data the relative atomic mass of the 'Fe' is calculated as follows,

Average mass of 100 atoms of Fe $= (54\times5.8) + (56\times91.7) + (57\times2.2) + (58\times0.3) = 5591$

Average mass of 1 atom of Fe $= 5591.2/100 = 55.91$ amu

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Consider another example of mass spectrum of chlorine.



Graph 24.2: Mass spectrum of chlorine

The two peaks in the above spectrum show that there are two isotopes of chlorine with relative atomic masses of 35 and 37. The relative abundance of chlorine-35 is 75.77% and that of chlorine-37 is 24.23%. The average atomic mass of chlorine can be calculated as:

Average mass of 100 atoms of chlorine $= (35\times75.77)+(37\times24.23)=3548$
Average mass of 1 atom of chlorine $= 3548.46/100 = 35.48$ amu

Applications of Mass Spectrometry

Mass spectrometry is one of the most important analytical techniques that is used in chemistry, biochemistry, medicine, pharmacy, agriculture, material science, food science and many related fields of science. Some important applications of mass spectroscopy are as:

i) It is used to determine the molecular mass of compounds by separating molecular ions on the basis of their mass-to-charge ratio.
ii) It is also used to determine molecular masses of peptides, proteins and oligonucleotides.
iii) It is used for characterization and sequencing of different proteins.
iv) It is used in materials science to identify the precise chemical composition of samples, which can help to explain why buildings or bridges collapse unexpectedly or why engineering components have suddenly failed.
v) It is used in forensic science to identify unusual substances found at a crime scene and match them precisely with similar substances found elsewhere.
vi) It is used to identify chemical, biological, radiological, nuclear, and explosive threats.

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vii) It can help us to understand our environment. We can use them to measure how quickly air and water pollution travels.

viii) Mass spectrometers are increasingly being used for things like drug testing and discovery, food contamination detection, virus and bacteria identification, pesticide residue analysis, isotope ratio determination, protein identification, and carbon dating.

Summary of Facts and Concepts

- The analytical chemistry deals with the analysis of matter. The analysis means to find out the chemical composition of the matter that is, what type of atoms constitutes the matter and how many atoms are forming that matter.
- The traditional methods of analysis are called classical methods of chemical analysis which are based on using the chemical reactions for analytical procedures. The traditional methods are time consuming and needs a lot of expertise.
- The modern methods of analysis are based on the use of different radiations. These analytical procedures are termed as the spectroscopy.
- The modern methods called spectroscopy are fast, require less amount of substance to be analyzed, and they use modern equipment like computers which make the results more accurate.
- The matter interact with the light or radiations and as result of this energy is absorbed and subsequently emitted by the electrons in the atoms and molecules of any substance under observation.
- The table of all known radiations is called electromagnetic spectrum.
- The Instrument that is used in spectroscopy is called the spectrometer.
- Mostly used radiations of spectrum include infrared rays, visible light, ultraviolet rays and the X-rays.
- Stretching (symmetric or asymmetric) involves the change in bond lengths and bending (scissoring, rocking, wagging, and twisting) involves the change in bond angles. The most useful bands in an infrared spectrum correspond to stretching frequencies.
- Compounds (organic or inorganic) having covalent bonds absorb electromagnetic radiations in the infrared region. The main use of the technique is to determine the functional groups in the molecule.
- Our eyes also serve as a visible spectrometer for identifying different substances.
- White light is made up of different colour radiations.
- The molecular formula of a substance is determined by the use of nuclear magnetic resonance (NMR) spectroscopy effectively.

