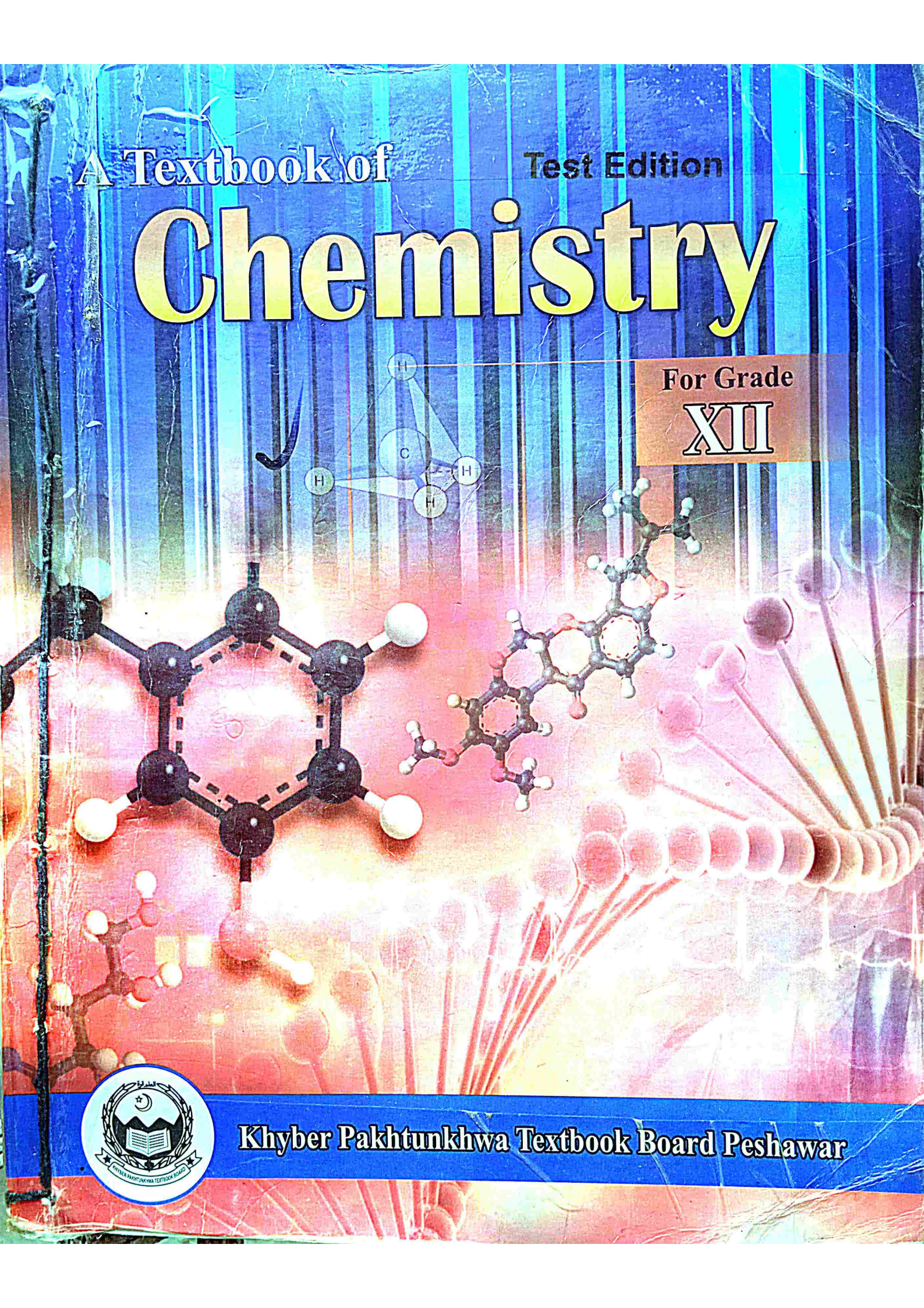
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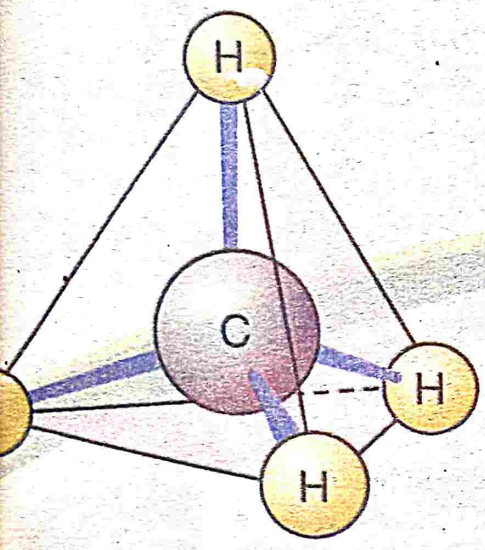


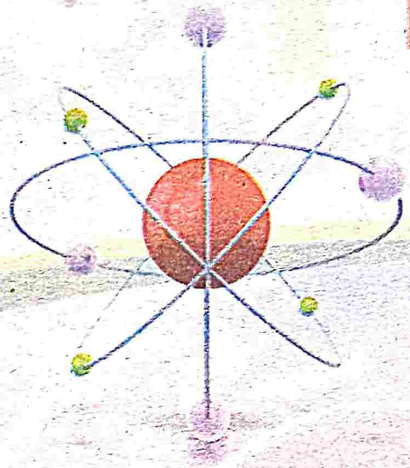
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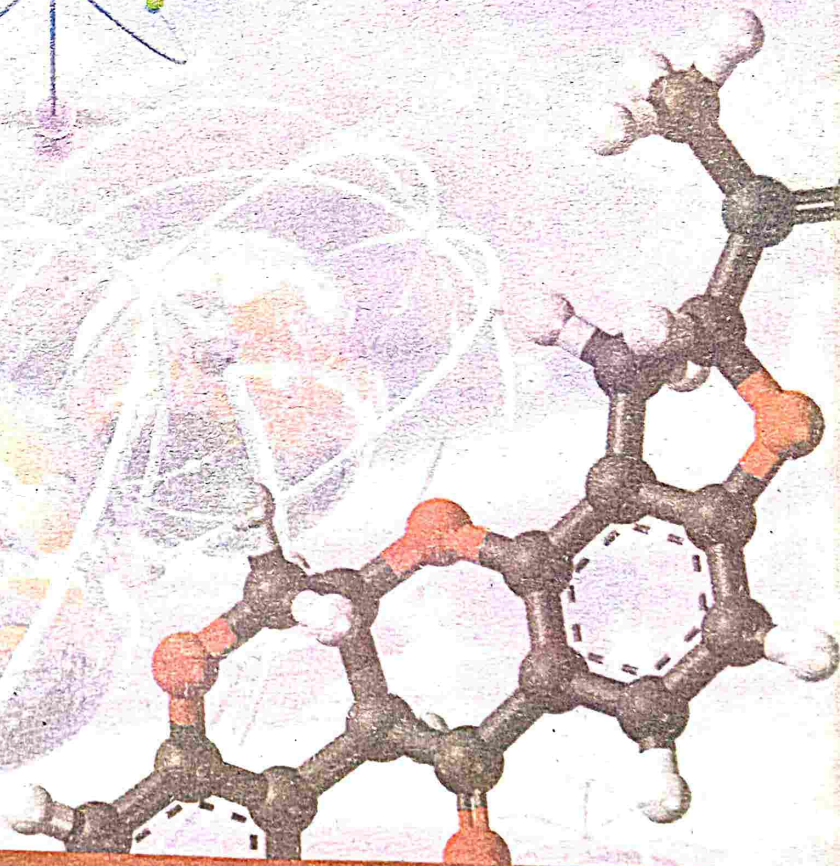
A Textbook of

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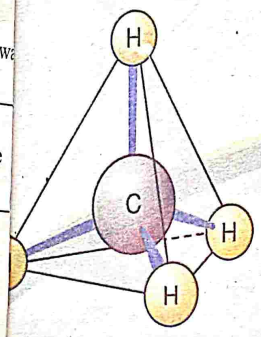
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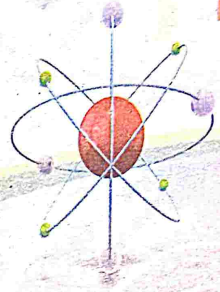
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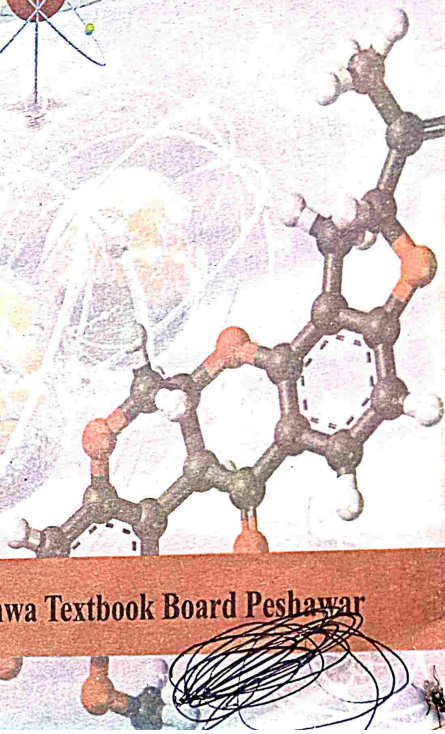
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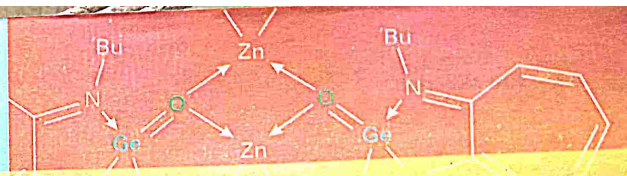


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Unit 13



s and p - Block Elements

Teaching	Assessment	Weightage %
25	3	22

After studying this unit, 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 and melting and boiling points of elements change within a group and within a period in the Periodic Table. (Analysing)
- 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. (Analysing)
- 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. (Analysing)
- Discuss the trends in thermal stability of the nitrates and carbonates of Group II elements. (Analysing)
- Differentiate beryllium from other members of its group. (Analysing)
- 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. (Analysing)
- Distinguish between an oxide and a peroxide. (Understanding)
- Write representative equations for the formation of oxides and sulphides. (Applying)
- Compare the outermost s and p orbital system of an element with its chemical properties. (Analysing)

Introduction

To easily understand the properties of the elements in the period table, the elements are placed in vertical columns and horizontal rows. The vertical columns are called groups or families and the horizontal rows are called the periods. The elements in the periodic table are divided into s, p, d and f blocks. Those elements in which last electrons occupy 's' subshell (orbital) are called s-block elements. The s-block elements are at the extreme left of the periodic table and placed in Group IA (alkali metals) and Group IIA (alkaline earth metals) elements. Those elements in which last electrons occupy p subshell are called p-block elements. The p-block elements are placed in Groups IIIA, IVA, VA, VIA, VIIA and VIIIA.

Both s-block and p-block elements are normal elements. s-block elements consist of only metals but p-block elements include both metals and non-metals.

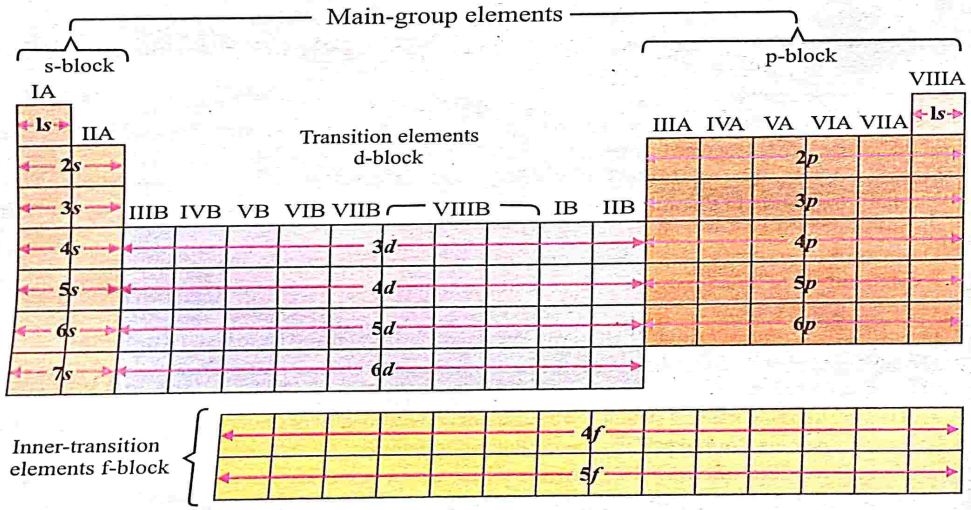


Figure 13.1 Demarcation of the Periodic Table.

In previous grades, you have learnt about the periodic classification of elements in groups and periods. You have also learnt the basics about the 1st, 2nd period elements. In this unit, you will study more detail about the periodic trends and some properties of period 3rd (Na to Ar), Groups IA, IIA, IVA and VIIA elements.

13.1 Period 3 (Na To Ar)

Period 3 elements consists of sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), phosphorous (P), sulphur (S), chlorine (Cl) and argon (Ar). Sodium and magnesium are metals and belong to s-block. Aluminum (metal), silicon (metalloid), phosphorus, sulphur, chlorine and argon are non-metals and belong to p-block.

13.1.1 Physical and Atomic Properties of the Elements

The properties of the atoms of the elements are called **atomic properties**. On moving from left to right, in a period and from top to bottom, in a group of the periodic table, atomic properties show a regular variations. Hence, these properties, are also called periodic properties. Certain important periodic and physical properties of period 3 elements have been discussed in this unit.

13.1.1.1 Electronic Structure

In third period of the periodic table electrons are successively filled in 3s and 3p orbital of atoms of elements (Na to Ar). The electronic configurations of these elements are given below where [Ne] represents the electronic configuration of neon.

Table 13.1 Elements, their Symbols and electronic configurations

Name of element	Symbol with atomic number	Electronic configuration
Sodium	$_{11}Na$	$[Ne]\ 3s^1$
Magnesium	$_{12}Mg$	$[Ne]3s^2$
Aluminium	$_{13}Al$	$[Ne]3s^2,3p^1$
Silicon	$_{14}Si$	$[Ne]3s^2,3p^2$
Phosphorus	$_{15}P$	$[Ne]3s^2,3p^3$
Sulphur	$_{16}S$	$[Ne]3s^2,3p^4$
Chlorine	$_{17}Cl$	$[Ne]3s^2,3p^5$
Argon	$_{18}Ar$	$[Ne]3s^2,3p^6$

13.1.1.2 Trend in Atomic Radius

The distance between the nucleus and the outermost shell of electrons of an atom or an ion is generally named as the atomic radius or ionic radius respectively. The exact position occupied by an electron cannot be defined with certainty. So the radius of an atom cannot be determined precisely. Thus, we deal with the radii of atoms linked together by some type of chemical bond.

1. Covalent Radius

It is defined as *"one-half of the distance between the nuclei of two identical atoms bonded together by a single covalent bond."* X-ray diffraction or spectroscopic measurements are used to determine the distance between the nuclei of any two bonded atoms. For example, the inter-nuclear distance in Cl_2 molecule is 198 pm. This means covalent radius of Cl atom is 99 pm.

2. Van der Waal's Radius

It is defined as *"one-half of the distance between the nuclei of two non-bonded and identical neighbouring atoms of two adjacent molecules in the solid state."* Since this radius corresponds to Van der Waal's forces of attraction between the molecules, its magnitude is always greater than that of covalent radius, e.g. Van der Waal's radius of hydrogen atom is 120 pm while its covalent radius is 37 pm.

3. Metallic Radius

This term is used for radius of metallic atoms e.g. Na, Mg, and Al. It is half of the total distance between nuclei of two adjacent atoms in the metallic cluster. The metallic radii are also smaller than Van der Waal's radii because metallic bonds are stronger than the Van der Waal's forces.

Periodic Trends

In general, atomic radii shows an increase in magnitude on moving from top to bottom in any group and decrease in magnitude on moving from left to right in any given period.

(a) Variation in a Group

As we move in a group from top to bottom, the number of shells and the effective nuclear charge increases but the effect of addition of new shell dominates over the effect of effective nuclear charge and hence the atomic size increases from top to bottom in a group. For example, see Table 13.2

Table 13.2 Trend in Atomic Radius of group IA

Elements of Group IA	Li	Na	K	Rb	Cs
Outer-shell electronic configuration	$[He]2s^1$	$[Ne]3s^1$	$[Ar]4s^1$	$[Kr]5s^1$	$[Xe]6s^1$
Atomic radius (pm)	152	186	227	248	265

(b) Variation in a Period

As we move in a period from left to right, the number of shells remains the same as the electrons are added in the same shell. However, the effective nuclear charge increases and pulls the electron cloud closer to the nucleus. As a result, the atomic size decreases from sodium (Na) to chlorine (Cl) in period third.

The atomic size of noble gas (Argon) is greater than the prior elements in the respective period (3rd period). This is due to the reason that in noble gases, Van der Waal's radius is determined, whose magnitude is larger than the covalent radius.

Table 13.3 Trend in Atomic Radius of 3rd Period Elements Na to Ar.

Symbol with atomic number	$_{11}Na$	$_{12}Mg$	$_{13}Al$	$_{14}Si$	$_{15}P$	$_{16}S$	$_{17}Cl$	$_{18}Ar$
Atomic radius (pm)	186	160	143	118	114	104	99	188

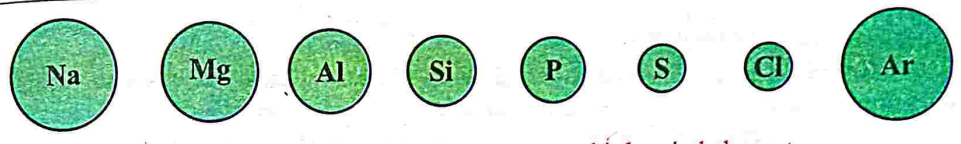


Figure 13.1 Atomic radius changes across third period elements.

13.1.1.3 Trend in First Ionization Energy

Ionization Energy (IE)

Ionization energy of an element is the minimum amount of energy (in kJ/mol) required to remove the outermost electron of an isolated gaseous atom to form an ion, the result is the formation of the gaseous cation, i.e.

$$Mg_{(g)} \longrightarrow Mg^+_{(g)} + e^- \qquad \Delta H = 737 kJ.mol^{-1}$$

Ionization energy for removal of first electron from the outermost shell of an atom is called 1st I.E. Similarly, the ionization energy for the removal of an electron from $M^+_{(g)}$ is called 2nd I.E.

$$Mg^+_{(g)} \longrightarrow Mg^{2+}_{(g)} + e^- \qquad \Delta H = 1476 kJ.mol^{-1}$$

Periodic Trends

In general, the ionization energy decreases in moving from top to bottom in a group and increases from left to right in a period.

(a) Variation in a Group

As we move in a group from top to bottom, there is an increase in the atomic size, nuclear charge and shielding effect. However, the combined effect of increase in atomic size and shielding effect dominates over the effect of increase in the nuclear charge. Hence, ionization energy decreases from top to bottom in a group with some exceptions.

Variation in a Period

As we move in a period from left to right, the number of shells remain the same but atomic size decreases as the electrons are added in the same shell, hence pulling the electrons closer towards the nucleus.

Thus, more energy is required to remove the electron from the outermost shell of the atom resulting in an increase of ionization energy. The first ionization energy values of period 3 elements are given below.

Table 13.4 First Ionization Energy Values of Period 3rd Elements

Elements of period 3rd	$_{11}$Na	$_{12}$Mg	$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl	$_{18}$Ar
1st ionization energy (kJ mol^{-1})	495	737	577	786	1011	1000	1251	1520

Tidbit

Screening effect or shielding effect

In a multi-electron atom, the electrons in the valence shell are attracted to the nucleus. Like same charges repel, so these electrons are repelled by the electrons present in the inner shells. On account of this, the force of attraction between the nucleus and the valence electrons decrease. This decrease in the force of attraction on the valence electrons due to the presence of electrons in the inner shells is called screening effect or shielding effect.

The magnitude of the screening effect depends upon the number of inner electrons higher the number of inner electrons greater shall be the value of the screening effect. As we move down ward in the group the number of shells increases gradually between the nucleus and the valence shell. These shells act like shields. These shells protect the electrons from the attraction of the nucleus.

13.1.1.4 Trend in Electronegativity

Electronegativity

The relative tendency of an atom to attract a shared electron pair towards itself is called its electronegativity.

Periodic Trends

In general, electronegativity decreases on moving from top to bottom in a group and increases from left to right in a period.

(a) Variation in a Group

As we move in a group from top to bottom, there is an increase in the atomic size, nuclear charge and shielding effect.

However, the combined effect of increase in atomic size, nuclear change and shielding effect results in decrease in the force of attraction of the nucleus for the shared pair of electron, thus electronegativity decreases.

(b) Variation in a Period

As we move in a period from left to right, there is no change in the number of shells but effective nuclear charge increases. This results in decrease in atomic size and hence electronegativity increases.

Fluorine (F) is the most electronegative element and Caesium (Cs) is the least electronegative element in the periodic table. Electronegativity values of period 3 elements are given in the table.