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Multiple Choice Questions

Four answers are given for each question. Select the correct answer.

i) Volumetric analysis method is aimed for:
   (a) Analyzing solutions (b) Analyzing liquids only
   (c) Analyzing solids only (d) Analyzing volume only

ii) The combustion analysis methods are:
   (a) Only limited to organic compounds
   (b) Only limited to Inorganic compounds
   (c) Covered both organic and inorganic compounds
   (d) Covered only physical characters of a chemical compound.

iii) The salt analysis covers:
   (a) Analysis of organic compounds
   (b) Analysis of Inorganic compounds
   (c) Both organic and inorganic compounds
   (d) Analysis the sodium chloride only.

iv) Mass spectrometers separates ions on which of the following:
   (a) Mass (b) Charge
   (c) Mass-to-charge ratio (d) Molecular mass

v) The Ultraviolet light has energy:
   (a) More than red light (b) Less than red light
   (c) More than X-rays (d) More than gamma rays

vi) The red light has wave length from:
   (a) 400-450nm (b) 450-550nm
   (c) 550-620nm (d) 620-800nm

vii) The portion of the fire that feels us warm is
   (a) Ultraviolet rays (b) Infrared rays
   (c) Visible radiations (d) Yellow light of fire

viii) The globar rod in IR spectrometer is made of:
   (a) Oxides of zirconium (b) Silver carbide
   (c) Oxides of cerium (d) Silicon carbide

ix) The colour of a chemical compound results from
   (a) Stretching of molecules (b) Bending of molecules
   (c) Release of energy (d) Electronic transitions

x) Mass spectroscopy is used to determine
   (a) Molecular masses (b) Functional group
   (c) Type of atoms (d) Unsaturation

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Short Answer Questions

Q.1. Define chemical analysis. What are the main types of chemical analysis?
Q.2. What is the importance of qualitative analysis and quantitative analyses?
Q.3. What are the different types of spectroscopy?
Q.4. What is the main use of IR spectroscopy?
Q.5. Why most chemist use wave number unit rather than wavelength in IR spectroscopy?
Q.6. How UV-Vis spectroscopy differs from IR spectroscopy?
Q.7. How does the detector in NMR spectrometer work?
Q.8. What are the principles of mass spectrometer?
Q.9. Name the factors that affect vibrational frequency.
Q.10 Give three applications of mass spectroscopy.

Long Answer Questions

Q.1. What is chemical analysis? Explain qualitative and quantitative analysis with at least one example.
Q.2. What do you know about classical and modern methods? Compare classical methods of analysis with modern methods.
Q.3. What is the difference between volumetric and gravimetric methods of analysis?
Q.4. What is combustion analysis? Discuss the procedure of combustion analysis.
Q.5. What are electromagnetic radiations? Describe the regions in electromagnetic spectrum in detail?
Q.6. Define and explain atomic absorption and emission spectra.
Q.7. Define spectroscopy. What are the applications of spectroscopy?
Q.8. What is UV-Vis spectroscopy? Explain the principle and applications of UV-Vis spectroscopy.
Q.9. Explain the various electronic transitions possible on the absorption of UV-Visible radiation.
Q.10. Write a note on infrared spectroscopy? Describe the principle and applications of IR spectroscopy.
Q.11. Explain the various vibrations possible when a molecule absorbs infrared radiation.

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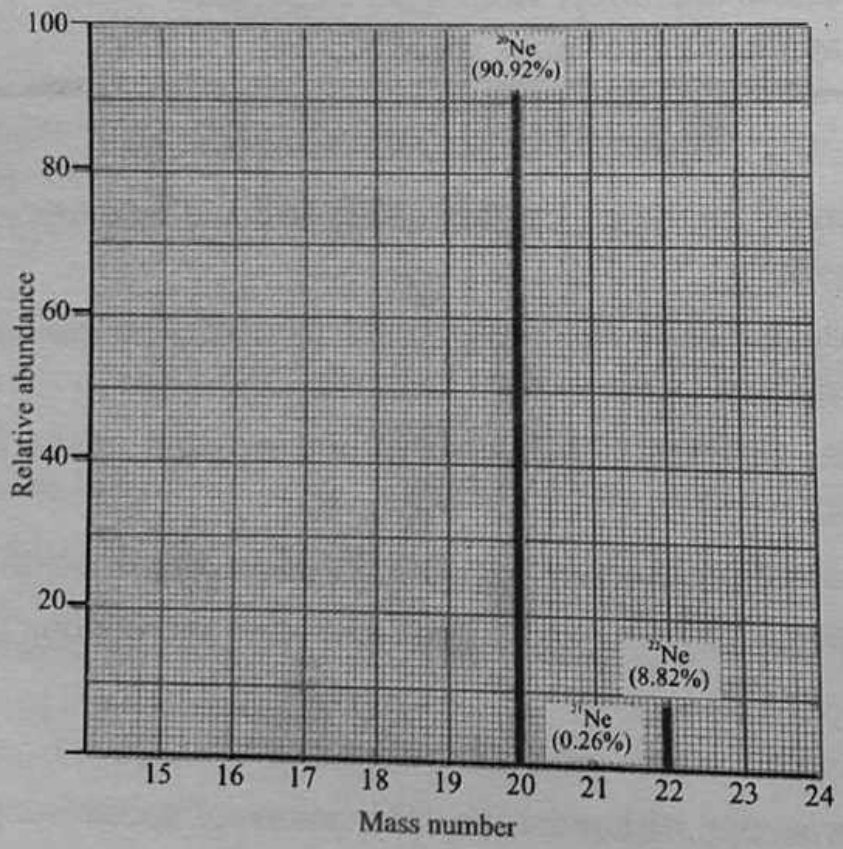
Problems

Q.1. When 2.203g of sample of an organic compound was burnt in a combustion tube, 4.401g of CO_2 and 1.802g of H_2O were produced. Determine the % age of carbon, hydrogen and oxygen atoms.

Q.2. An unknown compound contains 14.31% sodium, 9.97% sulphur, 6.22% hydrogen and 69.5% oxygen. Calculate the empirical formula of the compound.

Q.3. The empirical formula of glucose is CH_2O. It molecular mass is 180 amu. Determine it molecular formula.

Q.4. Calculate the average atomic mass of neon with the help of mass spectrum given below:



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Index

A

Acid-Base Behaviour of:
- Oxides of Group IVA, 39
- Oxides of Period 3 Elements, 18

Acid Anhydrdes:
- Introduction, 260
- Nomenclature, 264

Acid Rain, 344

Acyl Halides:
- Introduction, 260
- Nomenclature, 263

Adhesives:
- Introduction, 326
- Types, 326-328

Air Pollutants, 337

Alcohols:
- Acidity, 210
- Dehydration, 214
- Introduction, 206
- Isomerism, 209
- Nomenclature, 207-208
- Oxidation, 216
- Physical Properties, 209
- Preparation, 210-213
- Reactions, 214-217
- Reactivity, 213
- Structure, 209 - 210

Aldehydes:
- Introduction, 238
- Nomenclature, 239-240
- Physical Properties, 242
- Preparation, 243-244
- Reactions, 245-254
- Reactivity, 245
- Structure, 243

Alkaline Earth Metals, 29-35

Alkali Metals, 24-29

Alkane:
- Introduction, 107
- Nomenclature, 109-114
- Physical Properties, 115-116
- Reactivity, 119
- Stability, 118-119
- Structure, 118

Alkenes:
- Conjugation, 131-132
- Introduction, 122
- Nomenclature, 122-124
- Preparation, 125-127
- Reactions, 127-131
- Reactivity, 127
- Stability, 124-125
- Structure, 125

Alloy Formation of:
- Transition Elements, 60-61

Alkenyne:
- Definition, 140
- Nomenclature, 140

Alkyl Halides:
- Introduction, 174
- Nomenclature, 175-176
- Physical Properties, 177
- Preparations, 177-178
- Reactivity, 178-179
- Structure, 177

Alkyl Group, 111

Alkynes:
- Acidity, 143-144
- Addition Reactions, 144-146
- Introduction, 138
- Nomenclature, 138-139
- Physical Properties, 142
- Preparation, 142-143
- Reactivity, 143
- Relative Stability, 141
- Structure, 141-142