Table 13.5 Trend in Electronegativity of 3rd Period elements

Elements of period 3rd	$_{11}$Na	$_{12}$Mg	$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl	$_{18}$Ar
Electronegativity	0.93	1.31	1.61	1.90	2.19	2.58	3.16	–

Note that electronegativity of argon (Ar) is not included. As the electronegativity is related to the tendency of an atom to attract the shared pair of electrons. As, argon does not form covalent bond(s), so no electronegativity value is assigned to argon (Ar).

13.1.1.5 Trend in Electrical Conductivity

Electrical Conductivity

Electrical conductivity is the measure of the amount of electrical current a material can carry.

Electrical conductivity values of period 3 elements relative to aluminium are given below.

Table 13.6 Trend in Electrical Condutivity in 3rd Period Elements

Elements of period 3rd	$_{11}$Na	$_{12}$Mg	$_{13}$Al	$_{14}$Si	$_{15}$P	$_{16}$S	$_{17}$Cl	$_{18}$Ar
Electrical conductivity	0.55	0.61	1.00	0.10	0	0	0	0

Sodium, magnesium and aluminium are all metals and are good conductors of electricity. These metals conduct electricity because they contain free electrons. Going from sodium to aluminium, the number of free electrons increases and thus the electrical conductivity increases. Silicon has a giant covalent structure. It is a semiconductor, so it is not a good conductor. Phosphorus, sulphur, chlorine and argon are non-conductor as they are non-metals.

13.1.1.6 Trend in Melting and Boiling Points

The following table shows melting points and boiling points for the elements Na to Ar. Melting points and boiling points tell us how strongly the atoms in an element are held together.

Table 13.7 Trend in Melting and Boiling Points in 3rd Period Elements

Elements of period 3rd	Na	Mg	Al	Si	P	S	Cl	Ar
Melting point °C	98	651	660	1410	44(white)	119	–103	–189
Boiling point °C	883	1107	2470	2355	260	445	–35	–486

Sodium, magnesium and aluminium have metallic bonding, in which the nuclei of metal atoms are attracted by free electrons. Going from sodium to aluminium, the number of free electron increases and the melting and boiling points also increase. Silicon is a metalloid with a giant covalent structure. Silicon has a very high melting and boiling points because of strong covalent bonds. P, S, Cl and Ar in period 3 are non-metals and have low melting and boiling points because they have weak Van der Waal's forces between their molecules.

The strength of the Van der Waal's forces decreases as the size of the molecule decreases, so the melting and boiling points decreases in the order:

$$S_8 > P_4 > Cl_2 > Ar$$

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

i. Reactions of the Period 3rd Elements with Water

Sodium undergoes exothermic reaction with cold water producing hydrogen and a solution of sodium hydroxide.

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$

Magnesium reacts slowly with cold water but burns in steam. A clean coil of magnesium dropped into cold water eventually is covered with small bubbles of hydrogen, which floats it to the surface. Magnesium form a very thin layer of magnesium hydroxide on the surface, which tends to stop it from further reaction.

$$Mg_{(s)} + 2H_2O_{(l)} \longrightarrow Mg(OH)_{2(aq)} + H_{2(g)}$$

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

$$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$

Aluminium powder when heated in steam produces hydrogen and aluminium oxide. This reaction is relatively slow with bulk because of the formation of strong aluminium oxide layer on the metal and build-up of even more oxide during reaction.

$$2Al_{(s)} + 3H_2O_{(g)} \longrightarrow Al_2O_{3(s)} + 3H_{2(g)}$$

Silicon react with steam at red heat to produce silicon dioxide and hydrogen.

$$Si_{(s)} + 2H_2O_{(g)} \longrightarrow SiO_{2(s)} + 2H_{2(g)}$$

Chlorine dissolves in water to some extent to give a pale green solution. A reversible reaction takes place to produce a mixture of hydrochloric acid and chloric (I) acid (hypochlorous acid), which decompose to HCl on exposure to sunlight.

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HCl_{(aq)} + HOCl_{(aq)}$$

$$HOCl_{(aq)} \longrightarrow HCl_{(aq)} + \tfrac{1}{2} O_{2(g)}$$

Net reaction: $Cl_{2(g)} + H_2O_{(l)} \longrightarrow 2HCl_{(aq)} + \tfrac{1}{2} O_{2(g)}$

There is no reaction between argon and water.

ii. Reactions of the Period 3rd Elements with Oxygen

Sodium burns in a limited supply of air (oxygen) with a pale yellow flame to produce a white solid of sodium oxide. In sodium oxide, the oxidation state of oxygen is –2.

$$4Na_{(s)} + O_{2(g)} \longrightarrow 2Na_2O_{(s)}$$

Sodium burns in an excess of air (oxygen) with a flame to produce a pale yellow solid of sodium peroxide. In sodium peroxide the oxidation state of oxygen is –1.

$$2Na_{(s)} + O_{2(g)} \longrightarrow Na_2O_{2(s)}$$

When sodium peroxide react with oxygen at high temperature and pressure, it produces a yellow-orange solid of sodium superoxide (NaO_2). In sodium superoxide the oxidation state of oxygen is $-\tfrac{1}{2}$.

$$Na_2O_{2(s)} + O_{2(g)} \longrightarrow 2NaO_{2(s)}$$

Magnesium burns in oxygen with an intense flame to give white solid magnesium oxide.

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

Aluminium burns in oxygen, if it is powdered, otherwise, the strong oxide layer on aluminium tends to inhibit the reaction.

$$4Al_{(s)} + 3O_{2(g)} \longrightarrow 2Al_2O_{3(s)}$$

Silicon burns in oxygen if heated strongly enough. Silicon dioxide is produced.

$$Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}$$

White phosphorus catches fire spontaneously in air, burning with white flame and produces clouds of white smoke. A mixture of phosphorus trioxide (phosphorus (III) oxide) and phosphorus pentaoxide (phosphorous (V) oxide) is formed.

For phosphorus trioxide

$$P_{4(s)} + 3O_{2(g)} \longrightarrow P_4O_{6(g)}$$

For phosphorus pentaoxide

$$P_{4(s)} + 5O_{2(g)} \longrightarrow P_4O_{10(g)}$$

Sulphur burns in air or oxygen on gentle heating with a pale blue flame. It produces colourless sulphur dioxide gas.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

iii. Reactions of the Period 3rd Elements with Chlorine

Sodium burns in chlorine with a bright orange flame. White, solid sodium chloride is produced.

$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

Magnesium burns with its usual intense white flame to give white magnesium chloride.

$$Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)}$$

Aluminium reacts with chlorine by passing dry chlorine over aluminium foil heated in a long tube. Aluminium burns in stream of chlorine to produce pale yellow aluminium chloride.

$$2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(s)}$$

If chlorine is passed over silicon powder, in a heated tube, it reacts to produce a colourless liquid silicon tetrachloride.

$$Si_{(s)} + 2Cl_{2(g)} \longrightarrow SiCl_{4(l)}$$

White phosphorous burns in chlorine to produce a mixture of two chlorides. Phosphorus trichloride (Phosphorus (III) chloride) and phosphorus pentachloride (phosphorus (V) chloride). Phosphorus trichloride is colourless fuming liquid and

$$P_{4(s)} + 6Cl_{2(g)} \longrightarrow 4PCl_{3(l)}$$

phosphorous pentachloride is a straw-coloured solid.

$$P_{4(s)} + 10Cl_{2(g)} \longrightarrow 4PCl_{5(s)}$$

If a stream of chlorine is passed over some heated sulphur, it reacts to form an orange, foul smelling liquid disulphur dichloride (S_2Cl_2).

$$2S_{(s)} + Cl_{2(g)} \longrightarrow S_2Cl_{2(l)}$$

Society, Technology And Science

Body need a certain amount of iodine in order to make a chemical known as thyroid hormone. Thyroid hormone controls body metabolism and other important functions in the body.

Iodine is found primarily in seawater and in the soil especially in coastal areas. At high elevations, iodine is often deficient in the water and soil. Lack of iodine can cause an abnormal enlargement of the thyroid gland, known as a **goitre**.

A **goitre** is an abnormal enlargement of thyroid gland. Thyroid is a butterfly-shaped gland located at the base of neck. The most common cause of goitres worldwide is a lack of iodine in the diet. Iodine deficiency may be made worse by a diet high in hormone-inhibiting foods, such as cabbage, broccoli and cauliflower.

Our body does not naturally make iodine, so the only way to get this nutrient is through diet. Adults typically require 150µg per day. Pregnant and breastfeeding women need 200µg per day.

13.1.3 Physical Properties of the Oxides

The oxides of period 3rd elements are following.

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
-	-	-	-	P_4O_6	SO_2	Cl_2O

The oxides in the top row are the oxides where period 3 elements are in their highest oxidation state. In these oxides, all the outer electrons in period 3 elements are being involved in bonding from just one in sodium to all seven outer electrons of chlorine in Cl_2O_7.

The oxides (high oxidation state) of sodium, magnesium, aluminium, silicon, phosphorous are in solid state and those of sulphur and chlorine are in liquid state. The oxides having low oxidation state of sulphur and chlorine are in gaseous state.

13.1.3.1 Structure

Sodium, magnesium and aluminium oxides consist of giant structures containing metal ions and oxide ions. Magnesium oxide is similar in structure to sodium chloride. The crystalline aluminium oxide is known as corundum, in which oxygen ions form nearly hexagonal close-packed structure with the aluminium ions.

Tidbit

Corundum, naturally occurring aluminum oxide mineral (Al_2O_3) that is, after diamond, the hardest known natural substance.

Silicon dioxide is covalent oxide having giant structure. There are three different crystal forms of silicon dioxide; the most suitable structure is similar to that of diamond.

Phosphorus, sulphur and chlorine form molecular oxides. Some of these molecules are simple, while others are polymeric. Thus, the trend in structure in period is

Giant metallic ionic oxides ⟶ giant covalent oxide ⟶ molecular oxide.

13.1.3.2 Melting and Boiling Points

The giant structures (the metal oxides and silicon oxide) have high melting points and boiling points because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in their lattices. The oxides of phosphorous, sulphur and chlorine consist of individual molecules, some small and simple, others polymeric.

The attractive forces between these molecules will be dispersion forces and dipole-dipole interactions. The strength of the attractive forces depend on the size, shape and polarity of various molecules but are always much weaker than the ionic or covalent bonds present in a giant structure. These oxides are gases, liquids or low – melting solids.

Table 13.8 Melting and Boiling Points of Period 3rd Oxides

Oxides of period 3rd	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Melting point (°C)	1280	2900	2040	1610	340	– 17	– 92
Boiling point (°C)	1950	3600	2977	2230	360	45	82

13.1.3.3 Electrical Conductivity

None of the period 3rd oxides have any free or mobile electrons. It means that none of them will conduct electricity when they are in solid state. The ionic oxides can, however, conduct electricity in molten state because of the movement of ions towards the opposite electrodes.

13.1.4 Acid-Base Behaviour of the Oxides

Going across period 3, from left to right the nature of the oxides changes from basic (Na_2O,MgO) to amphoteric (Al_2O_3) and then to acidic (SiO_2,P_4O_6/P_4O_{10},SO_2/SO_3). The acidity of the oxides increases across the period.

13.1.4.1 Trend in Acid Base Behaviour

As we move in 3rd period from left to right, acidity of oxides increases, ranging from strongly basic oxides on the left to strongly acidic on the right side, with an amphoteric oxide (aluminium oxide) in the middle.

This trend applies only to the highest oxidation of the individual elements (see the top row of the table). For example, sulphur trioxide reacts with water to form sulphuric acid. They, however, also react with bases such as sodium hydroxide to form salts such as sodium sulphate.

Table 13.9 Trend in Acid Base Behaviour of Period 3 Oxides

Oxide of period 3	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} (P_4O_6)	SO_3 (SO_2)	Cl_2O_7 (Cl_2O)
Nature of oxide	Basic (alkaline)	Basic (weakly alkaline)	Amphoteric	Acidic	Acidic	Acidic	Acidic

13.1.4.2 Reactions of Oxides with Water, Acids and Bases

The period 3rd consists of elements Na to Ar. There occurs metals, metalloids and non-metals. Oxides of Period 3rd elements are basic to amphoteric to acidic.

Reaction of oxides with water

The oxides of period 3rd include oxides of metals such as Na_2O and MgO, which are basic in nature. They combine with water to form bases.

$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$
$$MgO_{(s)} + H_2O_{(l)} \longrightarrow Mg(OH)_{2(aq)}$$

Al_2O_3 does not react with H_2O, since the strength of ionic bonds holding Al_2O_3 molecules lattice together is too much strong.

Silicon dioxide does not react with H_2O. The covalent bonds holding the silicon and oxygen atoms together in the 3-dimensional lattice are too strong to be broken down by the water molecules.

Oxides of non-metals such as oxides of sulphur, phosphorous and chlorine react with water to form oxyacids.

Oxides of the phosphorus such as P_4O_{10}, react with water to produce acids.

$$P_4O_{10(s)} + 6H_2O_{(l)} \longrightarrow 4H_3PO_{4(l)}$$

Sulphur dioxide (SO_2) and sulphur trioxide (SO_3) react with water to produce sulphurous acid and sulphuric acid respectively.

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(l)}$$
$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(l)}$$

Chlorine forms several oxides, but only two are considered here. i.e. dichlorine heptoxide (Cl_2O_7), and dichlorine monoxide (Cl_2O).

Dichlorine heptoxide (Cl_2O_7) reacts with water to give the very strong acid, perchloric acid ($HClO_4$). While Cl_2O forms hypochlorous acid (HOCl)

$$Cl_2O_{7(l)} + H_2O_{(l)} \longrightarrow 2HClO_{4(aq)}$$
$$Cl_2O_{(g)} + H_2O_{(l)} \rightleftharpoons 2HOCl_{(aq)}$$

Reaction of Oxides with Acids and Bases

Na_2O and MgO react with acids to form salt and water.

$$Na_2O_{(s)} + 2HCl_{(aq)} \longrightarrow 2NaCl_{(aq)} + H_2O_{(l)}$$
$$MgO_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_2O_{(l)}$$

Aluminium oxide is amphoteric. It reacts with hot dilute hydrochloric acid and produces aluminium chloride and water.

As an Acid: $Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$

Aluminium oxide also reacts with bases. When concentrated sodium hydroxide solution is added to aluminium oxide, complex ion (sodium tetrahydroxoaluminate (III)) is formed.

As a Base: $Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \longrightarrow 2NaAl(OH)_{4(aq)}$

SiO_2 is chemically very inert and weakly acidic. It reacts with hot concentrated sodium hydroxide to produce sodium silicate and water.

$$SiO_{2(s)} + 2NaOH_{(l)} \longrightarrow Na_2SiO_{3(l)} + H_2O_{(g)}$$

Phosphorus oxides are acidic oxides, they react with alkalies to form salts and water Phosphorus trioxide reacts with sodium hydroxide to form sodium phosphite and water.

$$P_4O_{6(s)} + 12NaOH_{(aq)} \longrightarrow 4Na_3PO_{3(aq)} + 6H_2O_{(l)}$$

Phosphorus pentaoxide reacts with sodium hydroxide to form sodium phosphate and water.

$$P_4O_{10(s)} + 12NaOH_{(aq)} \longrightarrow 4Na_3PO_{4(aq)} + 6H_2O_{(l)}$$

Sulphur dioxide (SO_2) reacts with aqueous solution of sodium hydroxide and produces salt (sodium sulphite) and water. Sulphur trioxide (SO_3) reacts violently with water to produce sulphuric acid, which reacts with sodium hydroxide and produces salt (sodium sulphate).

$$SO_{2(g)} + 2NaOH_{(aq)} \longrightarrow Na_2SO_{3(aq)} + H_2O_{(l)}$$
$$H_2SO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$$

Dichlorine heptoxide (Cl_2O_7) reacts directly with sodium hydroxide to give sodium chlorate and water.

$$Cl_2O_{7(l)} + 2NaOH_{(aq)} \longrightarrow 2NaClO_{4(aq)} + H_2O_{(l)}$$

Dichlorine monoxide (Cl_2O) also reacts directly with sodium hydroxide to give sodium hypochlorite and water.

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

Argon (Ar) is noble gas and it does not form oxides.

13.1.5 Chlorides of the Period 3rd Elements

Chlorides are compounds formed between chlorine and another element. They are binary compounds, in which chlorine is combined with only one other element. The chlorides of Period 3rd elements Na (sodium) to S (sulphur) are given in the following table with their physical properties.

Table 13.10 Chlorides of the Period 3rd Elements and their Physical Properties

Chloride	NaCl	$MgCl_2$	Al_2Cl_6	$SiCl_4$	PCl_3	S_2Cl_2
Physical State(20°C)	Solid	Solid	Solid	Liquid	Liquid	Liquid
Melting Point(°C)	801	708	192.4	–69	–93.6	–80
Boiling Point (°C)	1465	1418	423	57	74	136

There are three chlorides of sulphur, but only one is mentioned here i.e. S_2Cl_2. Al_2Cl_6 is the dimer of aluminium chloride ($AlCl_3$).

13.1.5.1 Structure

NaCl and $MgCl_2$ are ionic and consist of giant ionic lattices at room temperature. $AlCl_3$ is complicated due to its structural changes as temperature increases. The structure is an ionic lattice – although with a lot of covalent character. PCl_5 is structurally more complicated. The chlorides of the other elements of this period are simple converts molecules.

13.1.5.2 Melting and Boiling Points

NaCl and $MgCl_2$ are ionic and solids with high melting and boiling points. Large amount of heat is needed to break the strong ionic attractions.

$AlCl_3$ is solid at room temperature, has an ionic lattice with a considerable covalent character. At 180 – 190°C (depending on the pressure), aluminium chloride converts to molecular form (dimeric form), Al_2Cl_6.

PCl_5 is a white solid, which sublimes at 163°C. As the temperature goes higher, the PCl_5 dissociates (splits up reversibly) to give PCl_3 and Cl_2.

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

The rest are low melting point liquids.

13.1.5.3 Electrical Conductivity

NaCl and $MgCl_2$ are ionic in nature. They do not conduct electricity in solid state. But in molten state in aqueous solution these compounds conduct electricity.
$AlCl_3$ and PCl_5 do not conduct electricity in solid state, as the ions are not free to move. In the liquid state, they are converted into a covalent form and hence do not conduct electricity.
The chlorides of rest of the elements of period 3rd do not conduct electricity because they do not have any free ions or any free electrons to conduct electricity.

13.1.5.4 Solubility in Water

NaCl dissolves in water and dissociates into ions to form a neutral solution of sodium chloride.

$$NaCl_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$$

$MgCl_2$ dissolves in water and dissociates into ions to form a solution of magnesium chloride

$$MgCl_{2(s)} \xrightarrow{H_2O} Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

$AlCl_3$ is hydrolysed (broken down by water) to give an acidic solution containing the complex species hexaaqua aluminium (III).

$$AlCl_{3(s)} + 6H_2O_{(l)} \longrightarrow [Al(H_2O)_6]^{3+}_{(aq)} + 3Cl^-_{(aq)}$$

The acidity is caused by the high charge density of aluminium ion (Al^{3+}) polarising the water ligands (attached molecules), releasing free hydrogen ions into solution:

$$[Al(H_2O)_6]^{3+}_{(aq)} \longrightarrow [Al(H_2O)_5OH]^{2+}_{(aq)} + H^+_{(aq)}$$

Silicon tetrachloride ($SiCl_4$), reacts very rapidly with water to form a strongly acidic solution. During the reaction, white fumes of hydrogen chloride gas are formed which dissolves in water forming hydrochloric acid.

$$SiCl_{4\,(l)} + 4H_2O_{(l)} \longrightarrow \underset{\text{silicic acid}}{Si(OH)_{4(aq)}} + 4HCl_{(g)}$$

Both of the phosphorus chlorides i.e. PCl_3 and PCl_5, violently react with water giving strongly acidic solutions. During the reaction, white fumes of hydrogen chloride gas are formed which dissolves in water forming hydrochloric acid.

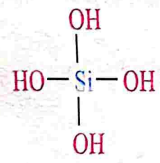
$$PCl_{3(l)} + 3H_2O_{(l)} \longrightarrow H_3PO_{3(aq)} + 3HCl_{(g)}$$
$$PCl_{5(s)} + 4H_2O_{(l)} \longrightarrow H_3PO_{4(aq)} + 5HCl_{(g)}$$

13.1.6 Hydroxides of the Period 3rd Elements

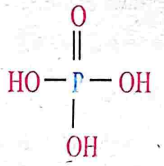
The word "hydroxide" refers to a compound which contains either a $\bar{O}H$ ion or an –OH group covalently bonded to the atom of an element. The sodium and magnesium hydroxides are simple basic hydroxides due to the presence of hydroxide ions. These hydroxide ions react with hydrogen ions of acid to form water.

Aluminium hydroxide, $Al(OH)_3$, like aluminium oxide, Al_2O_3, is amphoteric, it reacts with both acids and bases.

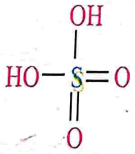
All the other elements e.g. Si, P, S and Cl, which have – OH groups covalently bonded to the atom of period 3 are acidic. They range from very weakly acidic silicic acid to the very strong sulphuric acid or perchloric acid.



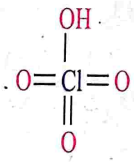
ortho salicic acid



phosphoric acid



sulphuric acid



perchloric acid

13.1.6.1 Sodium and Magnesium Hydroxides

Sodium hydroxide (NaOH) is a white solids having soapy touch. Skin contact with concentrated caustic soda can cause serious chemical burns. This is highly hygroscopic. Sodium hydroxide is only slightly soluble in alcohols. It is one of the most soluble substances in water evolving a considerable amount of heat.

Magnesium hydroxide, unlike sodium hydroxide, it is classified as a weak base, so it has no exothermic reaction with water. Magnesium hydroxide is obtained as a white precipitate when caustic potash (KOH) solution is added to a soluble magnesium salt. Both hydroxides react with acids to form salts. For example, with dilute hydrochloric acid, colourless solutions of sodium chloride or magnesium chloride are obtained.

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

$$Mg(OH)_{2(aq)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + 2H_2O_{(l)}$$

13.1.6.2 Aluminium Hydroxide

Aluminium hydroxide is amphoteric in nature. Like sodium or magnesium hydroxides, $Al(OH)_3$ reacts with acids which shows its basic nature. The $Al(OH)_3$ reacts with dilute hydrochloric acid and forms a colourless solution of aluminium chloride.

$$Al(OH)_{3(aq)} + 3HCl_{(aq)} \longrightarrow AlCl_{3(aq)} + 3H_2O_{(l)}$$

Aluminium hydroxide also shows acidic properties. It reacts with sodium hydroxide solution and forms a colourless solution of sodium tetrahydroxoaluminate (III).

$$Al(OH)_{3(aq)} + NaOH_{(aq)} \longrightarrow NaAl(OH)_{4(aq)}$$

Sodium tetrahydroxoaluminate (III).

13.1.6.3 Other Hydroxides

Other elements do not contain hydroxide ions but –OH group is covalently bonded to the atoms of period 3 elements. These compounds are acidic in nature because they can loss H^+ from –OH group.

Orthosilicic acid is very weak acid. Phosphoric acid is a weak acid but stronger than acetic acid. Sulphuric acid (H_2SO_4) and perchloric acids are very strong acids.

The strength of an acid depends on the stability of it's anion. Higher the stability of an anion, higher will be the acidic strength of compound.

13.2 Group – IA Elements

The elements lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), and francium (Fr) constitute group – IA of the periodic table. These are known as alkali metals since they form oxide and hydroxides which combine with water to produce alkaline solution. Only the first three of these are safe to keep in the school laboratory. The rest are violently reactive.

The characteristic feature of the sub-group – IA is the ns^1 arrangement in the outermost shell. The elements symbol and their electronic configuration are given in **Table 13.11.**

Table 13.11 Elements Symbol with Atomic No and their Electronic Configuration

Element symbol with atomic No.	Electronic configuration	
$_3Li$	$1s^2, 2s^1$	$[He]2s^1$
$_{11}Na$	$1s^2, 2s^2, sp^6, 3s^1$	$[Ne]3s^1$
$_{19}K$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$	$[Ar]4s^1$

$_{37}Rb$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^1$	$[Kr]5s^1$
$_{55}Cs$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^6, 6s^1$	$[Xe]6s^1$
$_{87}Fr$	$[Kr]\ 5s^2, 5p^6, 5d^{10}, 6s^2, 6p^6, 7s^1$	$[Rn]7s^1$

Like all metals, they are good conductor of heat and electricity. They are softer than other metals. They can be cut with a knife. They are lighter than other elements and have low melting points, boiling points and densities.

13.2.1 Atomic and Physical Properties

The elements in a group behave in similar way but they also show trends of variations in properties as given below.

13.2.1.1 Trend in Atomic Radius

As we move in group from lithium to caesium, an extra shell of electrons is added to next element. The addition of extra shells increases the atomic radius from Li to Cs.

Table 13.12 Trend in Atomic Radius in Group IA Elements

Elements	Li	Na	K	Rb	Cs
Atomic Radius (pm)	152	186	227	248	265

13.2.1.2 Trend in First Ionization Energy

As we move in group from lithium to caesium the ionization energy decreases, due to the addition of extra shells from Li to Cs. So the removal of electron become easier.

Table 13.13 Trend in First Ionization Energy in Group IA Elements

Elements	Li	Na	K	Rb	Cs
1st Ionization Energy (kJ/mol)	520	496	419	403	376

13.2.1.3 Trend in Electronegativity

Elements of group – IA are metals and are highly electropositive, so their electronegativity values are very low. As we move in group from lithium to caesium their electronegativities decrease in the same order.

Table 13.14 Trend in Electronegativity in Group IA Elements

Elements	Li	Na	K	Rb	Cs
Electronegativity	0.98	0.93	0.82	0.82	0.79

13.2.1.4 Trend in Melting and Boiling Points

The binding forces between the atoms in crystal lattice of these metals are relatively weak. So these metals are soft and possess low melting and boiling points, which decrease down the group.

Table 13.15 Trend in Melting and Boiling Points in Group IA Elements

Elements	Li	Na	K	Rb	Cs
Melting point (°C)	180.5	97.8	63.7	39.0	28.6
Boling point (°C)	1,326	883	756	688	690

13.2.1.5 Trend in Density

Density is *defined as mass per unit volume of a substance.*

Density increases with an increase in atomic mass and decreases with an increase in atomic volume.

Generally, we see that in alkali metals down the group, both the atomic size and atomic mass increase but the increase in atomic mass compensates the bigger atomic size. As a result, the density of alkali metals increases down the group. Potassium is, however, lighter than sodium.

Table 13.16 Trend in Density in Group IA Elements

Elements	Li	Na	K	Rb	Cs
Density at 20 °C (g/cm^3)	0.53	0.97	0.86	1.53	1.88

13.2.2 Trend in Reactivity with Water

Group – IA elements are very good reducing agents. They all react vigorously with water reducing it to hydrogen gas.

$$M_{(s)} \longrightarrow M^+_{(aq)} + 1e^-$$

$$H_2O_{(l)} + 1e^- \longrightarrow \frac{1}{2} H_{2(g)} + OH^-_{(aq)}$$

$$M_{(s)} + H_2O_{(l)} \longrightarrow MOH_{(aq)} + \frac{1}{2} H_{2(g)}$$

(Where M = Li, Na, K, Rb, Cs)

Lithium reacts slowly with water while sodium reacts vigorously. Potassium reacts even more vigorously, while Rb and Cs explode violently in contact with water. They all on reaction with water produce the respective hydroxides.

13.2.3 Reactions with Oxygen

Group – IA elements tarnish in air due to the formation of an oxide or hydroxide on th surface. These metals have to be stored without contact with air to prevent their oxidatio Their reactivity increases down the group.

Li, Na and K are stored in oil, Cs and Rb are normally stored in a sealed glass tubes t prevent air contact.

The group – IA elements react with oxygen to form normal oxides with general formul M_2O.

$$4M_{(s)} + O_{2(g)} \longrightarrow 2M_2O_{(s)}$$

(Where M = Li, Na, K, Rb, Cs)

13.2.3.1 Reactions with Air or Oxygen and the formation of Normal Oxides, Peroxides, Super Oxides and their Stability

When the group – IA elements are heated with excess of air or oxygen, lithium form normal oxide, Li_2O; sodium forms peroxide, Na_2O_2, whereas potassium, rubidium an caesium form superoxides having general formula MO_2

$$4Li_{(s)} + O_{2(g)} \longrightarrow 2Li_2O_{(s)}$$
lithium oxide

$$2Na_{(s)} + O_{2(g)} \xrightarrow{300^oC} Na_2O_2$$
sodium peroxide

$$K_{(s)} + O_{2(g)} \longrightarrow KO_2$$
potassium superoxide

"Rb" and "Cs" catch fire in air and produce superoxide such as RbO_2 and CsO_2 respectively. Thus, the reactivity of alkali metals with oxygen increases down the group.

13.2.3.2 Reactions of Oxides with Water and Dilute Acids

i. Reactions of Oxides with Water

Oxides of group – IA elements react with water to produce the respective bases. Group IA elements react with oxygen to form normal oxides, peroxides or superoxides. These oxides react with water in different ways.

Normal oxides

Normal oxide reacts with water and produce metal hydroxide. For example, Li_2O reacts with water and form lithium hydroxide.

$$Li_2O_{(s)} + H_2O_{(l)} \longrightarrow 2LiOH_{(aq)}$$

Peroxides

Peroxides (M_2O_2) react with water and produce metal hydroxide and hydrogen peroxide. For example, Na_2O_2 reacts with water and form sodium hydroxide and hydrogen peroxide.

$$Na_2O_{2(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_2O_{2(aq)}$$

Super oxides

Super oxides (MO_2) react with water and produce metal hydroxide, hydrogen peroxide and oxygen gas. For example, KO_2 reacts with water and forms potassium hydroxide, hydrogen peroxide and oxygen gas.

$$2KO_{2(s)} + 2H_2O_{(l)} \longrightarrow 2KOH_{(aq)} + H_2O_{2(aq)} + O_{2(g)}$$

ii. Reactions of Oxides with Dilute Acids

Oxides of group – IA elements react with dilute acids to produce the respective salts. Oxides of group – IA i.e. normal oxides, peroxides, or super oxides react with dilute acids as follows.

Normal oxides

Normal oxides such as Li_2O and Na_2O react with dilute sulphuric acid (H_2SO_4) and produce the respective salts and water.

$$Li_2O_{(s)} + H_2SO_{4(aq)} \longrightarrow Li_2SO_{4(aq)} + H_2O_{(l)}$$

$$Na_2O_{(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(l)}$$

Peroxides

Peroxides, such as Na_2O_2, react with dilute sulphuric acid (H_2SO_4) and produce sodium sulphate and hydrogen peroxide.

$$Na_2O_{2(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{2(l)}$$

Super oxides

Super oxides such as KO_2, react with dilute sulphuric acid (H_2SO_4) and produce potassium sulphate, hydrogen peroxide and oxygen gas.

$$2KO_{2(s)} + H_2SO_{4(l)} \longrightarrow K_2SO_{4(aq)} + H_2O_{2(aq)} + O_{2(g)}$$

13.2.4 Reactions with Chlorine

Group – IA elements react vigorously with chlorine to form metal chlorides. These metal chlorides are ionic crystalline solids. For example, sodium burns with an intense orange flame in chlorine in exactly the same way as it does in pure oxygen.

$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

$$2K_{(s)} + Cl_{2(g)} \longrightarrow 2KCl_{(s)}$$

Reactivity of alkali metals with particular halogens increases from Li to Cs.

13.2.5 Effect of Heat on Nitrates, Carbonates and Hydrogen-Carbonates explaining the Trend in Terms of the Polarizing Ability of the Positive Ion

Compounds of Group – IA elements are more stable to heat than the corresponding compounds of Group – IIA elements with the exception of lithium compounds.

Effect of Heat on Nitrates

In Group – IA the lithium nitrates decomposes on the same way as the nitrates of Group – IIA. Group – IIA nitrates tend to decompose on heating to produce metal oxide, nitrogen dioxide (brown fumes) and oxygen.

Tidbit

The ability of a cation to distort an anion is known as its **polarization power** and the tendency of the anion to become polarized by the cation is known as its **polarizability**.

Lithium nitrate on decomposition produces lithium oxide, nitrogen dioxide and oxygen.

$$4LiNO_{3(s)} \xrightarrow{\Delta} 2Li_2O_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

The rest of nitrates from sodium to caesium, however, do not decompose completely at low temperatures. At high temperature, the nitrates of these elements produce the respective metal nitrite (MNO_2) and oxygen, but no nitrogen dioxide. (Where M = Na, K, Rb and Cs)

$$2MNO_{3(s)} \xrightarrow{\Delta} 2MNO_{2(s)} + O_{2(g)}$$

As we go down the group, the decomposition of these metal nitrates becomes more difficult and higher temperature is required.

Effect of Heat on Carbonates

In Group – IA the lithium carbonate decomposes on the same way as the carbonates of Group – IIA. Group – IIA carbonates tend to decompose on heating to produce metal oxide and carbon dioxide.

In Group – IA, lithium carbonate behaves in the same way, producing lithium oxide and carbon dioxide

$$Li_2CO_{3(s)} \longrightarrow Li_2O_{(s)} + CO_{2(g)}$$

The rest of the Group – IA carbonates do not decompose at low temperature, although at higher temperature this becomes possible. The decomposition temperatures again increase down the group.

Effect of Heat on Hydrogen Carbonates

The hydrogen carbonates of Group – IIA such as calcium hydrogen carbonate are unstable to heat. They only exist in solution. Any attempt to separate them from solution causes them to decompose to the carbonate, carbon dioxide and water.

$$Ca(HCO_3)_{2(aq)} \longrightarrow CaCO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$$

The hydrogen carbonates of Group – IA are stable enough to exist as solid, although they do decompose easily on heating. For example,

$$2NaHCO_{3(s)} \longrightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$$

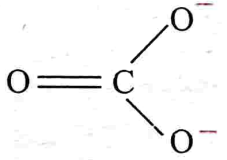
Explaining the Trend in Terms of the Polarizing ability of the Positive ion

A small positive ion has a large amount of charge packed into a small volume of space. An ion with a high charge density has a clear distorting effect on any nearby negative ions. A larger positive ion has the same charge spread over a larger volume of space. Its charge density is therefore lower and it causes less distortion to nearby negative ions.

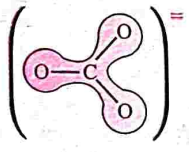
Polarizing the Carbonate ion

The molecular structure of carbonate is given below:

This figure shows two carbon-oxygen single bonds and one double bond, with two oxygen atoms each carrying a negative charge.



In carbonate, bonds are identical and the charges are delocalized.



The positive ion attracts the delocalized electrons in the carbonate ion towards itself. The carbonate ion becomes polarized.

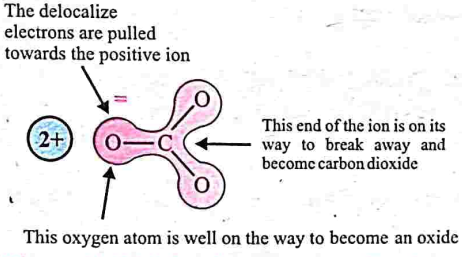


Figure 13.2 Molecular structure of carbonate.

When it is heated, the carbon dioxide gets free, leaving a metal oxide. The amount of heat required depends on the polarization of the ion. If the positive ion has only one positive charge, the polarizing effect is reduced. This is why the Group – IA compounds are more thermally stable than those in Group – IIA.

The smaller the positive ion, the higher the charge density and greater the effect on the carbonate ion. As we move down the group, the positive ions become bigger, so they have less effect on the carbonate ions near them. In other words, carbonates become more thermally stable down the group.

Extension to Nitrates and Hydrogen Carbonates

The phenomena of polarization is exactly the same for nitrates and hydrogen carbonates. The small positive ions at the top of the group polarize the nitrate or hydrogen carbonate ions to a greater extent than the larger positive ions at the bottom of the group. Again, the Group – IA compounds need more heat than those in Group – IIA because the Group – IA ions are less polarizing. Thus, thermal stability of anion of Group – I and Group – II increases down the group. The reason is increasing size and decreasing charge density of metal ions.

13.2.6 Flame Test: Origin of Flame Colours

The Group–IA elements and their salts impart a characteristic colour to the Bunsen flame. These colours differ from one another as shown below.

Table 13.17 Characteristic Colour to Bunsen Flame of Group – IA Elements

Elements	Lithium Li	Sodium Na	Potassium K	Rubidium Rb	Cesium Cs
Flame Colour	Crimson red	Golden yellow	Lilac	Red-violet	Blue-violet

On heating Group – IA elements or its salt (especially chlorides due to its more volatile nature in a flame), the electrons are excited easily to higher energy levels because of absorption of energy. When these electrons return to their ground states, they emit extra energy in the form of radiations, which fall in the visible region, thereby, imparting a characteristic colour to the flame.

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Bleaching powder is extensively applied to remove stains from fabrics or various surfaces. Besides, there are several other applications of bleaching powder. Some of their applications are as follows:

- Old items such as jewellery or showpieces made up of steel or metal can be cleaned with bleaching powder.
- Mixing equal parts of water and bleaching powder are used as a bathroom cleaner.
- Bleaching powder and soapy dishwater, clean the glass dishware, make it shining, clean and disinfect.
- Bleaching powder can be applied as a disinfectant.
- It can be used for cleaning and sterilizing kitchen and garden tools by washing them with bleaching powder.
- By mixing bleaching powder with detergent, make the plastic furniture; look new and free of germs.
- By adding some bleach in the vase, water can preserve the fresh cut flowers.
- By mixing, the bleaching powder with warm water can efficiently disinfect and clean thoroughly.
- Bleaching powder mixed in water can be used to clean and sanitize the doors, windows and floors in households, offices, hospitals, malls and other places. This removes the germs and bacteria from surfaces.
- Bleaching powder can be used in various industries and manufacturing units as an oxidizing agent. The chemical formula of bleaching powder is $CaOCl_2$. It reacts with dilute acids to release chlorine gas because chlorine is a strong oxidizing agent and contributes to the real action of bleaching powder.
- Bleaching powder can act as an oxidizing agent. It is used to prepare chloroform in laboratories by reacting with ethanol or acetone.

13.3 Group – IIA Elements

Group–IIA are commonly called alkaline earth metals. They do not exist free in nature. They exist in combined form. Magnesium and calcium are very abundant in the rocks of Earth's crust.

Elements of Group–IIA (alkaline earth metals) possess two electrons in the outermost (valence) *s*-orbital. They form *di*-positive ions by loss of both the electrons. The elements and their atomic number etc. are given in **Table 13.18** below.

Table 13.18 The Electronic Configuration of Group – IIA Elements

Elements symbol with atomic No	Electronic configuration	
$_4$Be	$1s^2, 2s^2$	$[He]2s^2$
$_{12}$Mg	$1s^2, 2s^2, 2p^6, 3s^2$	$[Ne]3s^2$
$_{20}$Ca	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$	$[Ar]4s^2$
$_{38}$Sr	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^2$	$[Kr]5s^2$
$_{56}$Ba	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 5s^2, 5p^6, 6s^2$	$[Xe]6s^2$
$_{88}$Ra	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{14}, 4f^{14}, 5s^2, 5p^6, 5d^{10}, 6s^2, 6p^6, 7s^2$	$[Rn]7s^2$

All Group – IIA metals except beryllium are white in colour. They are quite reactive and tarnish in air. The values of their densities, melting points and boiling points are higher than those of alkali metals.

13.3.1 Atomic and Physical Properties

13.3.1.1 Trend in Atomic Radius

The atomic radii increase down the group due to the successive addition of extra shell of electrons to each element from Be to Ba.

Table 13.19 Trend in Atomic Radius in Group – IIA Elements

Elements	Be	Mg	Ca	Sr	Ba
Atomic radius (pm)	112	150	197	215	217

13.3.1.2 Trend in First Ionization Energy

The first ionization energy of these elements decreases with increase of atomic radii from Be to Ba.

Table 13.20 Trend in First Ionization Energy in Group IIA Elements

Elements	Be	Mg	Ca	Sr	Ba
1^{st} Ionization energy (kJ/mol)	899.5	737.7	589.8	549.5	502.6

13.3.1.3 Trend in Electronegativity

The electronegativity values of these elements are small and decrease from Be to Ba.

Table 13.21 Trend in Electronegativity in Group IIA Elements

Elements	Be	Mg	Ca	Sr	Ba
Electronegativity	1.57	1.31	1.00	0.95	0.89

13.3.1.4 Trend in Melting and Boiling Points

Melting point: If we exclude the magnesium, there is a general decrease in melting point going down Group – IIA. However, if you include magnesium, you will see that its melting point is lower than the melting point of calcium, the next element. If you include magnesium, there is no obvious trend in melting points

Boiling point: There does not appear to be a trend in boiling points going down the group. Again magnesium is an anomaly.

Table 13.22 Trend in Melting and Boiling points in Group – IIA Elements

Element	Be	Mg	Ca	Sr	Ba
Melting point (°C)	1278	651	843	769	725
Boiling point (°C)	2477	1110	1487	1380	1640

13.3.2 Trend in Reactivity with Water

Beryllium is the only alkaline earth metal, which does not react with water even at red heat due to much less electropositive character. The other elements of Group – IIA react with water, though slowly.

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

$$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$

Calcium, strontium and barium react even with cold water to form the corresponding hydroxides.

$$Ca_{(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$

Group – IIA elements become more reactive towards water as we go down the group.

13.3.3 Reactions with Oxygen and Nitrogen

Group – IIA elements react with oxygen to produce the respective metal oxide.

13.3.3.1 Simple Oxides

Ca, Sr and Ba being more electropositive, react with air readily to form a mixture of their respective oxides. The reactivity towards oxygen increases as we go down the group.

$$2Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)}$$

Beryllium does not react below 600°C, but in powdered form burns brilliantly. Beryllium has very strong layer of BeO on its surface, which prevents any more oxygen reaching the underlying beryllium to react with it.

Thus, Ca, Ba and Sr are stored in paraffin but Be and Mg are not because they form protective oxide layer on their surface.