Amides:
- Introduction, 260
- Nomenclature, 263

Amines:
- Basicity, 196-197

Scanned with CamScanner

Introduction, 193
Nomenclature, 193-195
Physical Properties, 195-196
Preparation, 197-198
Reaction, 198-200
Reactivity, 198
Structure, 196
Aromatics, 321
Atmosphere, 334
Analytical Chemistry, 358
Atomic Absorption Spectrum, 381
Atomic Emission Spectrum, 381-382
Atomic Radius of:
Alkali Metals, 25
Alkaline Earth Metals, 30
Halogens, 42
Period 3 elements, 10
Auxochrome, 317

B

Binding Energy of Transition Elements, 57
Blocks of Elements:
s-block Elements, 8
p-block Elements, 8
d-block Elements, 8
f-block Elements, 9
Benzene:
Explanation, 146
Nomenclature, 147-151
Physical Properties, 151
Reactions, 154-161
Reactivity, 154
Resonance Energy, 153-154
Stability, 153-154
Structure, 152
Biochemistry, 286
Biosphere, 334
Bond Enthalpies in:
Halogens, 43
Hydrogen Halides, 43
Boiling Points of:
Alkali Metals, 26
Alkaline Earth Metals, 31
Chlorides of Period 3 Elements, 22
Halogens, 42-43
Oxides of Period 3 Elements, 17
Period 3 elements, 12-13
Bucky Ball (or Fullerene), 95

C

Carboxylic Acids:
Acidity, 265-266
Introduction, 259
Nomenclature, 260-263
Physical Characteristics, 264-265
Preparation, 266-268
Reactions, 268-276
Reactivity, 268
Structure, 265
Carbohydrates:
Classification, 286-288
Function, 288-289
Introduction, 286
Nutritional Importance, 289-290
Catalytic Activity of:
Iron, 79
Transition Elements, 58-59
Vanadium, 72-73
Central Metal Atom, 62
Chemical Analysis, 359
Chemical Industry, 313-314
Chiral Centres, 133
Chlorides of:
Group IVA Elements, 37
Period 3 Elements, 21-23
Chromophore, 317
Coal, 89-90
Colour of:
Complexes, 69-71
Combustion Analysis, 360-361
Constitutional Isomers, 136-138

Scanned with CamScanner

Coordination Compounds:
Component, 62-64
Definition, 62
Nomenclature, 65-68
Coordination Number, 64
Coordination Sphere, 64
Cosmetics, 322-326
Cycloalkane:
Definition, 107
Explanation, 107
Nomenclature, 114-115
Physical Properties, 117
Reactivity, 119
Stability, 118-119
Structure, 118

D

Density of:
Alkali Metals, 26
Destructive Distillation of Coal, 92-93
Detection of:
Halogens, 100
Nitrogen, 99
Sulphur, 100
Dissolved Solids, 348
Dyes:
Chemical Composition, 317
Classification, 318
Introduction, 316

E

Effect of Heat on:
Nitrates of Alkali Metals, 28
Nitrates of Alkaline Earth Metals, 33
Carbonates of Alkali Metals, 28
Carbonates of Alkaline Earth Metals, 33
Bicarbonates of Alkali Metals, 29
Electrical Conductivity of:
Chlorides of Period 3 Elements, 22
Oxides of Period 3 Elements, 17-18
Period 3 elements, 12
Electromagnetic Radiations, 364-365
Electromagnetic Spectrum, 365-367
Electron Affinity of:
Halogens, 42
Electronegativity of:
Alkali Metals, 25
Alkaline Earth Metals, 31
Halogens, 42
Period 3 elements, 11-12
Electronic structure of:
Period 3 elements, 9
Transition Elements, 56-57
Electronic Transitions, 368-369
Elimination Reactions, 185-187
Empirical Formula:
Determination, 362-363
Environment, 333-334
Environmental Chemistry, 332-333
Enzymes:
Application, 297-298
Factors, 296-297
Introduction, 295
Role, 295-296
Ethers:
Introduction, 229-230
Nomenclature, 230-231
Physical Properties, 231
Preparations, 231
Reactions, 232
Reactivity, 231-232