13.3.3.2 Formation of Peroxides on Heating with Oxygen

Be, Mg and Ca do not form peroxide when heated with oxygen. However, Sr and Ba react in oxygen to form peroxide.

Barium forms barium peroxide on heating with oxygen, but strontium reacts with oxygen to form strontium peroxide, when it is heated with oxygen under high pressure.

$$Ba_{(s)} + O_{2(g)} \longrightarrow BaO_{2(s)}$$

$$Sr_{(s)} + O_{2(g)} \longrightarrow SrO_{2(s)}\ .$$

13.3.3.3 Formation of Nitrides on Heating in Air

All the Group – IIA elements burn in nitrogen to form ionic nitrides of the general formula, M_3N_2.

$$3M_{(s)} + N_{2(g)} \xrightarrow{\Delta} M_3N_{2(s)}$$

$$3Mg_{(s)} + N_{2(g)} \xrightarrow{\Delta} Mg_3N_{2(s)}$$

$$3Be_{(s)} + N_{2(g)} \xrightarrow{\Delta} Be_3N_{2(s)}$$

The nitrides of Group – IIA elements are ionic and solid in nature except beryllium nitride (Be_3N_2) which is covalent and volatile.

13.3.4 Trend in Solubility of the Hydroxides, Sulphates and Carbonates

i. Solubility of the Hydroxides

Group–II metal hydroxides become more soluble in water as we go down the group.

Magnesium hydroxide appears to be insoluble in water. However, if it is shaken in water and filtered, the solution is slightly basic (pH = 9.0). This is because some magnesium hydroxide has been dissolved.

Calcium hydroxide is partially soluble in water. A suspension of calcium hydroxide in water will appear at more alkaline (pH = 11) than magnesium hydroxide as it is more soluble so there will be more hydroxide ions present in solution of magnesium hydroxide.

Barium hydroxide is soluble enough to produce a solution with a concentration around 0.1 mol dm^{-3} at room temperature. The hydroxide ions present would make the solution strongly alkaline.

$$Ba(OH)_{2(s)} \xrightarrow{H_2O} Ba^{2+}_{(aq)} + 2OH^-_{(aq)}$$

Tidbit

- Magnesium hydroxide is used in medicine (in suspension as milk of magnesia) to neutralise excess acid in the stomach and to treat constipation.

$$Mg(OH)_{2(aq)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + 2H_2O_{(l)}$$

- An aqueous solution of calcium hydroxide is called limewater and can be used as a test-reagent for carbon dioxide.

ii. Solubility of the Sulphates

Group – IIA sulphates become less soluble as we move down the group. $BaSO_4$ is the least soluble. This simple trend is true provided that hydrated beryllium sulphate is considered, but not for the anhydrous beryllium sulphate. The anhydrous beryllium sulphate, $BeSO_4$ is insoluble, whereas the hydrated form, ($BeSO_4.4H_2O$), is soluble. Solubility of magnesium sulphate and calcium sulphate also depends on whether the salt is hydrated or not.

iii. Solubility of the Carbonates

The carbonates become less soluble down the group. All the Group – IIA carbonates are sparingly soluble, while all dissolve in acids. The trend to lower solubility is, however, broken at the bottom of the group.

Barium carbonate is slightly more soluble than strontium sulphate. As we move downward in the group, the energy required to break the lattice of carbonates decreases, because the positive ions get larger. The larger the ions, the more distance there is between ions. Thus, the forces holding these ions together become weaker. This increases the solubility.

On the other hand, when the size of the positive ions become larger downward in the group, the energy released by the ions during hydration also falls because bigger ions are not so strongly attracted to the water molecules. This decreases the solubility of carbonates.

The effect of decrease in hydration energy is greater than decrease in lattice energy in case of carbonates of IIA down the group. Thus, the solubility of carbonates decreases.

13.3.5 Trend in Thermal Stability of the Nitrates and Carbonates

i. Thermal Stability of the Group – IIA Nitrates

All the nitrates of this group undergo thermal decomposition to the metal oxide, nitrogen dioxide and oxygen gas. Thermal decomposition means the splitting up of a compound by heating. The following reactions describe the thermal decomposition of the nitrates (Where M = Be, Mg, Ca, Ba and Sr).

$$2M(NO_3)_{2(s)} \longrightarrow 2MO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

$$2Ca(NO_3)_{2(s)} \longrightarrow 2CaO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

The nitrates become more thermally stable down the group, i.e. they require more heating to decompose.

ii. Thermal Stability of the Group – IIA Carbonates

All the carbonates of this group undergo thermal decomposition, to the metal oxide and carbon dioxide gas.

The following reactions describe the decomposition of the carbonate (Where M = Be, Mg, Ca, Ba and Sr).

$$MCO_{3(s)} \longrightarrow MO_{(s)} + CO_{2(g)}$$

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

The carbonates become more thermally stable down the group, they require more heating to decompose.

13.3.6 How Beryllium Differs from other Members of its Group?

Beryllium differs from other Group – IIA metals in many respects. This is partly due to its small size and partly due to its high electronegativity.

- Beryllium is the lightest of all the Group – IIA metals.
- Beryllium has higher melting and boiling point compared to other elements in Group – IIA.
- Beryllium unlike other Group – IIA metals is not easily affected by dry air
- Beryllium does not react with water or steam at red heat.
- The oxide of beryllium, BeO is amphoteric whereas, other oxides of Group – IIA metals are strong bases.
- Oxides, nitrides, chlorides etc. of Group–IIA elements are ionic, while those of beryllium are covalent.
- Salts of beryllium do not impart any colour during flame test unlike its other family members.
- Beryllium oxide is insoluble in water unlike oxide of other members of its family.
- Beryllium does not liberate hydrogen from acids as observed in other Group – IIA metals.

13.3.6.1 Why is Beryllium Chloride Covalent and not Ionic?

Beryllium at the top of the group has high electronegativity (1.57) compared with the rest of the group members. High electronegativity means that it attracts a bonding pair of electrons towards itself more strongly than the rest of the Group – IIA elements. This gives covalent character to $BeCl_2$.

13.3.6.2 Amphoteric Beryllium Hydroxide

Beryllium hydroxide can act both as an acid and as a base.

i. Beryllium Hydroxide as an Acid

Beryllium hydroxide reacts with concentrated solution of sodium hydroxide to produce sodium tetrahydroxoberyllate.

As an acid: $Be(OH)_{2(aq)} + 2NaOH_{(aq)} \longrightarrow Na_2[Be(OH)_4]_{(aq)}$

sodium tetrahydroxoberyllate

ii. Beryllium Hydroxide as a Base

Beryllium hydroxide reacts with dilute hydrochloric acid producing beryllium chloride as neutralization product.

As a base: $Be(OH)_{2(aq)} + 2HCl_{(aq)} \longrightarrow BeCl_{2(aq)} + 2H_2O_{(l)}$

13.4 Group – IVA Elements

The Group – IVA of the periodic table is often referred to as the carbon group. This group consists of five elements carbon (C), silicon (Si), germanium (Gr), tin (Sn) and lead (Pb). This group is present in the middle of periodic table forming a link between more electropositive elements of Group – IA to IIIA and more electronegative elements of Group VA to VIIA. Each element in this group contains four valence electrons. The elements of group – IV A evidentially exhibit an intermediate character. The general electronic configuration of Group – IVA elements in valence shell is ns^2, np^2, where n varies from 2 (for carbon) to 6 (for lead), for example, the electronic configuration of carbon is $1s^2, 2s^2, 2p^2$.

13.4.1 Physical Properties: Melting and Boiling Points

The melting point of carbon is extremely high. The melting and boiling points of silicon and germanium are very high because these elements have a very stable arrangement of solid structure (diamond-type lattice). Sn and Pb have a lower melting point because only two electrons are involved in bond formation instead of four, due to inert pair effect.

Table 13.23 Melting and Boiling Points of Group IVA Elements

Elements	C	Si	Ge	Sn	Pb
Melting point (°C)	3550 (Diamond)	1410	937	232	328
Boiling point (°C)	4827	2355	2830	2260	1744

13.4.2 The Trend from Non-Metal to Metal

The change from non-metallic to metallic character with the increase of atomic number is best illustrated in this group e.g. C and Si are non-metals. Ge is metalloid, Sn and Pb exhibit metallic character.

13.4.3 Oxidation State

Oxidation state is the apparent charge (positive or negative) on an atom of an elemen molecule or ion.

Carbon and silicon show +4 oxidation states in carbonates and silicates. The rema members can show +2 as well as +4 oxidation states. Since, the electronegativity of elements is low; they do not have such a high tendency to form negative ions.

13.4.4 Possible Oxidation States

Oxidation state of group – IVA elements may be positive or negative depending upo nature of the compounds. The typical oxidation state shown by elements of Groups – is +4, found in compounds like CCl_4, $SiCl_4$ and SnO_2. However, as we move down group, there are more and more examples, where the oxidation state is +2, such as Sn $PbCl_2$ and PbO.

However, carbon forms C^{-4} and C_2^{-2} ions in certain compounds, such as Be_2C (C = Be = +2), Na_2C_2 (C_2 = –2, Na = +1) etc. Besides this, CH_4, is not an example of ca with an oxidation state of +4. Because carbon is more electronegative than hydrogen its oxidation state is –4.

13.4.4.1 Inert Pair Effect in Formation of Ionic Bonds

The tendency of the two electrons in the outermost atomic s–orbital to remain unshare compounds is called inert pair effect. For example, C and Si show a covalence of four to sp^3 hybridization. However, hybridization may not always be feasible in case of lower elements of Group – IV. For hybridization to be energetically feasible, net enth change involved in the following two processes should be negative.

i. Promotion of one electron of the *s*–orbital into higher energy *p*–orbital. Ene must be provided for this process.

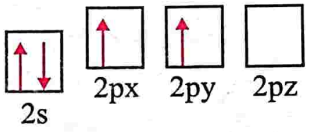
ii. Formation of four covalent bonds by the four hybrid orbitals, energy is relea in this process.

If energy release in the formation of four bonds is more than energy absorbed in promo of *s*–electron then hybridization is feasible. This happens in case of C and Si and also Ge in most cases. However, Sn and Pb form weak covalent bonds due to their larger ato radius. So, the energy released in the formation of four covalent bonds may be less the energy needed to promote *s*–electrons. So, hybridization will not occur and *s*–electrons remain paired. They are called inert pair and effect is called inert pair ef thus, Sn and Pb show oxidation state of 2 in addition to four.

13.4.4.2 Inert Pair Effect and the Formation of Covalent Bonds

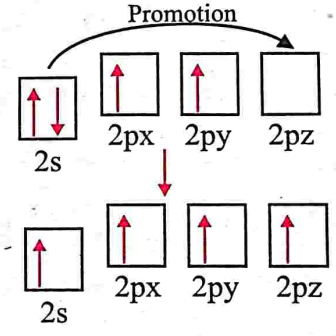
Carbon normally forms four covalent bonds rather than two. The outer electronic structure of carbon is,

Ground state (C)



There are two unpaired electrons in 2px and 2py orbitals. In order to form bonds, however, carbon promotes one 's' electron to the empty 2pz orbital.

Excited state (C*)



This produces 4 unpaired electrons which (after hybridization) can form four covalent bonds. To promote the 's' electron to 'p' orbital requires energy. During the covalent bond formation each bond releases energy and this energy is enough for the promotion of 's' electron to 'p' orbital.

The other members of Group – IVA, such as lead show reluctance to do the same; this is due the decrease in bond energies down the group. Bond energies decreases as atomic size increases and the bonding pair move away from the two nuclei and also because of screening effect. For example, the energy released by two extra Pb–Cl bonds may not be enough to cater the extra energy needed to promote a 6s electron into the empty 6p orbital.

13.4.5 Chlorides of Carbon, Silicon and Lead

Carbon, silicon and lead give tetrachlorides, which are simple covalent molecules. They exist in liquid state at room temperature with the general formula of MCl_4. (where M = C, Si, Pb).

13.4.5.1 Structures and Stability

i. Structure

The MCl_4 have a tetrahedral shape with a bond angle of 109.5°. A typical example is carbon tetrachloride.

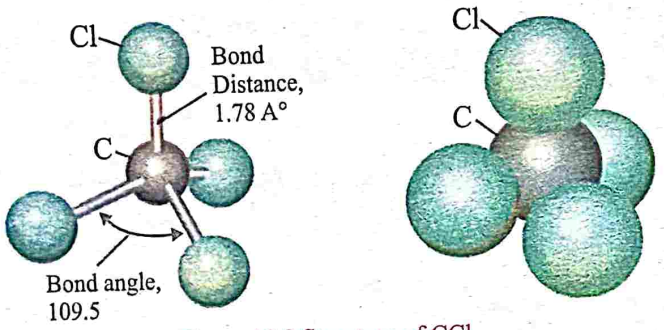


Figure 13.3 Structure of CCl_4.

ii. Stability

When we move down the Group, compounds with a +2 oxidation state in Group – IV element become more stable.

This means that the +4 oxidation is less favourable while the +2 oxidation state is more favourable down the Group.

Thus, stability decreases from CCl_4 to $PbCl_4$. Lead tetrachloride ($PbCl_4$) at room temperature, tends to decompose to give lead dichloride ($PbCl_2$) and chlorine gas.

$$PbCl_{4(s)} \longrightarrow PbCl_{2(s)} + Cl_{2(g)}$$

13.4.5.2 Reactions with Water

Carbon tetrachloride (CCl_4) does not react with water. This is due to bulky nature of chlorine atoms around small carbon atom. As a result, oxygen of water cannot penetrate to reach carbon atom.

$SiCl_4$ to $PbCl_4$ react violently with water to produce their respective oxides and fumes of HCl.

$$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$$

$$PbCl_{4(l)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4HCl_{(g)}$$

$PbCl_2$ is ionic in nature and sparingly soluble in cold water but more soluble in hot water. The solubility in water involves breakup of the ionic lattice and the hydration of Pb^{2+} and Cl^- ions.

$$PbCl_{2(s)} \xrightarrow{H_2O_{(l)}} Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

13.4.6 Oxides

Group –IVA elements form two types of oxides i.e. monoxide and dioxide. This is because the elements have two possible oxidation states, +2 and +4.

Monoxide, include carbon monoxide (CO), silicon monoxide (SiO), germanium monoxide (GeO), tin monoxide (SnO) and lead oxide (PbO), while the dioxide includes carbon dioxide (CO_2), silicon dioxide (SiO_2), germanium dioxide (GeO_2), tin dioxide (SnO_2) and lead dioxide (PbO_2).

The oxide of carbon and silicon are non-metal oxides and are covalent in nature, whereas, oxides of germanium, tin and lead are metal oxide and are ionic in nature.

13.4.6.1 Structure of Carbon Dioxide and Silicon Dioxide

Carbon and silicon have four electrons in their valence shells. They are both tetravalent. It means that the structure of CO_2 and SiO_2 should be similar. But the structure of SiO_2 and CO_2 are quite different from each other. The physical properties of carbon dioxide differ significantly from those of silicon dioxide. Carbon dioxide is a gas whereas silicon dioxide is a hard, high-melting point solid. The other oxides of Group – IV are also solids.

i. Structure of Carbon dioxide

In CO_2 molecule, one electron from 2s orbital moves to 2p level. The hybridization in CO_2 is sp, two sp hybrid orbitals are arranged in linear form with an angle of 180°as shown in Figure 13.4.

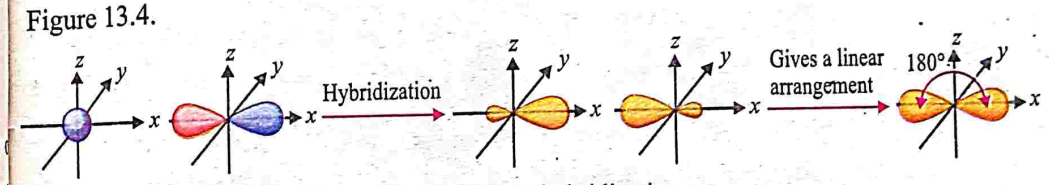


Figure 13.4 sp hybridization.

These sp hybrid orbitals are used to form the σ-bond between the carbon and the oxygen atoms. The two 2p orbitals remain unhybridized on the sp hybridized carbon. These are used to form the π-bond with the oxygen atoms.

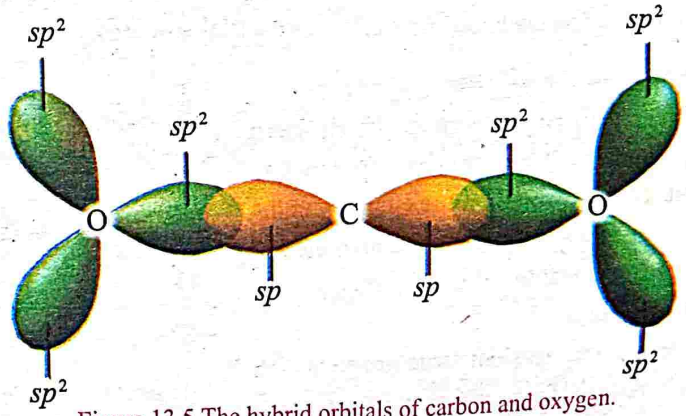


Figure 13.5 The hybrid orbitals of carbon and oxygen.

In CO_2 molecule, each oxygen atom is sp^2 hybridized. One 'p' orbital on each oxygen atom remains unchanged and is used for the π-bond formation with the carbon atom.

The sp orbitals on carbon atom form σ-bonds with the sp^2 orbitals on the two oxygen atoms as shown in **Figure 13.6**. The remaining sp^2 orbitals on the oxygen atoms hold lone pairs. The π-bonds between the carbon atom and each oxygen atom are formed by the overlap of parallel 2p orbitals. The sp hybridized carbon atom has two unhybridized p orbitals **(Figure 13.6)**.

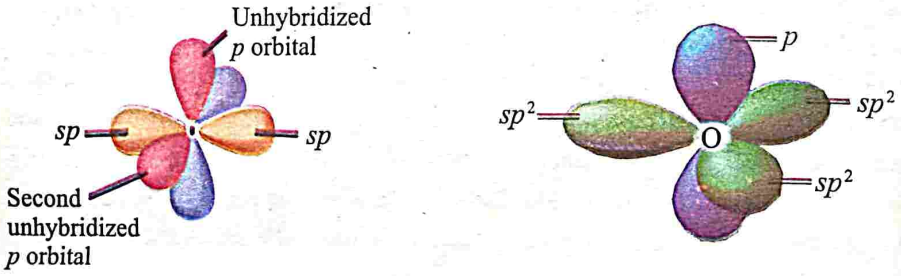


Figure 13.6 Each of these p orbitals is used to form a π-bond with an oxygen atom.

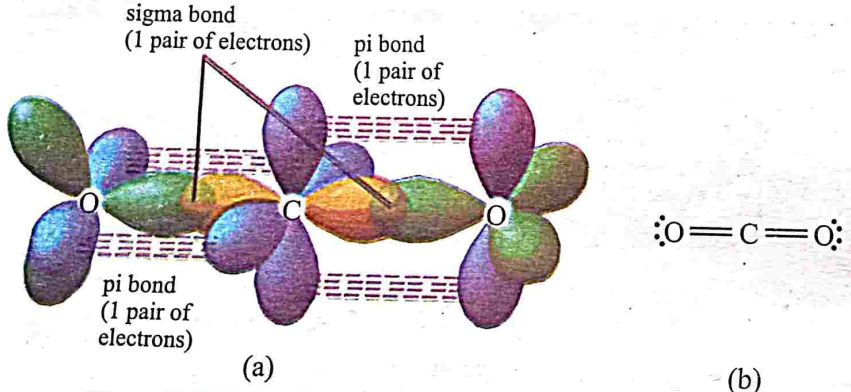


Figure 13.7 The total bonding picture for the CO_2 molecule.

ii. The Structure of Silicon dioxide

Silicon atoms are bigger than carbon atoms, which mean that silicon – oxygen bond will be long as compared to carbon – oxygen bond. The 'p' orbital on the silicon and the oxygen are not quite close enough together to allow enough side wise overlap to give us a stable 'π' bond. Thus, silicon – oxygen bond is a single bond.

The SiO_2 molecule is a giant covalent structure in which each silicon atom is bonded to four oxygen atoms through

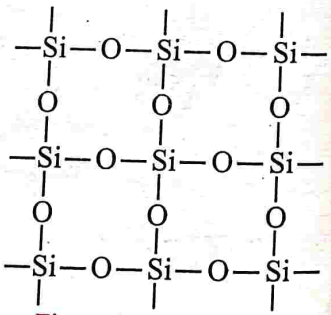


Figure 13.8 Structure of Silicon dioxide.

ingle covalent bonds whereas each oxygen atom is bonded to two silicon atoms.

3.4.6.2 Acid Base Behaviour of Group IV Oxides

he oxides of group – IVA elements are acidic, but their acidity decreases as we move own the group. Acid – base reactions of these oxides are given below.

Group – IVA monoxides

arbon monoxide is treated as neutral oxide but it is slightly acidic. It does not react with ater. It reacts with hot and concentrated sodium hydroxide (NaOH) to produce sodium ethanoate (HCOONa).

$$CO_{(g)} + NaOH_{(aq)} \longrightarrow HCOONa_{(aq)}$$

ermanium, tin and lead monoxides are amphoteric oxides. They can act as an acid as well a base.

s a base: $SnO_{(s)} + 2HCl_{(aq)} \longrightarrow SnCl_{2(aq)} + H_2O_{(l)}$

s an acid: $SnO_{(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SnO_{2(aq)} + H_2O_{(l)}$

Group – IVA dioxides

arbon dioxide is a slight acidic oxide. It reacts with water to a slight extent to produce ydrogen ions and hydrogencarbonate ions.

$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

arbon dioxide reacts with cold sodium hydroxide (NaOH) to give either sodium carbonate sodium hydrogencarbonate solution, depending on the proportion.

$$CO_{2(g)} + 2NaOH_{(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \quad \text{or}$$

$$CO_{(g)} + NaOH_{(aq)} \longrightarrow NaHCO_{3(aq)}$$

licon dioxide is weakly acidic. It reacts with hot and concentrated sodium hydroxide to ve sodium silicate. However, it does not react with water due to its strong covalent nds.

$$SiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_{3(aq)} + H_2O_{(l)}$$

ermanium, tin and lead dioxides are amphoteric oxides. They can act as an acid as well a base.

s a base: $SnO_{2(s)} + 4HCl_{(aq)} \longrightarrow SnCl_{4(aq)} + 2H_2O_{(l)}$

For germanium and tin dioxides, hot and concentrated hydrochloric acid is used. However, for lead dioxide, cold hydrochloric acid is used. This is because, lead dioxide will decompose if the temperature increases.

As an acid: $SnO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SnO_{3(aq)} + H_2O_{(l)}$

For all reactions, hot and concentrated sodium hydroxide is used.

13.5 Group – VIIA Elements: Halogens

Group – VIIA comprise the elements fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). The elements are collectively known as halogens due to their salts forming tendency. All these elements are non-metals.

13.5.1 Atomic and Physical Properties

Elements of Group – VIIA (halogens) possess seven electrons in the outermost (valence) shell, the characteristics feature being 'ns^2np^5' in the outer most shell. The elements and their atomic number etc. are given in **Table 13.24.**

Table 13.24 Elements Symbol with Atomic no and Their Electronic Configuration

Elements	Electronic Configuration	
$_9F$	$1s^2, 2s^2, 2p^5$	[He] 2s, $2p^5$
$_{17}Cl$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$	[Ne] $3s^2$, $3p^5$
$_{35}Br$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^5$	[Ar]$3d^{10}$, $4s^2$, $4p^5$
$_{53}I$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^5$	[Kr]$4d^{10}$, $5s^2$, $5p^5$

Halogens in the uncombined state exist as diatomic covalent molecules (F_2, Cl_2 etc). These discrete molecules are held together by weak Van der Waals's forces, which explain the volatile nature of these elements. These elements are also poisonous in nature.

13.5.1.1 Trend in Atomic Radius

Atomic radii of Group – VII A elements increase down the group as shown in **Table 13.25.**

Table 13.25 Trend in Atomic Radius in Group –VIIA elements

Halogen	$_9F$	$_{17}Cl$	$_{35}Br$	$_{53}I$
Covalent Radius (pm)	71	99	114	133

13.5.1.2 Trend in Electronegativity

Electronegativity of Group – VII A elements decreases gradually from fluorine to iodine down the group as shown below.

Tidbit

Fluorine is the most electronegative element of the periodic table.

Table 13.26 Trend in Electronegativity in Group –VIIA Elements

Halogen	F	Cl	Br	I
Electronegativity	4.0	3.0	2.8	2.5

13.5.1.3 Trend in Electron Affinity

Electron affinity greatly influences the chemical behaviour of atoms by accepting one or more electrons. Electron affinity of an element is defined as *"the amount of energy released when an electron is accepted by an atom in the gaseous state to form an anion,"* i.e.

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \qquad \Delta H = -349 kJmol^{-1}$$

As the energy is released, so electron affinity is given the negative sign. Electron affinity is the measure of the attraction of the nucleus of an atom for the extra electron.

Periodic Trends

(a) Variation in a Group

As we move in a group from top to bottom, there is an increase in the atomic size, nuclear charge and shielding effect. However, the combined effect of increase in atomic size and shielding effect dominates over the effect of increase in the nuclear charge. Hence, force of attraction of the nucleus for the electron to be added decreases resulting in a decrease in electron-affinity values.

However, it has been seen that fluorine has lower electron affinity than chlorine because fluorine has very small size and high charge density which opposes the electron to be added. Electron affinity generally decreases in the following order (I < Br < F < Cl).

(b) Variation in a Period

As we move in a period from left to right, there is no change in the number of shells but atomic size decreases due to the increase in nuclear charge, thereby increasing the force of attraction of the nucleus for the electron to be added and hence electron affinity increases. This trend is given below.

Table 13.27 Trend in Electron Affinity in Group–VIIA Elements

Halogen	F	Cl	Br	I
Electron Affinity (kJ/mol)	–328.0	–349.0	–324.6	–295.2

13.5.1.4 Trend in Melting and Boiling Points

The melting and boiling points of Group – VIIA increases down the group due to increase in strength of the Van der Waals forces. This trend is given below.

Table 13.28 Trend in Melting and Boiling Points in Group–VIIA Elements

Halogen	F	Cl	Br	I
Melting point (°C)	–220.0	–101.0	–7.2	+114.0
Boling point (°C)	–188.0	–35.0	+58.8	+184.0

13.5.1.5 Bond Enthalpies

Bond enthalpy is the amount of heat required to break one mole of covalent bonds to form *individual atoms*. It begins with the original substance in a gaseous state and ending with gaseous atoms.

$$Cl\text{–}Cl_{(g)} \xrightarrow{\Delta} 2Cl_{(g)}$$

13.5.1.5.1 Bond Enthalpies in Halogens

Bond breaking is an endothermic process and bond enthalpy involved is given positive sign. The bond enthalpies of halogens are given below.

Table 13.29 Bond Enthalpies in Halogens

Bond	F – F	Cl – Cl	Br – Br	I – I
Bond length (pm)	144	199	228	267
Bond enthalpy (kJ/mol)	159	243	193	151

The abnormal behavior in F – F bond is due to its smaller size and strong repulsion amongst the non-bonded electrons (lone pair) of fluorine atoms. Hence bonds become weak, though bond is short. Thus, enthalpy of fluorine is less than the other halogens.

13.5.1.5.2 Bond Enthalpies in Hydrogen Halides

Down the group the halogen atoms get bigger, the bonding pair of electrons get more and more distant from the nucleus, the attraction is less and the bond becomes weaker. So the bond enthalpies of hydrogen halides decreases down the group. The bond enthalpies are very important in the thermal stability of hydrogen halides.

H – F and H – Cl are stable to heat and they do not decompose easily. H – Br decomposes slightly into hydrogen and bromine on heating and H – I decomposes to an even greater extent. As the bonds get weaker, they are more easily broken. Bond enthalpies of halides are given below.

Table 13.30 Bond Enthalpies in Hydrogen Halides

Hydrogen Halide	H – F	H – Cl	H – Br	H – I
Bond enthalpy (kJ/mol)	+568.2	+ 431.9	+ 366.1	+ 298.3

13.5.2 Strength of Halogens as Oxidizing Agents

An oxidizing agent is a substance that removes electrons from other substances during a redox reaction.

The oxidizing agent takes these electrons for itself, thus gaining electrons and getting reduced. An oxidizing agent is thus an electron acceptor. The halogen accepts electron during the reaction and acts as oxidizing agent.

$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2Na^{+}Cl^{-}_{(s)}$$

For example, fluorine is a powerful oxidizing agent. Fluorine is the most electronegative, so forming F^- is the most energetically favourable of the reductions. This makes fluorine the most powerful oxidizing agent.

Chlorine has the ability to take electrons from bromide ions and oxidize/change them to bromine in potassium bromide solution.

$$Cl_{2(g)} + 2Br^{-}_{(aq)} \longrightarrow 2Cl^{-}_{(aq)} + Br_{2(l)}$$

The bromine appears as an orange solution.

Chlorine can also oxidize iodide ions to iodine in potassium iodide solution.

$$Cl_{2(g)} + 2I^{-}_{(aq)} \longrightarrow 2Cl^{-}_{(aq)} + I_{2(aq)}$$

The iodine appears either as a red solution or as a dark grey precipitate if the chlorine is in excess.

Bromine and iodine cannot regain those electrons from the chloride ions formed. This indicates that chlorine is more powerful oxidizing agent than either bromine or iodine. In short, oxidizing ability decreases down the group.

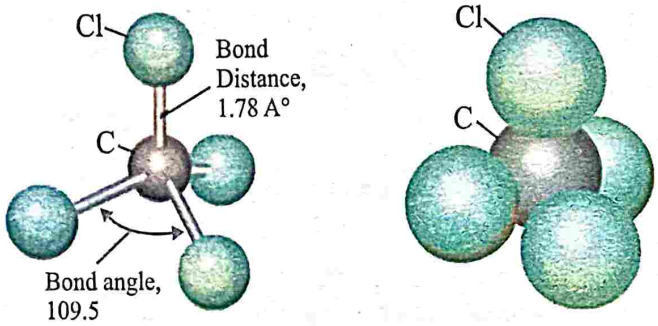


Figure 13.3 Structure of CCl_4.

ii. Stability

When we move down the Group, compounds with a +2 oxidation state in Group – element become more stable.

This means that the +4 oxidation is less favourable while the +2 oxidation state is favourable down the Group.

Thus, stability decreases from CCl_4 to $PbCl_4$. Lead tetrachloride ($PbCl_4$) at temperature, tends to decompose to give lead dichloride ($PbCl_2$) and chlorine gas.

$$PbCl_{4(s)} \longrightarrow PbCl_{2(s)} + Cl_{2(g)}$$

13.4.5.2 Reactions with Water

Carbon tetrachloride (CCl_4) does not react with water. This is due to bulky natur chlorine atoms around small carbon atom. As a result, oxygen of water cannot penetra reach carbon atom.

$SiCl_4$ to $PbCl_4$ react violently with water to produce their respective oxides and fum HCl.

$$SiCl_{4(l)} + 2H_2O_{(l)} \longrightarrow SiO_{2(s)} + 4HCl_{(g)}$$

$$PbCl_{4(l)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4HCl_{(g)}$$

$PbCl_2$ is ionic in nature and sparingly soluble in cold water but more soluble in hot w The solubility in water involves breakup of the ionic lattice and the hydration of Pb^{2+} Cl^- ions.

$$PbCl_{2(s)} \xrightarrow{H_2O_{(l)}} Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

13.4.6 Oxides

Group –IVA elements form two types of oxides i.e. monoxide and dioxide. This is bec the elements have two possible oxidation states, +2 and +4.

Monoxide, include carbon monoxide (CO), silicon monoxide (SiO), germanium monoxide (GeO), tin monoxide (SnO) and lead oxide (PbO), while the dioxide includes carbon dioxide (CO_2), silicon dioxide (SiO_2), germanium dioxide (GeO_2), tin dioxide (SnO_2) and lead dioxide (PbO_2).

The oxide of carbon and silicon are non-metal oxides and are covalent in nature, whereas, oxides of germanium, tin and lead are metal oxide and are ionic in nature.

13.4.6.1 Structure of Carbon Dioxide and Silicon Dioxide

Carbon and silicon have four electrons in their valence shells. They are both tetravalent. It means that the structure of CO_2 and SiO_2 should be similar. But the structure of SiO_2 and CO_2 are quite different from each other. The physical properties of carbon dioxide differ significantly from those of silicon dioxide. Carbon dioxide is a gas whereas silicon dioxide is a hard, high-melting point solid. The other oxides of Group – IV are also solids.

i. Structure of Carbon dioxide

In CO_2 molecule, one electron from 2s orbital moves to 2p level. The hybridization in CO_2 is sp, two sp hybrid orbitals are arranged in linear form with an angle of 180°as shown in Figure 13.4.

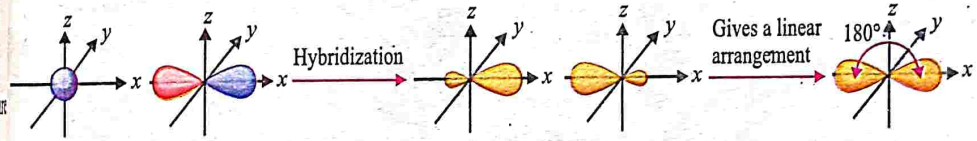


Figure 13.4 sp hybridization.

These sp hybrid orbitals are used to form the σ-bond between the carbon and the oxygen atoms. The two 2p orbitals remain unhybridized on the sp hybridized carbon. These are used to form the π-bond with the oxygen atoms.

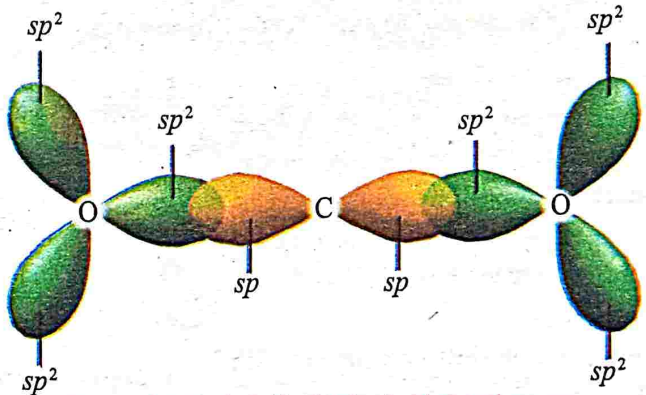


Figure 13.5 The hybrid orbitals of carbon and oxygen.

In CO_2 molecule, each oxygen atom is sp^2 hybridized. One 'p' orbital on each oxygen atom remains unchanged and is used for the π-bond formation with the carbon atom. The sp orbitals on carbon atom form σ-bonds with the sp^2 orbitals on the two oxygen atoms as shown in **Figure 13.6**. The remaining sp^2 orbitals on the oxygen atoms hold lone pairs. The π-bonds between the carbon atom and each oxygen atom are formed by the overlap of parallel 2p orbitals. The sp hybridized carbon atom has two unhybridized p orbitals **(Figure 13.6)**.

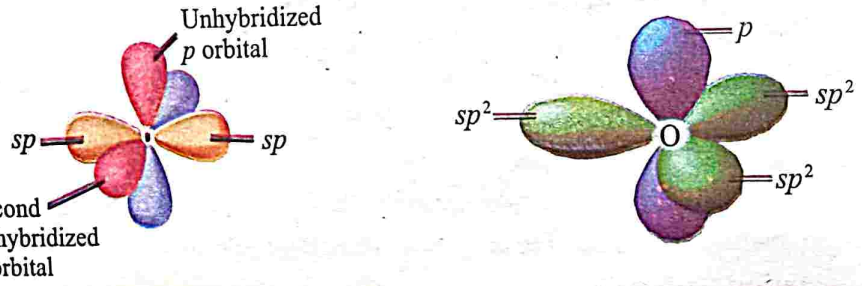


Figure 13.6 Each of these p orbitals is used to form a π-bond with an oxygen atom.

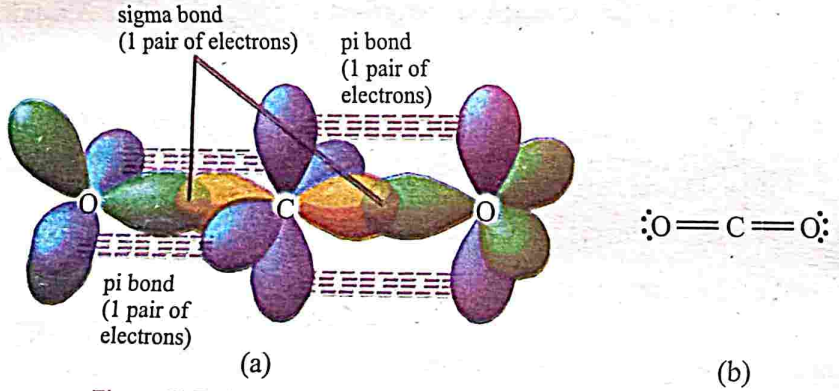


Figure 13.7 The total bonding picture for the CO_2 molecule.

ii. The Structure of Silicon dioxide

Silicon atoms are bigger than carbon atoms, which mean that silicon – oxygen bond will be long as compared to carbon – oxygen bond. The 'p' orbital on the silicon and the oxygen are not quite close enough together to allow enough side wise overlap to give us a stable 'π' bond. Thus, silicon – oxygen bond is a single bond.

The SiO_2 molecule is a giant covalent structure in which each silicon atom is bonded to four oxygen atoms through

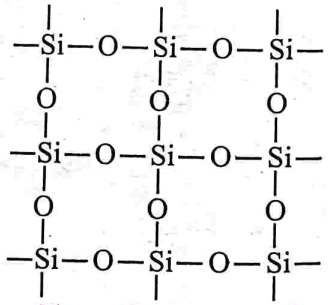


Figure 13.8 Structure of Silicon dioxide.

ngle covalent bonds whereas each oxygen atom is bonded to two silicon atoms.

3.4.6.2 Acid Base Behaviour of Group IV Oxides

he oxides of group – IVA elements are acidic, but their acidity decreases as we move own the group. Acid – base reactions of these oxides are given below.

Group – IVA monoxides

arbon monoxide is treated as neutral oxide but it is slightly acidic. It does not react with ater. It reacts with hot and concentrated sodium hydroxide (NaOH) to produce sodium ethanoate (HCOONa).

$$CO_{(g)} + NaOH_{(aq)} \longrightarrow HCOONa_{(aq)}$$

ermanium, tin and lead monoxides are amphoteric oxides. They can act as an acid as well a base.

s a base: $SnO_{(s)} + 2HCl_{(aq)} \longrightarrow SnCl_{2(aq)} + H_2O_{(l)}$

s an acid: $SnO_{(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SnO_{2(aq)} + H_2O_{(l)}$

Group – IVA dioxides

rbon dioxide is a slight acidic oxide. It reacts with water to a slight extent to produce drogen ions and hydrogencarbonate ions.

$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

rbon dioxide reacts with cold sodium hydroxide (NaOH) to give either sodium carbonate sodium hydrogencarbonate solution, depending on the proportion.

$$CO_{2(g)} + 2NaOH_{(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \quad \text{or}$$

$$CO_{(g)} + NaOH_{(aq)} \longrightarrow NaHCO_{3(aq)}$$

licon dioxide is weakly acidic. It reacts with hot and concentrated sodium hydroxide to ve sodium silicate. However, it does not react with water due to its strong covalent nds.

$$SiO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_{3(aq)} + H_2O_{(l)}$$

ermanium, tin and lead dioxides are amphoteric oxides. They can act as an acid as well a base.

s a base: $SnO_{2(s)} + 4HCl_{(aq)} \longrightarrow SnCl_{4(aq)} + 2H_2O_{(l)}$

For germanium and tin dioxides, hot and concentrated hydrochloric acid is used. However for lead dioxide, cold hydrochloric acid is used. This is because, lead dioxide will decompose if the temperature increases.

As an acid: $SnO_{2(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SnO_{3(aq)} + H_2O_{(l)}$

For all reactions, hot and concentrated sodium hydroxide is used.

13.5 Group – VIIA Elements: Halogens

Group – VIIA comprise the elements fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). The elements are collectively known as halogens due to their salt forming tendency. All these elements are non-metals.

13.5.1 Atomic and Physical Properties

Elements of Group – VIIA (halogens) possess seven electrons in the outermost (valence) shell, the characteristics feature being 'ns^2np^5' in the outer most shell. The elements and their atomic number etc. are given in **Table 13.24.**

Table 13.24 Elements Symbol with Atomic no and Their Electronic Configuration

Elements	Electronic Configuration	
$_9F$	$1s^2, 2s^2, 2p^5$	[He] $2s, 2p^5$
$_{17}Cl$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$	[Ne] $3s^2, 3p^5$
$_{35}Br$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^5$	[Ar]$3d^{10}, 4s^2, 4p^5$
$_{53}I$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 5s^2, 5p^5$	[Kr]$4d^{10}, 5s^2, 5p^5$

Halogens in the uncombined state exist as diatomic covalent molecules (F_2, Cl_2 etc). These discrete molecules are held together by weak Van der Waals's forces, which explain the volatile nature of these elements. These elements are also poisonous in nature.

13.5.1.1 Trend in Atomic Radius

Atomic radii of Group – VII A elements increase down the group as shown in **Table 13.25.**

Table 13.25 Trend in Atomic Radius in Group –VIIA elements

Halogen	$_9F$	$_{17}Cl$	$_{35}Br$	$_{53}I$
Covalent Radius (pm)	71	99	114	133

13.5.1.2 Trend in Electronegativity

Electronegativity of Group – VII A elements decreases gradually from fluorine to iodine down the group as shown below.

Tidbit

Fluorine is the most electronegative element of the periodic table.

Table 13.26 Trend in Electronegativity in Group –VIIA Elements

Halogen	F	Cl	Br	I
Electronegativity	4.0	3.0	2.8	2.5

13.5.1.3 Trend in Electron Affinity

Electron affinity greatly influences the chemical behaviour of atoms by accepting one or more electrons. Electron affinity of an element is defined as *"the amount of energy released when an electron is accepted by an atom in the gaseous state to form an anion,"* i.e.