F

Flame Tests of:
Alkali Metals, 29
Fossil Remains, 89-90
Functional Group, 95-97

G

General Features of Transition Elements, 55-56

Scanned with CamScanner

Global Warming, 343
Green Chemistry:
Goal, 352
Introduction, 352
Principles, 352-353
Green House Effect, 342
Grignard's Reagent:
Introduction, 189
Preparation, 189
Reactions, 190-192
Reactivity, 190
Groups, 8
Group 14 (IVA) Elements, 35

H

Hair Dyes:
Introduction, 325
Side Effects, 326
Types, 325-326
Halide Ions as Reducing Agents, 45-46
Halogens, 41
Halogens as Oxidizing Agents, 43-44
Homologous Series:
Definition, 97
General Characteristics, 98
Hydrocarbons:
Introduction, 106
Types, 106-107
Hydrogen Halides:
Acidity, 44-45
Hydrosphere, 333-334
Hydroxides of:
Period 3 Elements, 23-24

I

Industrial Chemistry:
Introduction, 313
Industrial Smog, 341
Infrared Spectroscopy:
Application, 377
Introduction, 371-372
Instrumentation, 375-376
Principle, 372
Ionic Character of:
Oxides of Period 3 Elements, 16
Ionization Energy of:
Alkali Metals, 25
Alkaline Earth Metals, 30-31
Period 3 elements, 10-11
Ionization Sphere, 64
Isomerism, 132-133

K

Ketones:
Introduction, 238
Nomenclature, 240-241
Physical Properties, 242
Preparation, 243-245
Reactions, 245-254
Reactivity, 245
Structure, 243

L

Ligand, 62-64
Lipids:
Classification, 298-299
Importance, 301
Introduction, 298
Properties, 299-300
Structure, 299
Lipsticks, 323
Lithosphere, 3333

M

Magnetic Behaviour of:
Transition Elements, 59-60
Markovnikov's Rule, 128
Mass Spectroscopy:
Application, 386-387
Introduction, 383
Instrumentation, 383-386
Principle, 383

Scanned with CamScanner

Melting Points of:
Alkali Metals, 26
Alkaline Earth Metals, 31
Chlorides of Period 3 Elements, 22
Halogens, 42-43
Oxides of Period 3 Elements, 17
Period 3 elements, 12-13
Metallic Character of:
Group IVA Elements, 36
Minerals:
Introduction, 306
Sources, 306-307
Biolobical Significance, 307-308
Molecular Formula:
Determination, 363
Molecular Vibrations, 373-375
Monosaccharides, 386-387

N

Nail Varnish, 323-324
Nail Varnish Remover, 324
Natural Gas, 90
Natural Polymers, 321
Natural Product Chemistry, 90
NMR Spectroscopy:
Application, 381
Introduction, 377
Instrumentation, 380
Principle, 378-379
Nomenclature:
Definition, 108
Common system, 108
IUPAC system, 108-109
Nucleic Acids, 302-306
Nucleophilic Substitution Reactions, 179-185
Nylon:
Formation, 322
Properties, 322
Uses, 322

O

Olefins, 321
Oligosaccharides, 287-288
Optical Activity, 134
Optical Isomers, 134-135
Organic Chemistry, 89
Organic Compounds:
Characteristics, 93-94
Definition, 89
Sources, 89-92
Uses, 94
Organometallic Compounds, 189
Oxidation State of:
Chromium, 73
Copper, 81
Group IVA Elements, 36
Iron, 78-79
Manganese, 76-77
Transition Elements, 57-58
Vanadium, 72
Oxides of:
Group IVA Elements, 38-39
Ozone:
Depletion, 346-347
Destruction, 345
Introduction, 339
Harmful Effects, 339
Production, 345

P

Partial and Total Synthesis, 91-92
Peculiar Behaviour of:
Beryllium, 33-34
Periods, 8
Pesticides:
Classification, 319
Introduction, 318-319
Petrochemicals, 319-321
Petroleum, 90

Scanned with CamScanner

Phenols:
Acidity, 224
Introduction, 220
Nomenclature, 220-222
Physical Properties, 223-224
Preparations, 224-226
Reactions, 226-227
Reactivity, 226
Structure, 223
Photochemical Smog, 342
Physical Properties of:
Group IVA Elements, 36
Oxides of Period 3 Elements, 8
Polymers, 321-322
Polysaccharides, 288
Polyvinyl Chloride (PVC):
Formation, 321
Uses, 322
Potassium Dichromate as an Oxidizing Agent, 75
Potassium Manganate(VII) as an Oxidizing Agent, 77
Proteins:
Classification, 291
Importance, 294
Introduction, 291
Properties, 294
Structure, 292-293

Q

Qualitative Analysis, 359
Quantitative Analysis, 359-360

R

Radical Substitution Reactions, 119-121
Raw Materials, 314-315
Reactions of:
Alkali Metals with Oxygen, 27
Alkali Metals with Halogens, 28
Alkaline Earth Metals with Oxygen, 32
Alkaline Earth Metals with Nitrogen, 32
Hexaaquacopper (II) with Hydroxide Ions, 81
Hexaaquacopper (II) with Ammonia, 82
Hexaaquacopper (II) with Carbonate Ions, 82
Hexaaquairon (II) and (III) with Water, 79-80
Hexaaquairon (II) and (III) with Ammonia, 80
Iron (II) with Carbonates Ions, 80
Iron (II) with Thiocyanate Ions, 80-81
Iron (III) with Carbonates Ions, 80
Iron (III) with Thiocyanate Ions, 80-81
Oxides of Period 3 Elements with Water, 19
Oxides of Period 3 Elements with Acids, 19-20
Oxides of Period 3 Elements with Bases, 20-21
Period 3 Elements with Water, 13-14
Period 3 Elements with Oxygen, 14-15
Period 3 Elements with Chlorine, 15-16
Resonance, 152-153

S

Sedimats, 348
Series of Transition Elements, 54-55
Sewage Treatment, 351-352
Shapes of:
Complex Ions, 68-69
Smog, 341-342
Solubility in Water of:
Carbonates of Alkaline Earth Metals, 33
Chlorides of Period 3 Elements, 23
Hydroxides of Alkaline Earth Metals, 32
Sulphates of Alkaline Earth Metals, 33
Spectroscopy, 367

Scanned with CamScanner

Stereoisomers, 135-136
Stratosphere, 345-347
Structure of:
Carbon Dioxide, 38
Chlorides of Period 3 Elements, 21-22
Oxides of Period 3 Elements, 16
Silicon Dioxide, 38-39
Suspended Solids, 348
Synthesis Gas, 321
Synthetic Polymers, 321-322

T

Thermal Pollution, 348-349
Thiols:
Acidity, 220
Introduction, 218
Nomenclature, 218-219
Physical Properties, 219
Structure, 219-220
Transition Elements, 54
Troposphere, 334-335

U

UV-Vis Spectroscopy:
Application, 371
Introduction, 367
Instrumentation, 369-371
Principle, 367-368

W

Water Pollution, 347
Water Treatment, 347

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Glossary

Acetals. Acetals are formed when hemiacetals react with second molecule of alcohol.

Achiral: A molecule that is superimposable on its mirror image. It has a lack of handedness.

Activating group: The electron donating groups that increase the reactivity of the aromatic ring towards electrophilic substitution such as hydroxyl group (—OH).

Acylation: The replacement of hydrogen of benzene by an acyl group (—COR) is called alkylation.

Addition Reactions: The most important reactions of alkenes are the addition reactions.

Alcohols: Alcohols are organic compounds in which hydroxyl group is attached to alkyl group.

Alkanes: Alkanes are saturated hydrocarbons containing single bonds between carbon atoms.

Alkenes: Unsaturated hydrocarbons containing one or more carbon-carbon double bonds in their structures.

Alkylation: The replacement of hydrogen of benzene by an alkyl group (—R) is called alkylation.

Alkyl Group: Alkyl group is formed by the removal of one hydrogen atom from an alkane.

Alkyl Halides: Organic compounds in which one or more hydrogen atom(s) of an alkane are replaced by one or more halogen atom(s).