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \qquad \Delta H = -349 kJmol^{-1}$$

As the energy is released, so electron affinity is given the negative sign. Electron affinity is the measure of the attraction of the nucleus of an atom for the extra electron.

Periodic Trends

(a) Variation in a Group

As we move in a group from top to bottom, there is an increase in the atomic size, nuclear charge and shielding effect. However, the combined effect of increase in atomic size and shielding effect dominates over the effect of increase in the nuclear charge. Hence, force of attraction of the nucleus for the electron to be added decreases resulting in a decrease in electron-affinity values.

However, it has been seen that fluorine has lower electron affinity than chlorine because fluorine has very small size and high charge density which opposes the electron to be added. Electron affinity generally decreases in the following order ($I < Br < F < Cl$).

(b) Variation in a Period

As we move in a period from left to right, there is no change in the number of shells but atomic size decreases due to the increase in nuclear charge, thereby increasing the force of attraction of the nucleus for the electron to be added and hence electron affinity increases. This trend is given below.

13.27 Trend in Electron Affinity in Group–VIIA Elements

Halogen	F	Cl	Br	I
Electron Affinity (kJ/mol)	–328.0	–349.0	–324.6	–295.2

13.5.1.4 Trend in Melting and Boiling Points

The melting and boiling points of Group – VIIA increases down the group due to increase in strength of the Van der Waals forces. This trend is given below.

Table 13.28 Trend in Melting and Boiling Points in Group–VIIA Elements

Halogen	F	Cl	Br	I
Melting point (°C)	–220.0	–101.0	–7.2	+114.0
Boling point (°C)	–188.0	–35.0	+58.8	+184.0

13.5.1.5 Bond Enthalpies

Bond enthalpy is the amount of heat required to break one mole of covalent bonds to form individual atoms. It begins with the original substance in a gaseous state and ending with gaseous atoms.

$$Cl\text{–}Cl_{(g)} \xrightarrow{\Delta} 2Cl_{(g)}$$

13.5.1.5.1 Bond Enthalpies in Halogens

Bond breaking is an endothermic process and bond enthalpy involved is given positive sign. The bond enthalpies of halogens are given below.

Table 13.29 Bond Enthalpies in Halogens

Bond	F – F	Cl – Cl	Br – Br	I – I
Bond length (pm)	144	199	228	267
Bond enthalpy (kJ/mol)	159	243	193	151

The abnormal behavior in F – F bond is due to its smaller size and strong repulsion amongst the non-bonded electrons (lone pair) of fluorine atoms. Hence bonds become weak, though bond is short. Thus, enthalpy of fluorine is less than the other halogens.

13.5.1.5.2 Bond Enthalpies in Hydrogen Halides

Down the group the halogen atoms get bigger, the bonding pair of electrons get more and more distant from the nucleus, the attraction is less and the bond becomes weaker. So the bond enthalpies of hydrogen halides decreases down the group. The bond enthalpies are very important in the thermal stability of hydrogen halides.

H – F and H – Cl are stable to heat and they do not decompose easily. H – Br decomposes slightly into hydrogen and bromine on heating and H – I decomposes to an even greater extent. As the bonds get weaker, they are more easily broken. Bond enthalpies of halides are given below.

Table 13.30 Bond Enthalpies in Hydrogen Halides

Hydrogen Halide	H – F	H – Cl	H – Br	H – I
Bond enthalpy (kJ/mol)	+568.2	+ 431.9	+ 366.1	+ 298.3

13.5.2 Strength of Halogens as Oxidizing Agents

An oxidizing agent is a substance that removes electrons from other substances during a redox reaction.

The oxidizing agent takes these electrons for itself, thus gaining electrons and getting reduced. An oxidizing agent is thus an electron acceptor. The halogen accepts electron during the reaction and acts as oxidizing agent.

$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2Na^{+}Cl^{-}_{(s)}$$

For example, fluorine is a powerful oxidizing agent. Fluorine is the most electronegative, so forming F^- is the most energetically favourable of the reductions. This makes fluorine the most powerful oxidizing agent.

Chlorine has the ability to take electrons from bromide ions and oxidize/change them to bromine in potassium bromide solution.

$$Cl_{2(g)} + 2Br^{-}_{(aq)} \longrightarrow 2Cl^{-}_{(aq)} + Br_{2(l)}$$

The bromine appears as an orange solution.

Chlorine can also oxidize iodide ions to iodine in potassium iodide solution.

$$Cl_{2(g)} + 2I^{-}_{(aq)} \longrightarrow 2Cl^{-}_{(aq)} + I_{2(aq)}$$

The iodine appears either as a red solution or as a dark grey precipitate if the chlorine is in excess.

Bromine and iodine cannot regain those electrons from the chloride ions formed. This indicates that chlorine is more powerful oxidizing agent than either bromine or iodine. In short, oxidizing ability decreases down the group.

The order of decreasing power of halogens as oxidizing agent is

$$F_2 > Cl_2 > Br_2 > I_2$$

13.5.3 The Acidity of Hydrogen Halides

According to Bronsted and Lowery, an acid is a proton donor. Hydrogen chloride gas is soluble in water; its solvated form is hydrochloric acid. HCl is soluble in water and produces H_3O^+ and Cl^- ions.

$$HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

This reaction shows that HCl completely dissociates in water. Hydrochloric acid is therefore a strong acid. An acid is strong if it is fully ionized in solution.

Hydrogen bromide and hydrogen iodide dissolve in (and react with) water and completely dissociate in water. Therefore, both HBr and HI are strong acids.

Hydrofluoric acid is an exception to strong halogen acids. Although hydrogen fluoride dissolves in water, but hydrofluoric acid is only a weak acid. In strength, it is similar to organic acids like methanoic acid.

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

The trend in reducing power of the halide ions is opposite to the trend in oxidizing power of the halogen elements. This means that the iodide ion is the best reducing agent.

The more reactive halogen will displace the ions of a less reactive halogen from its solution. This is a redox reaction with the halogen acting as an oxidizing agent and the halide ion as a reducing agent. Chlorine oxidizes iodide ions to iodine and is itself reduced to chloride ions.

$$2I^-_{(aq)} + Cl_{2(g)} \longrightarrow 2Cl^-_{(aq)} + I_{2(aq)}$$

Beside this, Br^- reduces sulphuric acid (H_2SO_4) to SO_2, which results in a decrease of oxidation state of sulphur from '+6' in H_2SO_4 to '+4' in SO_2.

$$H_2\overset{+6}{S}O_{4(aq)} + 2H^+_{(aq)} + 2Br^-_{(aq)} \longrightarrow Br_{2(aq)} + \overset{+4}{S}O_{2(aq)} + 2H_2O_{(l)}$$

Iodide (I^-) is stronger reducing agent than bromide ion (Br^-), as it reduces H_2SO_4 to H_2S in which oxidation state of 'S' changes from +6 to –2.

$$H_2\overset{+6}{S}O_{4(aq)} + 8H^+_{(aq)} + 2I^-_{(aq)} \longrightarrow I_{2(aq)} + H_2\overset{-2}{S}_{(g)} + 4H_2O_{(l)}$$

The reducing agents, halides show the following trend in reducing strength:

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

Key Points

- Group – IA and Group – IIA elements belong to s-block.
- Group – IVA and Group – VIIA elements belong to p-block.
- Atomic radius of all the groups increases down the group.
- Period 3rd consists of metals (Na, Mg and Al), metalloid (Si) and non-metals (P, S, Cl and Ar).
- Atomic radius decreases in period 3 up to chlorine but argon does not follow this trend.
- All the elements of period 3rd react with oxygen and form the oxides, except argon.
- Period 3rd oxides do not conduct electricity in solid state.
- The chlorides of period 3rd i.e. NaCl, $MgCl_2$ and Al_2Cl_6 are in solid state, while the $SiCl_4$, PCl_3 and S_2Cl_2 are in liquid state.
- Density of Group – IA elements increases down the group.
- Normal oxides of Group – IA on reaction with dilute acids produce slats and water.
- The carbonates of Group – IA do not decompose on heating except lithium carbonate.
- Group – IA metals give characteristics colours to the Bunsen flame.
- Beryllium is the only alkaline earth metal, which does not react with water even at red heat.
- Be, Mg and Ca on reaction with oxygen form normal oxides.
- Sr and Ba react with oxygen and form peroxide.
- BeO are amphoteric whereas other oxides of Group – IIA metals are strong bases.
- Inert pair effect is the non-participation of the two 's' electrons in bonding.
- In CO_2 molecule, carbon atom is sp and each oxygen atom is sp^2 hybridized.
- Silicon dioxide is weakly acidic.
- Electron affinity is the amount of energy released when an electron is added to an isolated gaseous atom to form an anion.
- In Group–VIIA the electron affinity generally decreases in the order (I < Br < F < Cl).
- In Group–VIIA the order of decreasing power as oxidizing agent is $F_2 > Cl_2 > Br_2 > I_2$.

Exercise

Q1. Choose the correct one from the given options.

1. Electronegativity of Be is approximately equal to that of
   a. Al b. Mg c. B d. Na
2. The elements which are most abundant in earth crust are:
   a. Si and Al b. Ca and Mg c. B and Ar d. B and Al
3. Carbonates of Li are not stable like that of sodium due to
   a. low electronegativity. b. low electropositivity.
   c. high charge density of Li^+. d. low charge density of Li^+.
4. Which one of the following metal sulphates is not soluble in water
   a. Na_2SO_4 b. K_2SO_4 c. $BaSO_4$ d. $ZnSO_4$
5. Which of the following alkali metal forms only normal oxide with O_2?
   a. Li b. K c. Na d. Rb
6. Strongest reducing agent among the halogens is
   a. Cl_2 b. F_2 c. Br_2 d. I_2
7. Which of the following has the lowest electron affinity?
   a. F b. I c. Cl d. Br
8. Which of the following halide has the highest melting point?
   a. NaCl b. NaBr c. NaF d. NaI
9. The highest boiling point of HF amongst the hydrogen halides is due to
   a. lowest electronegativity of F. b. highest electronegativity of F.
   c. lowest atomic weight of F. d. lowest atomic radius of F.
10. Which of the following is acidic in nature?
    a. Al_2O_3 b. CO_2 c. SnO_2 d. CaO
11. Third period element that initially reacts rapidly with oxygen to form a protective oxide coating that prevents further reactions is
    a. Na b. Al c. Si d. Mg
12. Which of the following has a greater affinity for oxygen?
    a. B b. Na c. K d. Mg
13. Which of the following is the strongest base
    a. $Si(OH)_4$ b. $Be(OH)_2$ c. $Mg(OH)_2$ d. $Al(OH)_3$
14. The inert pair effect dominates in
    a. Pb b. Sn c. C d. Si
15. The elements of Group–IVA which have no tendency to form a dichloride are
    a. C and Si b. P and Sn c. Ga and C d. Sn and Si

Q2. Write short answers of the following questions.

i. Give the reason that the nitrates and carbonates of Group –IIA elements are thermally stable.
ii. Write down at least four characteristics of Group-IIA elements.
iii. Give reason(s) that why carbonates of Group – IA elements are more thermally stable than those of Group – IIA.
iv. Justify that beryllium chloride is different from the chlorides of its group.
v. Explain the structure and stability of chlorides of Group – IVA elements.
vi. Why fluorine is stronger oxidizing agent than chlorine?
vii. How would you test and confirm the amphoteric nature of $Be(OH)_2$.
viii. Why the atomic radius of argon is larger than all the member of third period?
ix. Why there is a fall in ionization energy at Al and Si in same period?
x. Give the reason(s) that the compounds of Sn^{4+} are covalent in nature while those of Sn^{2+} are ionic.

Q3. Write detail answers of the following questions.

1. (a). Explain halide ions as reducing agents and discuss their trends in reducing strength.
   (b). Why the bond enthalpy is important in the thermal stability of hydrogen halides?
2. (a). Give the reason(s) that why simple oxides, peroxides and superoxide of Group – II A elements are formed?
   (b). What is meant by inert pair effect? Explain inert pair effects in formation of ionic and covalent bond.
3. (a). Discuss the effect of heat on nitrates, carbonates and hydrogen carbonates of Group –II A elements?
   (b). Discuss in detail acid base behaviour of Group – IVA oxides.
4. (a). Explain acid-base behaviour of oxides of third period elements.
   (b). Enlist the properties of hydroxides of third period elements.
5. (a). Explain the bond enthalpies in halogens and bond enthalpies in hydrogen halides.
   (b). Analyse the halide ions as reducing agents and trends in reducing strength of halides ions.

Project

Perform an experiment that will enable you to differentiate and identify the elements present in salt using flame test. Record your observation in the table form.

Salt name				
Colour of the salt				
Colour of the flame				
Element identified				

Unit

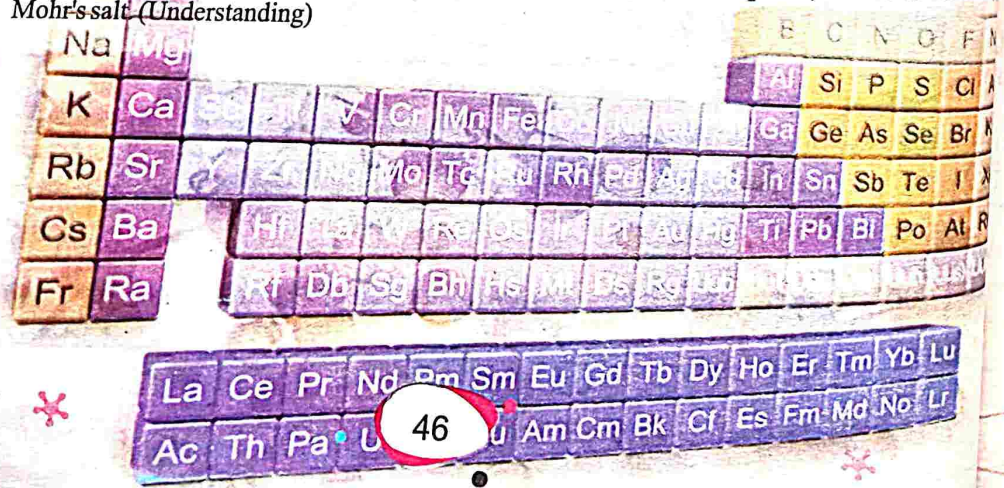
14

d and f - Block Elements: Transition Elements

Teaching	Assessment	Weightage %
9	1	6

After studying this unit, 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. (Analysing)
- Describe important reactions and uses of Vanadium, Chromium, Manganese, Iron and Copper. (Understanding)
- Explain shapes, origin of colours 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. (Analysing)
- 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

Transition elements are those elements, which have partially filled d or f orbitals either in their atomic or in any common oxidation states. The transition elements occupy the central part of the periodic table, bridging the gap between the s-block metals of Groups–IA and IIA on the left and the p-block metals metalloid and non-metals of Groups–IIIA to VIIIA on the right **(Figure 14.1)**.

Generally, these elements have partly filled (n – 1)d subshell in the ground state of their free atom or in their common oxidation states. The elements of groups IB to VIII B (groups 3 –12) are known as d-block elements. Each d–subshell consists of five orbitals and can accommodate 10 electrons, so each transition series consists of 10 elements. The **first series** extends from scandium to zinc (Sc – Zn). These elements have partially filled 3d orbitals. The **second series** runs from yttrium to cadmium (Y – Cd). These elements have partially filled 4d orbitals and the **third series** runs from the element lanthanum (La) and the elements hafnium through mercury (Hf – Hg). All these elements have partially filled 5d orbitals. In addition, there is a **fourth transition series** starts up from the unstable, radioactive elements actinium (Ac), which also includes Rutherfordium (Rf) through the recently discovered element 112, copernicium (Cn). These elements have partially filled 6d orbitals.

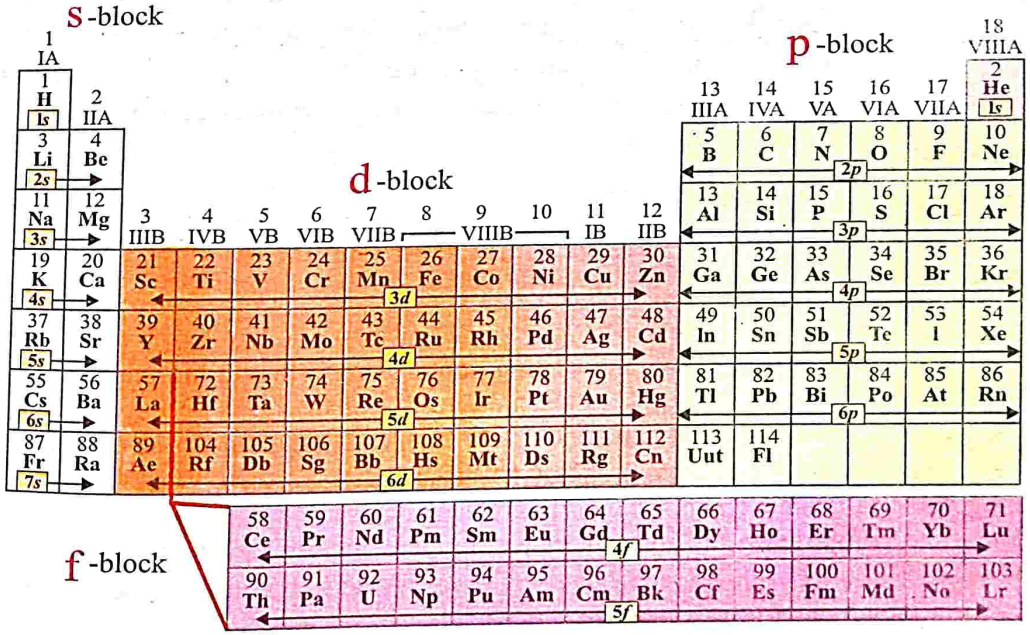


Figure 14.1 Demarcation of the Periodic Table

Elements from caesium (atomic number 58) to lutetium (atomic number 71) make first series of f – block elements known as lanthanides. In this series of 14 metallic elements, 4f subshell are progressively filled. Elements from thorium (atomic number 90) to lawrencium (atomic number 103) make the second series of f – block elements, the actinides, in which the 5f subshell is progressively filled. The lanthanides and actinides together comprise the f-block elements, or inner transition elements.

Tidbit

Typical and Non-Typical Transition Elements

Group **IIB Elements (Zn, Cd and Hg)** do not have a partially filled d-subshell either as elements or in any of their ionic state. Neither do they show typical properties of transition elements to any appreciable extent (except complex formation).

Similarly, **IIIB (Sc, Y and La)** is another group of elements, which do not show many of the properties associated with typical transition elements.

In order to maintain a rational classification, the elements of group **IIB and group IIIB** are referred to as **Non-Typical Transition Elements** and the elements in the remaining transition series are called **Typical Transition Elements.**

In previous unit, you have studied the s-block and p-block elements. In this unit, you will study the d-block elements, their general features, coordination compounds and chemistry of some important transition elements in detail. The transition elements,for the sake of convenience, are divided into two main categories.

i. the main transition elements or the 'd' block elements
ii. the 'f' block elements (inner transition elements)

Here, we will discuss the main transition elements or the 'd' block elements only.

14.1 General Features

14.1.1 General Features of Transition Elements

The General Features of Transition Elements are,

- They are all hard metals.
- They have high melting and boiling points. This is due to high nuclear charge and small atomic radius.
- They form alloys with one another and also with the elements of other blocks.
- They are good conductors of heat and electricity.
- Most of these elements show variable valencies or oxidation states.
- The compounds and ions of transition elements are mostly coloured in solid state and in solution respectively. Colour is due to the incomplete "d" orbitals in which electronic transition is possible.

- Some of the transition elements form paramagnetic compounds because of the presence of unpaired electrons.
- They have the ability to form complexes because of the involvement of vacant d-orbitals.

14.1.2 Electronic Structure

Generally, the electronic configuration of transition elements is $(n-1)\,d^{1-10}ns^{1-2}$.

Scandium ($Z = 21$), the first transition metal n this series, has the configuration Ar]$3d^1,4s^2$. Addition of electron to the 3d ub-shell continues until, at zinc ($Z = 30$), the d sub-shell is filled, with the 4s sub-shell till containing two electrons. However, here are two irregularities, one at chromium ($Z = 24$) and the other at copper ($Z=29$). he electronic configuration of chromium $Z = 24$) is [Ar]$3d^5$, $4s^1$ and not [Ar]$3d^4,4s^2$; we might expect. A similar break in the ttern is observed for copper, whose electronic configuration is [Ar] $3d^{10},4s^1$, rather an [Ar] $3d^9,4s^2$.

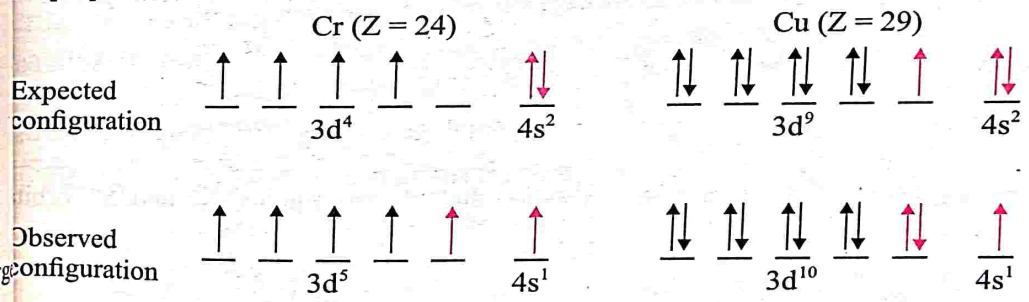
Tidbit

Aufbau Principle

The word 'Aufbau' is derived from the German language and can be translated as construct or build up.