Alkynes: Unsaturated hydrocarbons containing one or more carbon-carbon triple bonds in their structures.

Amines: Organic compounds in which one or more hydrogen atom(s) of ammonia are replaced by alkyl or aryl groups.

Ammonolysis: The process of cleavage of the carbon-halogen bond by ammonia molecule.

Anomers: Similar molecules differing in the configuration at the hemiacetal (anomeric) carbon (carbon–1 atom of an aldose or the carbon–2 atom of a 2–ketose).

Apoenzyme: The proteinaceous part of enzyme.

Bond angle: The angle formed between two adjacent bonds.

Bond Enthalpy: Bond enthalpy, also known as bond energy, is the amount of energy required to break one mole of covalent bonds in a gaseous substance.

Carbocation: Carbocations are carbon atoms in an organic molecule bearing positive charge.

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Carbohydrate: Polyhydroxyaldehyde or polyhydroxyketones or compounds which give such compounds on hydrolysis. They include sugars, starches, celluloses, and gums and serves as a major energy source in the diet of animals.
Carbolic Acid: The 5% aqueous solution of phenol.
Carbonyl Group: A functional group composed of a carbon atom doubly bonded to an oxygen atom (C═O)
Catenation: The self-linking property of atoms of an element to form chains and rings.
Catalytic Hydrogenation: The addition of hydrogen across a double or triple bond of an unsaturated hydrocarbon in the presence of catalyst.
Chiral: A molecule that is not super imposable on its mirror image. It has handedness. The objects that show handedness are golf clubs, scissors, shoes and a corkscrew.
Chiral carbon atom: A carbon atom that is bonded to four different atoms or groups.
Chiral centers: Tetrahedral atoms usually carbon atoms having four different substituents.
Cis-trans Isomers: Compounds having same molecular and structural formulas but restricted rotation about certain bonds.
Coenzyme: The non- proteinaceous part of the enzyme.
Complex Ion: An ion in which a central metal atom or ion is surrounded by ligands (group of ions or molecules).
Deactivating group: The electron withdrawing groups that decrease the reactivity of the aromatic ring towards electrophilic substitution such as nitro group (—NO_2).
Decarboxylation: The loss of carbon dioxide from the carboxyl group of a molecule.
Dehydration: A chemical reaction that involves the loss of a water molecule from the reacting molecule. The alcohols can be dehydrated to produce alkenes.
Delocalization: The distribution of electron density over more than two atoms that are bonded together.
Delocalization energy: See resonance energy.
Dextrorotatory: A substance that rotates plane polarized light in a clockwise direction.
Diamagnetism: A form of magnetism whereby certain materials are slightly repelled by an external magnetic field.
Electrophile: Positively charged or neutral specie that can accept an electron pair in a reaction.
Elimination Reaction: A chemical reaction that involves the removal of two atoms or group of atoms from two adjacent carbon atoms of a substrate molecule.
Electromagnetic Spectrum: The entire range of wavelengths or frequencies of electromagnetic radiation extending from the highest energy gamma rays to the lowest energy radio waves.

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Empirical Formula: The simplest formula that indicates the relative proportion of atoms present in a compound. It does not show actual number or arrangement of atoms.

Enzymes: Biological molecules that act as catalysts within living cells.

Epoxidation: The addition of oxygen (O_2) to alkene is called epoxidation.

Esterification: An equilibrium reaction in which an alcohol and an acid (carboxylic acid) form an ester as the reaction product.

Ethers: A class of organic compounds that consist of an oxygen atom bonded to two alkyl or/and aryl groups.

Fat: Triesters of glycerol and fatty acids. They are generally soluble in organic solvents and largely insoluble in water.

Fibres: Thin threads of natural or artificial substances from which a vegetable tissue, mineral substance, or textile is formed. Natural fibres include cotton, hair, fur, silk, and wool. Natural fibres are of plant or animal origin. The most important synthetic fibres are dacron, nylon, orlon, and polypropylene.

Fatty Acids: A carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated.