Aufbau principle states that electrons are filled into atomic orbitals in the increasing order of orbital energy level.

According to the Aufbau principle, the available atomic orbitals with the lowest energy state are occupied before those with higher energy state.



e reason for these irregularities is that a slightly greater stability is associated with half-filled ($3d^5$) and completely filled ($3d^{10}$) subshells.

hen the first-row transition metals form cations, electrons are removed first from the orbitals and then from the 3d orbitals.

e second, third and fourth transition metal series correspond to the filling of the 4d , and 6d sub-shells respectively.

Table 14.1 Electronic Configuration of Three Series of *d* – block Elements

3d-elements		4d-elements		5d-elements	
Elements	Electronic configuration	Elements	Electronic configuration	Elements	Electronic configuration
$_{21}Sc$	$[Ar]3d^1, 4s^2$	$_{39}Y$	$[Kr]4d^1, 5s^2$	$_{57}La$	$[Xe]5d^1, 6s^2$
$_{22}Ti$	$[Ar]3d^2, 4s^2$	$_{40}Zr$	$[Kr]4d^2, 5s^2$	$_{72}Hf$	$[Xe],4f^{14},5d^2,6$
$_{23}V$	$[Ar]3d^3, 4s^2$	$_{41}Nb$	$[Kr]4d^4, 5s^1$	$_{73}Ta$	$[Xe],4f^{14},5d^3,6$
$_{24}Cr$	$[Ar]3d^5, 4s^1$	$_{42}Mo$	$[Kr]4d^5, 5s^1$	$_{74}W$	$[Xe],4f^{14},5d^4,6$
$_{25}Mn$	$[Ar]3d^5, 4s^2$	$_{43}Tc$	$[Kr]4d^5, 5s^2$	$_{75}Re$	$[Xe],4f^{14},5d^5,6$
$_{26}Fe$	$[Ar]3d^6, 4s^2$	$_{44}Ru$	$[Kr]4d^7, 5s^1$	$_{76}Os$	$[Xe],4f^{14},5d^6,6$
$_{27}Co$	$[Ar]3d^7, 4s^2$	$_{45}Rh$	$[Kr]4d^8, 5s^1$	$_{77}Ir$	$[Xe],4f^{14},5d^7,6$
$_{28}Ni$	$[Ar]3d^8, 4s^2$	$_{46}Pd$	$[Kr]4d^{10}, 5s^0$	$_{78}Pt$	$[Xe],4f^{14},5d^9,6$
$_{29}Cu$	$[Ar]3d^{10}, 4s^1$	$_{47}Ag$	$[Kr]4d^{10}, 5s^1$	$_{79}Au$	$[Xe],4f^{14},5d^{10},$
$_{30}Zn$	$[Ar]3d^{10}, 4s^2$	$_{48}Cd$	$[Kr]4d^{10}, 5s^2$	$_{80}Hg$	$[Xe],4f^{14},5d^{10},$

In the lanthanide and actinide series valence shell electrons go to '4f' and '5f' or respectively.

14.1.3 Binding Energy

Transition metals are generally tough having great mechanical strength due to s metallic bonding. This is because, apart from 's' electrons of the outermost shel unpaired electrons of underlying *d*–orbitals also participate in binding to form m bonds.

In moving from left to right in any transition series, the number of unpaired ele increases up to Group – VB and VIB, after that pairing takes place and the num unpaired electrons goes on decreasing until it becomes zero at Group – IIB.

Table 14.2 No. of Unpaired Electrons in the 1st Transition Series

Elements	3d orbital electronic structure	No. of unpaired electrons
Sc^{3+}		0
Ti^{3+}	↑	1
V^{3+}	↑ ↑	2
Cr^{3+}	↑ ↑ ↑	3
Mn^{3+}	↑ ↑ ↑ ↑	4
Mn^{2+}, Fe^{3+}	↑ ↑ ↑ ↑ ↑	5
Fe^{2+}	↑↓ ↑ ↑ ↑ ↑	4
Co^{2+}	↑↓ ↑↓ ↑ ↑ ↑	3
Ni^{2+}	↑↓ ↑↓ ↑↓ ↑ ↑	2
Cu^{2+}	↑↓ ↑↓ ↑↓ ↑↓ ↑	1
Zn^{2+}	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	0

Therefore, binding energy increases upto Group – VIB and then progressively decreases upto Group – IIB. For example, in 3d transition series binding energy increases upto vanadium and then decrease upto zinc.

14.1.4 Variable Oxidation States

Most of the transition metals show variable oxidation states and form compounds showing more than one (variable) oxidation states because energy levels of ns and (n–1)d are very close. The involvement of the d-electrons in addition to 'ns' electrons in bond formation also take place. The oxidation state of 3d series is from +2 to +7 (except Cr and Cu).

Tidbit

Valency

The combining capacity of an atom is known as its valency.

Variable Valency

Some elements differ in their capacity to combine with other elements depending on the nature of the reaction; this property is called variable valency. For example, the iron in ferrous oxide shows a valency of +2, whereas in ferric oxide, it has a valency of +3.

The lowest oxidation states of these elements

electrons.

As the number of unpaired electrons in 3d orbital increases the number of oxidation state also increases form Sc^{3+} to Mn^{7+}.

After Mn, the number of oxidation states decreases as the electrons starts pairing in 3d orbital and hence fewer unpaired electrons are available for bond formation, so oxidation states decreases from Fe to Zn. From iron to zinc only the weakly held electrons of "4s" subshell are involved in oxidation state.

Table 14.3 Commonly Occurring Oxidation States of the 1st Transition Series

Element name	Atomic number	Electronic configuration	Oxidation states						
Scandium(Sc)	21	$[Ar]3d^1, 4s^2$		2	3				
Titanium(Ti)	22	$[Ar]3d^2, 4s^2$		2	3	4			
Vanadium(V)	23	$[Ar]3d^3, 4s^2$		2	3	4	5		
Chromium(Cr)	24	$[Ar]3d^5, 4s^1$		2	3	4	5	6	
Manganese(Mn)	25	$[Ar]3d^5, 4s^2$	1	2	3	4	5	6	7
Iron(Fe)	26	$[Ar]3d^6, 4s^2$	1	2	3	4	5	6	
Cobalt(Co)	27	$[Ar]3d^7, 4s^2$		2	3	4	5		
Nickel(Ni)	28	$[Ar]3d^8, 4s^2$		2	3	4			
Copper(Cu)	29	$[Ar]3d^{10}, 4s^1$	1	2	3				
Zinc(Zn)	30	$[Ar]3d^{10}, 4s^2$		2					

14.1.5 Catalytic Activity

Many transition metals and their compounds are used as catalysts, which influence the rate of chemical reaction.

Some common examples are platinum (Pt), nickel (Ni), iron (Fe), chromium (Cr) and vanadium pentoxide (V_2O_5) etc. They are used as catalyst either because of their ability to change oxidation state or in the case of metals adsorbs other substance on their surface and activate them in the process.

Transition metals have variable oxidation states and hence are capable of forming intermediate compounds, which help in the formation of desired product. For example, finely divided iron is used as a catalyst in Haber's process for the synthesis of ammonia, while V_2O_5 is used in the conversion of SO_2 to SO_3 for the manufacture of H_2SO_4 by contact process. $TiCl_4$ is used in the polymerization of ethene to polythene polymer.

The application of nickel (Ni), palladium (Pd) or platinum (Pt) in the catalytic hydrogenation of unsaturated hydrocarbons and the use of copper (Cu) in the oxidation of ethanol to acetaldehyde are example of catalytic properties of transition elements.

14.1.6 Magnetic Behaviour

Substances show two different types of behaviours when subjected to an external magnetic field. If a substance is weakly attracted by a strong magnetic field, it is called paramagnetic substance, whereas a substance weakly repelled by magnetic field is called diamagnetic substance.

Paramagnetic behaviour of a substance is due to interaction of magnetic field produced by spinning of one or more unpaired electrons in an atom, ion or molecule with external magnetic field.

In diamagnetic substances the electrons are paired up due to which magnetic field of oppositely spinning electrons cancel each other.

Metals like Fe, Co and Ni possess very high paramagnetic nature and attain permanent magnetic moment hence, they are ferromagnetic as shown by Fe^{3+} and Mn^{2+} ions which have five unpaired electrons each.

14.1.7 Alloy Formation

An alloy is a mixture of a metal with another element, either metal or non-metal. Transition metals have another great characteristic that they easily mix with each other. This is because all the *d*-block metals have similarity in their atomic sizes. Some transition metal atoms allow to replace easily in crystal lattice.

An alloy in which one of the components is mercury is known as amalgam. In alloys the chemical properties of the component elements are retained but certain physical properties are improved. Alloys are more shiny, stronger and harder than the pure metal. They are rigid, light weight, durable, thermally more stable, less reactive and corrosion resistant as compared to its component elements.

Table 14.4 Important Alloys and Their Uses

Alloys	Compositions	Uses
Brass	Cu + Zn	In making utensils.
Bronze	Cu + Sn	In making coins, bell and utensils.
German Silver	Cu + Zn + Ni	In making utensils.
Rolled Gold	Cu + Al	In making cheap ornaments.
Gun Metal	Cu + Sn + Zn + Pb	In making guns, barrels, gears and bearings.
Duralumin	Al + Cu + Mg + Mn	For making utensils.
Solder	Pb + Sn	For soldering.
Bell metal	Cu + Sn	For casting bells and statues.
Stainless steel	Fe + Cr + Ni + C	For making utensils and surgical cutlery.
Nickel steel	Fe + Ni	For making electrical wire, automobile parts.

14.2 Coordination Compounds

Coordination compounds are those compounds in which a central atom or ion is attached with a fixed number of groups or molecules (ligands) through coordinate covalent bonds.

These compounds can be divided into two classes depending on their behaviour in aqueous solution.

1. Those which Lose their Identity in Solution i.e. Double Salts

These compounds exist as stable compounds only in the solid crystalline state and break up into constituent units in aqueous solution. For example, when crystals of potash alum are dissolved in water, Al^{3+}, K^+ and SO_4^{2-} ions are produced. This aqueous solution shows the same physical and chemical properties as a mixture of aqueous solution of aluminium sulphate and potassium sulphate. Some examples of double salts are,

Mohr's salt: $FeSO_4.(NH_4)_2SO_4.6H_2O$

Potash alum: $Al_2(SO_4)_3.K_2SO_4.24H_2O$

These compounds lose their identity in the solution.

2. Coordination or Complex Compounds

These compounds exist as a stable compounds in the solid state and retain their identity in the solution. For example, when potassium ferrocyanide is dissolved in water, the aqueous solution does not show the characteristic test of Fe^{2+} and CN^- ions.

The physical and chemical properties of the aqueous solution is entirely different from those of free Fe^{2+} and CN^- ions.

In coordination compounds, a central metal atom or ion is bonded to the surrounding electron-pair donors called ligands, through a coordinate bond. These compounds are also known as metal complexes because of the presence of complex metal ions. Some common examples of coordination compounds are,

Potassium ferrocyanide $K_4[Fe(CN)_6]$

Sodium nitroprusside $Na_2[Fe(CN)_5NO].2H_2O$

Terminology Used in Coordination Compounds

The important terms used to define a complex compound are as follows:

4.2.1 Complex Ion

1. Complex Ion

A complex ion as a positively or negatively charged species containing a central metallic atom or ion surrounded by a suitable number of ligands.

For example, when the aqueous solutions of $Fe(CN)_2$ and KCN are mixed together and evaporated a new compound is obtained. When the compound is dissolved in aqueous solution, it does not ionize as Fe^{2+} and CN^- ions but ionizes as K^+ ion and $[Fe(CN)_6]^{4-}$ ion (Ferrocyanide ion). On this basis it has been given a formula $K_4[Fe(CN)_6]$

$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6]$$

$$K_4[Fe(CN)_6] \xrightarrow{\text{Ionization}} 4K^+ + [Fe(CN)_6]^{4-}$$

Here $[Fe(CN)_6]^{4-}$ is called a complex ion. In the complex compound $K_4[Fe(CN)_6]$, the complex ion is present consisting of the central iron ion, Fe^{2+}, surrounded by six CN^- ions acting as ligands.

2. Central Metal Atom or Ion

Every complex ion contains a metal atom or ion to which one or more neutral molecules or ions are attached. This is known as the central metal atom or ion. For example, $K_4[Fe(CN)_6]$, $[Ag(NH_3)_2]Cl$. In these examples, Fe^{2+} and Ag^+ are the central metal ions.

3. Ligand

The atoms, ions, or neutral molecules, which surrounds the central metal ion and donate electron pairs to it, are called ligands. They may be anions or neutral molecules. For example, $K_4[Fe(CN)_6]$, $[Ag(NH_3)_2]Cl$. In these examples, the CN^- is anionic and NH_3 is the neutral ligand.

Depending upon the number of donor atoms (or site), the ligands may be classified into various categories as follows.

i. Monodentate or Unidentate Ligands

The ligands which possess only one donor site are called monodentate or unidentate ligands. Some examples are CN^-, F^-, Cl^-, OH^-, CO, NH_3, H_2O etc.

ii. Multidentate or Polydentate Ligands

The ligands, which possess more than one donor sites are called multidentate, or polydentate ligands. Depending on the number of coordinating donor atoms, these are called bidentate (two), tridentate (three), tetradentate (four), pentadentate(five) and hexadentate (six) ligands. For example, ethylene diamine tetra acetic acid EDTA is an important hexadentate ligand.

4. Coordination Number

It refers to the total number of coordinate covalent bonds formed by the central metal ion with the ligands. For example, in $[CoCl_2(NH_3)_4]Cl$, $[Cu(NH_3)_6]Cl_2$, $K_3[Cr(C_2O_4)_3]$ and $K_4[Fe(CN)_6]$, six coordinate covalent bonds are formed between the ligands and the central metal ion and the coordination number is six, while in $[Cu(NH_3)_4]SO_4$, four coordinate covalent bonds are in between the ligand NH_3 and the central metal ion and the coordination number is four.

5. Coordination Sphere

The central atom along with the surrounding ligands are enclosed in a square bracket and forms coordination sphere. It may be anionic, cationic or neutral. For example, in $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$, and $[Ni(CO)_4]$. In these examples, $[Fe(CN)_6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, and $[Ni(CO)_4]^0$ are ionic, cationic and neutral coordination sphere and K^+ and SO_4^{2-} is the ionization sphere in **Figure 14.2.**

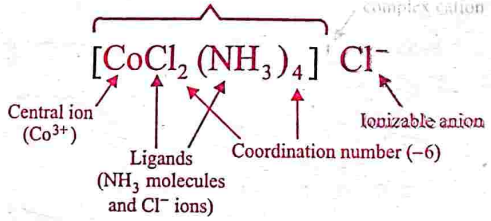


Figure 14.2 Coordination sphere.

The part present outside the bracket is called ionization sphere as it is ionisable in solution.

6. Charge on the Coordination Sphere

It is the algebraic sum of the charges present on the central metal ion and the total charge on the ligands. For example, '$Fe(CN)_6]^{4-}$

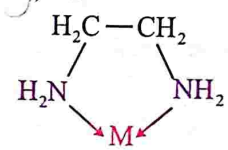
Charge on iron, Fe = + 2

Total charge on six CN^- ions = – 6

Charge on the Coordination Sphere = – 6 + 2 = – 4

7. Chelates

The bonding of a polydentate ligand to a metal ion through more than one site is called chelating ligand. These ligands produce a ring like structure called chelate. The polydentate ligand is called a chelating agent, the process of chelate formation is called chelation and the compounds formed are known as chelate compounds. Chelation increases the stability of complex. For example, ethylene diamide acts as a bidentate chelating ligand.



ethylene diamide

14.2.2 Nomenclature of Coordination Compounds

The systematic names of complex compounds are based on rules recommended by the Inorganic Nomenclature Committee of International Union of Pure and Applied Chemistry (IUPAC). The rules for naming the coordination compounds are as follows:

1. The cation is named before the anion, as in other ionic compounds. For example, in the $K_3[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$ compounds, we name the K^+ and $[Co(NH_3)_4Cl_2]^+$ cations first, respectively.

$K_4[Fe(CN)_6]$ is named potassium hexacyanoferrate(II)

cation anion

$[Co(NH_3)_6]Cl_3$ is named hexaamminecobalt(lll) chloride

cation anion

2. In naming the complex ion, the ligand names are written in alphabetical order, before the name of the central metal ion. There should be no space between the name of the ligand and the name of the central metal ion.
3. Numerical prefixes di, tri, tetra etc., are used for indicating the number of the same kind of ligand. Thus, the ligands in the cation $[Co(NH_3)_4Cl_2]^+$ are "tetraamminedichloro". If the ligand already contains a Greek prefix (e.g. ethylendiamine) if it is polydenate ligands the prefixes, bis-, tris-, tetrakis-, pentakis- are used instead. Numerical prefixes are not considered for determination of alphabetical order.

$[Fe(CN)_6]^{4-}$ or hexacyanoferrate(II) ion

6 CN ligands

$[Co(NH_3)_6]^{3+}$ or hexaamminecobalt(III) ion

6 NH_3 ligands

4. The oxidation number of the central metal ion is indicated in parentheses by Roman numerals following the name of the metal. For example, the Roman numeral III is used to indicate the +3 oxidation state of chromium in $[Cr(NH_3)_4Cl_2]^+$, which is called tetraamminedichlorochromium(III) ion. No space is provided between the name of the metal and the parentheses.

hexacyanoferrate(II) hexaamminecobalt(III)

ferrum – iron | oxidation number 2

indicates an anion

(metal name) (oxidation number 3)

5. The names of anionic ligands end with the letter 'O', for example, hydroxo (OH), carbonato (CO_3^{2-}), whereas the names of neutral ligands are written as such. The exceptions are H_2O (aqua), CO (carbonyl), and NH_3 (ammine). Table 14.5 lists some common ligands.

Table 14.5 Names of Common Ligands in Coordination Compounds

Ligand	Name of Ligand in Coordination Compound
Bromide, Br^-	Bromo
Chloride, Cl^-	Chloro
Cyanide, CN^-	Cyano
Hydroxide, OH^-	Hydroxo
Oxide, O^{-2}	Oxo
Carbonate, CO_3^{2-}	Carbonato
Nitrite, NO_2^-	Nitro
Oxalate, $C_2O_4^{2-}$	Oxalato
Ammonia, NH_3	Ammine
Carbon monoxide, CO	Carbonyl
Water, H_2O	Aqua

6. After naming the ligands, name the central metal. If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix -ate. For example, in $K_4[Fe(CN)_6]$ the anion $[Fe(CN)_6]^{4-}$ is called hexacyanoferrate (II) ion. For example, Co in a complex anion is called cobaltate and Pt is called palatinate. For some metals, the Latin names are used in the complex anions (e.g. Fe is called ferrate and not ironate). The Roman numeral II indicates the oxidation state of iron. Table 14.6 gives the names of anions containing metal atoms.

Table 14.6 Names of Anions Containing Metal Atoms

Metal	Name of Metal in Anionic Complex
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Manganese	Manganate
Molybdenum	Molybdate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate

7. Some coordination compounds are called by their common names. For example, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ are named ferricyanide and ferrocyanide respectively and $Fe(CO)_5$ is called iron carbonyl.

Examples: The systematic names for some coordination compounds are,

Complex Formula	Complex Name
$[Cr(NH_3)_3(H_2O)_3]Cl_3$	triamminetriaquachromium(III) chloride
$[Pt(NH_3)_5Cl]Br_3$	pentaamminechloroplatinum(IV) bromide
$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II)
$Na_2[NiCl_4]$	sodium tetrachloronickelate(II)
$Pt(NH_3)_2Cl_4$	diammine tetrachloroplatinum(IV)
$Fe(CO)_5$	pentacarbonyliron(0)
$(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$	ammonium diaquabis(oxalato)nickelate(II)
$[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$	dichlorobis(ethylenediamine)platinum(IV) chloride
$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(III) sulphate

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

Coordination compounds have definite geometrical shapes because the bond formed between central metal atom and the ligands are directional in nature. Hence, the ligands are arranged around central metal atom in a clear spatial arrangement. This arrangement depends on the number of ligands (co-ordination number) and the relative sizes of the metal ion and the ligands. As the ligand gets larger, fewer of them can coordinate to the metal ion. Thus, iron(III) is able to coordinate to six fluorides in $[FeF_6]^{3-}$ but to only four chlorides in $[FeCl_4]^-$

There are various geometries for the coordination complexes. The most common geometries for coordination complexes are tetrahedral geometry, square planar geometry and octahedral geometry. Complexes in which the coordination number is 4 have two geometries—tetrahedral and square planar. Complexes with a coordination number of 6 always have an octahedral geometry. The coordination complex ions with coordination number 2, 4 and 6 is discussed here in detail.

i. 2-Coordinated Complex Ions

This arrangement is not very common for first row transition metal ion complexes. These complex ions can have only two possible arrangements, i.e. linear or bent. The linear arrangement is adopted by the central ion with two hybrid orbitals and is most commonly shown by complexes of Cu(I), Ag(I) and Au(I). For example, $[CuCl_2]^-$, $[Cu(NH_3)_2]^+$, $[Ag(NH_3)_2]^+$, $[Au(CN)_2]^-$, etc.