Fullerenes: An allotrope of carbon in the form of a hollow sphere, ellipsoid, tube, and many other shapes.

Functional Group: An atom or group of atoms within a molecule which confers specific properties to a compound. It is the reactive part of the molecule. Each functional group has its characteristic reactivity.

Grignard Reagents: Alkyl magnesium halides (RMgX) are commonly known as Grignard Reagents.

Groups: Columns of elements in the periodic table.

Halohydration: The addition of hypohalous acid to alkenes.

Heat of Hydrogenation: The amount of heat evolved when one mole of an alkene is hydrogenated.

Hemiacetals: These compounds are formed by the addition of an alcohol molecule to carbonyl group. On the other hand, acetals are formed when hemiacetals react with second molecule of alcohol.

Homologous Series: A series of compounds with the same functional group in which each member differs from the next member by a methylene ($—CH_2—$) group in their formula.

Hydration: The addition of water to an unsaturated compound particularly an alkene or alkyne.

Hydrohalogenation: The addition of HX to alkenes.

Hydrocarbons: Compounds containing atoms of carbon and hydrogen only.

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Hydrogenation: The addition of hydrogen across a double or triple bond of an unsaturated hydrocarbon.

Isomers: Compounds having same molecular formula but different structures.

Laevorotatory: A substance that rotates plane polarized light in an anticlockwise direction.

Lipids: They include fatty acids, neutral fats, waxes and steroids (like cortisone). They are soluble in organic solvents such as alcohol, ether and chloroform. They are insoluble in water.

Markovnikov's Rule: According to this rule, the negative part of the polar reagent (unsymmetrical molecule) like HX adds to that carbon of double bond of an unsymmetrical alkene which has minimum number of hydrogen(s).

Mercapto Group: A functional group containing a sulphur atom bonded to a hydrogen atom. Its general formula is —SH. It is also known as thiol group or sulfhydryl group.

Monomers: They are the building blocks from which polymers are made.

Ozonolysis: The reaction of ozone (O_3) with alkene to break carbon-carbon double bond.

Peptides: They are short chain of amino acids monomers linked by peptide bonds.

Period: Rows of elements in the periodic table.

Periodic Table: A table of elements in which elements are arranged into groups and periods in the increasing order of atomic numbers.

Phosphodiester Bond: A covalent bond in RNA or DNA that holds a polynucleotide chain together by joining a phosphate group at position 5 in the pentose sugar of one nucleotide to the hydroxyl group at position 3 in the pentose sugar of the next nucleotide.

Phosphodiester Linkage: See phosphodiester bond.

Polarimeter: An instrument used to measure the optical activity of a compound.

Polymerization: The chemical process of formation of large molecule by joining together of two or more small molecules by chemical bonds.

Proteins: They are composed of long chains of amino acids. They are essential part of all living organisms.

Resonance Energy: The resonance energy of a compound is a difference between the energy of the actual molecule and the most stable resonance structure. It is also known as delocalization energy.

Resonance: The process in which two or more structures are written for a compound which differ only in the arrangement of electrons is called resonance.

Saturated Hydrocarbons: Hydrocarbons with only single covalent bonds.

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Shelf Life: The period of time that a product can be stored and remain fresh, useful or suitable for consumption.

Steric Hindrance: The prevention or retardation of chemical reaction because of the blocking of the reactive site of a molecule by adjacent atoms or groups of atoms.

Stereoisomerism: Compounds that have same connectivity but different arrangement of atoms or group of atoms in space are called stereoisomers and the phenomenon is known as stereoisomerism.

Spectroscopy: The study of the interaction between matter and electromagnetic radiation is called spectroscopy.

Substrate: A substrate is a molecule undergoing a reaction. It may also be defined as: the molecule that is attacked in a chemical reaction.

Sulfhydryl Group: See mercapto group.

Tautomerism: The isomers of a compound which differ only in the position of protons and electrons are called tautomers and the phenomenon is known as tautomerism.

Unsaturated Hydrocarbons: Hydrocarbons with multiple (double or triple) covalent bonds.

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