Figure 14.3 Coordinated complex.

Bent arrangement is found in case of [Ag(SCN)] which exists as a polymer in the solid state.

ii. 4-Coordinated Complex Ions

These are far less common and they can take up one of two different shapes.

a. Tetrahedral Complexes

Tetrahedral geometry is the most common geometry adopted by complexes of transition as well as non-transition elements. For example, $[CuCl_4]^{2-}$, $[CoCl_4]^{2-}$, etc. The copper (II) and cobalt (II) ions have four chloride ions bonded to them rather than six, because the chloride ions are too big to fit any more around the central metal ion.

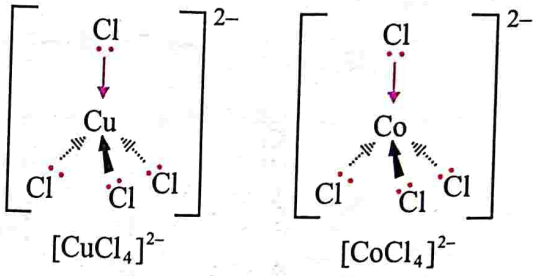


Figure 14.4 Tetrahedral ion geometry.

b. Square Planer Complexes

Occasionally a 4 – coordinate complex turns out to be square planer. There is no easy way of predicting that this is going to happen. The only one you might possibly come across at this level is cisplatin (*cis*-diamminedichloroplatinum (II)), which is used as an anti-cancer drug.

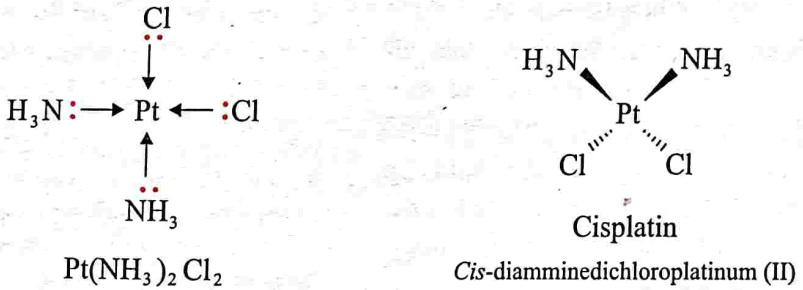
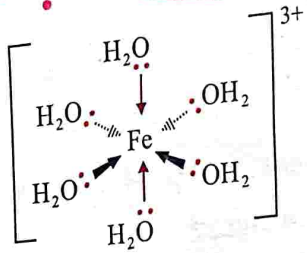


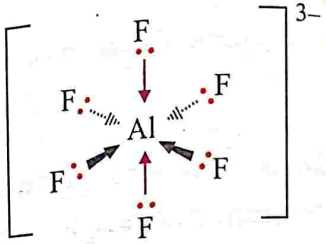
Figure 14.5 Square planer complex.

iii. 6-Coordinated Complex Ions

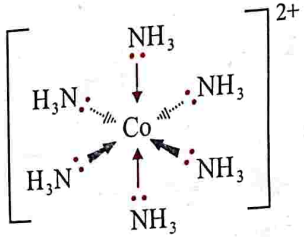
These are complex ions in which the central metal ion is forming six co-ordinate covalent bonds or in simple words the central metal ion is attached to six ligands. These ions have an octahedral shape. Four of the ligands are in one plane, while the fifth one above the plane and the sixth one below the plane. The shapes of four examples of 6 – coordinated complex ions.



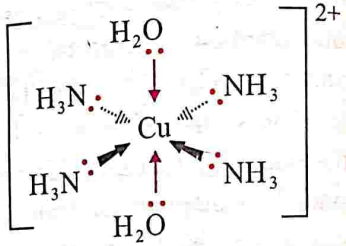
$[Fe(H_2O)_6]^{3+}$



$[AlF_6]^{3-}$



$[Co(NH_3)_6]^{2+}$



$[Cu(NH_3)_4(H_2O)_2]^{2+}$

Figure 14.6 Geometrical shapes of complexes.

14.2.4 Colour of Complexes

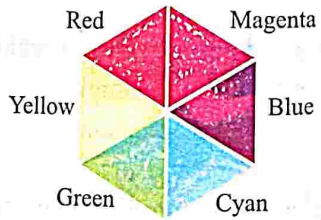
Most of the compounds of the transition metals are coloured in solid or solution state. In transition elements, the d orbitals are responsible for the development of colour in the transition compound. When these orbitals form bonds with the ligands, they splits up, e.g in octahedral complexes they divide into two energy levels, one set has higher energy than the other. The electrons residing in low energy d-orbital absorb a part of the visible light and jump to higher energy *d*–orbital. This process is called d – d transition.

When light is allowed to fall on a substance, it absorbs from it the light of a particular colour whose wavelength is in the visible region (4000 – 7000Å) and reflects or transmits back the remaining light which is

Tidbit

Complementary Colours

Colours directly opposite each other on the colour wheel are said to be complementary colours. Blue and yellow are complementary colours; red and cyan are complementary; and so are green and magenta. Copper (II) sulphate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum. Thus, cyan is the complementary colour of red.



the colour complementary to that of the absorbed light. The colour of the transmitted light is different from the colour of the absorbed light and is known as the complementary colour of the absorbed light. The colour of the transition metal complex is the colour of this transmitted light.

If the complex absorbs all colours except orange, the complex appears orange. The complex will also appear orange if it absorbs only light of the colour blue. In a complementary manner, if the complex ion absorbed only orange, it would appear blue. Blue and orange are referred to as complementary colours. In $[Ti(H_2O)_6]^{3+}$, yellow and green lights are absorbed, while most of the blue and red lights are transmitted, therefore the solution of $[Ti(H_2O)_6]^{3+}$ ions looks purple in colour.

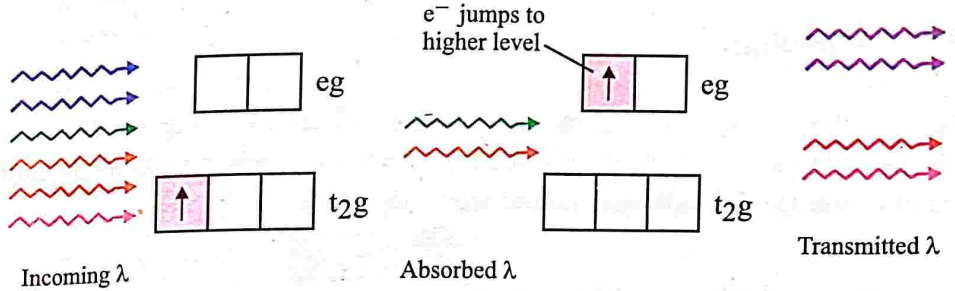


Figure 14.7 Absorbance and transmittance of light in $[Ti(H_2O)_6]^{3+}$ and splitting of d–orbital.

The ions which have completely filled or empty *d*–orbitals are colourless e.g. complexes of $Cu^+(3d^{10})$, $Zn^{2+}(3d^{10})$ and $Sc^{3+}(3d^0)$, $Ti^{4+}(3d^0)$ are colourless.

Table 14.8 Colours and outer Electronic Configurations of Transition Metal Ions

Ion	Outer configuration	Colour
Sc^{3+}	$3d^0$	Colourless
Ti^{3+}	$3d^1$	Purple
Ti^{4+}	$3d^0$	Colourless
V^{3+}	$3d^2$	Green
Cr^{3+}	$3d^3$	Violet
Mn^{2+}	$3d^5$	Light pink
Mn^{3+}	$3d^4$	Violet
Fe^{2+}	$3d^6$	Light yellow
Fe^{3+}	$3d^5$	Yellow

Co^{3+}	$3d^7$	Pink
Ni^{2+}	$3d^8$	Green
Cu^{+}	$3d^{10}$	Colourless
Cu^{2+}	$3d^9$	Blue
Zn^{2+}	$3d^{10}$	Colourless

14.3 Chemistry of Some important Transition Elements

14.3.1 Vanadium

Vanadium symbol 'V', silvery white metallic element with an atomic number of 23 and atomic mass 50.941 a.m.u. **Vanadium is used for vanadium steels, a particularly hard alloy employed for knife blades and various workshop tools.**

14.3.1.1 Oxidation States

Oxidation states of atoms depend upon unpaired electrons in d-orbitals. Compounds of vanadium in +5, +4, +3 and +2 oxidation states are important.

The compounds in the lower oxidation state are good reducing agents. They also have ionic character and due to incomplete electron sub–shell they are also coloured.

The compounds in the higher oxidation states are generally colourless due to the empty electron shell. When a colourless compound of $V^{5+}(3d^0, 4s^0)$ is reduced by suitable reducing agent, it first turns blue VO^{2+} $(3d^1, 4s^0$ then green $V^{3+}(3d^2, 4s^0)$ and finally violet $V^{2+}(3d^3, 4s^0)$. Vanadium also shows +1,0 oxidation states in the compounds $[V(dipy)_3]^{1+}$, $V(CO)_6$ and $[V(CO)_6]^{1-}$ respectively

Tidbit

Difference between Valency and Oxidation Number

Valency is different from the oxidation number. Thus, the valency of nitrogen is 3, whereas it can have oxidation numbers from –3 to +5. The oxidation number is the hypothetical charge of an atom in a molecule or ion, and it is a measure of its apparent capacity to gain or lose electrons within that species.

14.3.1.2 As Catalyst in Contact Process

The contact process is the common method of producing sulphuric acid in high concentrations needed for industrial process.

Vanadium pentoxide (V_2O_5) is used as catalyst in various oxidation reaction involving the use of oxygen (O_2) as the oxidizing agent e.g. conversion of SO_2 to SO_3 in the manufacture of H_2SO_4.

$$2SO_{2(g)} + O_{2(g)} \underset{}{\overset{V_2O_5\,(400-450^\circ C)}{\rightleftharpoons}} 2SO_{3(g)}$$

14.3.2 Chromium

Chromium, symbol Cr, atomic number 24 and atomic mass is 51.99 a.m.u, is a shiny metallic element. **Chromium metal provides a shiny protective coating for iron and steel surfaces due to brilliant and corrosion resistant nature. Chromium metal is not inert in itself; instead, it forms a very thin, tough and transparent oxide coating that gives protection.**

14.3.2.1 Oxidation States

Chromium forms three common oxidation states in its compounds, +2, +3 and +6. Chromium in +3 oxidation state is most stable, while Cr(+2) compounds are not much stable and are strong reducing agents, while those of Cr(+6) compounds are strong oxidizing agents.

With the increase in oxidation state of the chromium,

a. The acidic character of its oxides also increases.

Oxides	**CrO**	**Cr_2O**	**CrO_3**
Oxidation state of Cr	+2	+3	+6
Nature	Basic	Amphoteric	Acidic

b. Similarly the covalent character of the compounds also increases. Thus, Cr(+2) compounds are ionic, Cr(+3) compounds ionize to some extent, while those of Cr(+6) are covalent.

The compounds in which chromium shows +2 oxidation state are called chromous salts. These salts are unstable and tend to oxidize on exposure to air into corresponding Cr(+3) compounds. Some of chromous salts are $CrCl_2$, CrS, $CrSO_4.7H_2O$, $CrCO_3$ etc.

The compounds in which chromium shows +3 oxidation state are called chromic compounds. These may be derived from chromic oxide, Cr_2O_3. These are formed as chromate or dichromate. Examples of chromic compounds are chromic chloride ($CrCl_3$), chromic sulphate, $Cr(SO_4)_3.18H_2O$.

The compounds in which chromium shows +6 oxidation state are chromium trioxide (CrO_3), potassium chromate (K_2CrO_4) and potassium dichromate ($K_2Cr_2O_7$) etc.



14.3.2.2 Chromate – Dichromate Equilibrium

When solid potassium chromate, K_2CrO_4 is dissolved in water it forms a yellow solution. When solid potassium dichromate, $K_2Cr_2O_7$ is dissolved in water the resulting solution is orange. The colours come from the negative ions $CrO_4^{2-}{}_{(aq)}$ and $Cr_2O_7^{2-}{}_{(aq)}$. However, in solution these ions are actually in equilibrium as indicated by the equation:

$$2CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \rightleftharpoons Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$

This is dynamic equilibrium and sensitive to the acidity and basicity of solution. According to Le-Chatelier's principle, the addition of acid to the reactant shifts the equilibrium towards right and yields more dichromate (orange). On the other hand, the addition of base promotes the conversion of dichromate to chromate.

$$\underset{\text{Yellow}}{CrO_4^{-2}} \rightleftharpoons \underset{\text{Orange}}{Cr_2O_7^{-2}}$$

14.3.2.3 Reduction of Chromate (VI) Ions with Zn and an Acid

Dichromate (VI) ions (for example, in potassium dichromate (VI) solution) can be reduced to chromium (III) ions and chromium (II) ions using zinc and either dilute sulphuric acid or hydrochloric acid.

Acidic potassium dichromate solution reacts with zinc forming Cr^{3+} ions and colour of the solution changes from orange to green.

For reduction from +6 to +3,

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

and then after further reduction by the zinc, Cr^{+2} ions are formed and colour changes from green to blue.

For reduction from +3 to +2

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

14.3.2.4 Potassium Dichromate as an Oxidizing Agent in Organic Chemistry

Potassium dichromate (VI) is used as an oxidizing agent in **organic** reactions. The solution of potassium dichromate (VI) isacidified with dilute sulphuric acid. When oxidation occurs, the orange solution containing the dichromate (VI) ions is reducedto a green solution containing chromium (III) ions.

i. Primary Alcohols

Primary alcohol are oxidized to either aldehydes or carboxylic acids depending on the reaction conditions.

In the case of the formation of carboxylic acids, the alcohol is first oxidized to an aldehyde, which is then oxidized further to the acid.

Partial Oxidation to Aldehydes

We get an aldehyde if we use an excess of alcohol and remove aldehyde as soon as it is formed in order to avoid further oxidation.

$$\underset{\text{primary alcohol}}{3CH_3CH_2OH} + Cr_2O_7^{2-} + 8H^+ \longrightarrow \underset{\text{Acetaldehyde}}{3CH_3CHO} + 2Cr^{3+} + 7H_2O$$

Full Oxidation to Carboxylic Acids

The alcohol is heated with an excess of the oxidizing agent i.e. potassium dichromate (VI), on completion of the reaction, the carboxylic acid is produced.

$$\underset{\text{primary alcohol}}{3CH_3CH_2OH} + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow \underset{\text{ethanoic acid}}{3CH_3COOH} + 4Cr^{3+} + 11H_2O$$

ii. Secondary Alcohols

Secondary alcohols are oxidized to ketones. When the secondary alcohol, 2-propanol is heated with potassium dichromate (VI) solution acidified with dilute sulphuric acid, ketone (propanone) is produced.

$$\underset{\text{2-propanol(Secondary alcohol)}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-H} + [O] \xrightarrow[\text{Conc. } H_2SO_4]{K_2Cr_2O_7} \underset{\text{ketone}}{CH_3-\overset{\overset{O}{||}}{C}-CH_3} + H_2O$$

iii. Tertiary Alcohols

Tertiary alcohols are not oxidized by acidified sodium or potassium dichromate(VI) solution.

14.3.2.5 Potassium Dichromate as an Oxidizing Ag

In redox titration, a standard solution of potassium dichromate ($K_2Cr_2O_7$) is used to determine the unknown concentration of a solution of Fe^{2+}. Dichromate ion reduces to chromium (III) ions.

The half-equation for the dichromate (VI) ion is:

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

and Fe(II) is oxidized to Fe(III)

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$

Combining these equations gives:

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 6Fe^{2+} + 14H^+ \longrightarrow \underset{\text{Green}}{2Cr^{3+}} + 6Fe^{3+} + 7H_2O$$

The molecular form of the equation can be written as,

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

Tidbit

Mohr's salt

Ferrous ammonium sulphate or Mohr's salt [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$].

Determining the unknown concentration of a solution of Fe^{2+}, is actually titration against the Mohr's salt.

14.3.3 Manganese

Manganese is the third most abundant transition metal after iron and titaniu Manganese, (Mn), is silvery white, brittle metallic element used principally in maki alloys. The atomic number of manganese is 25 and atomic mass 54.938 a.m.u.

14.3.3.1 Oxidation States

According to the electronic configuration of manganese ($3d^5, 4s^2$), it shows a maximu oxidation state of +7. In addition to this state, it also shows lower oxidation states su as +6, +4, +3 and +2.

- Manganese compounds in which 'Mn' is in +7 oxidation state, are restricted the unstable oxide Mn_2O_7 and compounds of intensely purple permangana ion (MnO_4^{-1}) and are powerful oxidizing agents.
- Mn^{6+} is present in MnO_3 in the salt of manganic acid (H_2MnO_4). The free ac is unknown. Its salts are called manganates e.g. K_2MnO_4.
- The compounds having Mn^{4+} are very limited in number. The most famili compound of Mn^{4+} is MnO_2.

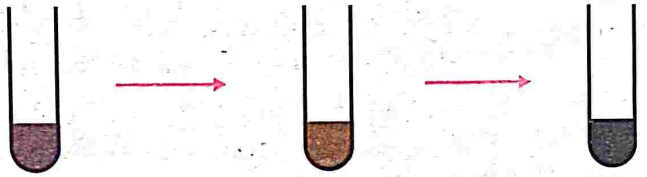
- The compound of Mn^{3+} is called manganic compound. In aqueous solution Mn^{3+} ions is quite unstable since it is easily reduced to Mn^{2+} ions e.g. $H_2Mn_2O_4$, $Mn_2(SO_4)_3$.

$$Mn^{3+} + 1e^- \longrightarrow Mn^{2+}$$

- +2 is the most stable oxidation state of Mn in neutral or acidic solution. Mn^{2+} ion exists as pale pink hexaaquamanganese(II) $[Mn(H_2O)_6]^{2+}$, which is quite stable to oxidation. The stability of Mn^{2+} is due to half-filled 3d orbital. The compounds of Mn^{2+} are called manganous compounds such as MnO, $MnCO_3$, $MnSO_4$, $MnCl_2$ etc.

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

Potassium manganate (VII) is a powerful oxidizing agent. It is usually used in neutral or alkaline solution in organic chemistry. Acidified potassium manganate (VII) tends to be destructively strong oxidizing agent, breaking carbon-carbon bonds. The potassium manganate (VII) solution is usually made mildly alkaline with sodium carbonate solution and the typical colour changes are:



Original dark purple manganate (VII) ion MnO_4^-

Reduced to dark green manganate (VI) ion Mn_4^{2-}

Further reduced to black precipitate of MnO_2

i. In Testing for a C=C Double Bond

Potassium manganate (VII) oxidizes carbon-carbon double bonds and so goes through the colour changes. The colour change depends on whether the potassium manganate (VII) is used under acidic or alkaline conditions. Ethene, for example, is oxidized to ethane-1,2-diol.

$$CH_2 = CH_2 + H_2O + [O] \longrightarrow \begin{matrix} CH_2 - CH_2 \\ | \quad\quad | \\ OH \quad OH \end{matrix}$$

- Under **acidic conditions**, the manganate (VII) ions are reduced to manganese (II) ions.

$$5CH_2=CH_2 + 2H_2O + 2MnO_4^- + 6H^+ \longrightarrow 5CH_2(OH)-CH_2(OH) + 2Mn^{2+}$$

Under **alkaline condition,** the manganate (VII) ions (MnO_4^-) are first reduced green manganate (VI) ions.

$$CH_2=CH_2 + 2MnO_4^- + 2OH^- \longrightarrow CH_2(OH)-CH_2(OH) + 2MnO_4^{2-}$$

Dark green solution

Then dark brown solid manganese (IV) oxide MnO_2 (manganese dioxide) is formed as a result of further reduction of MnO_4^{-2}.

$$2CH_2=CH_2 + 2MnO_4^{2-} + 4H_2O \longrightarrow 2CH_2(OH)-CH_2(OH) + 2MnO_2 + 4OH^-$$

Dark brown precipitate

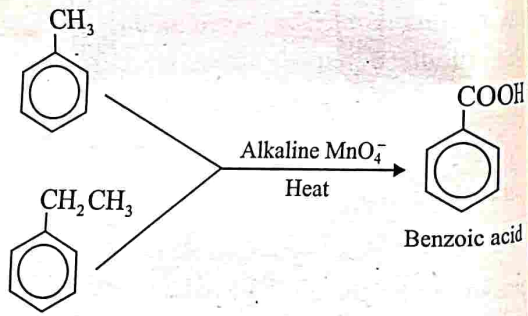
The net reaction is given as,

$$3CH_2=CH_2 + 2MnO_4^- + 4H_2O \longrightarrow 3CH_2(OH)-CH_2(OH) + 2MnO_2 + 2OH^-$$

Dark brown precipitate

ii. In the Oxidation of Aromatic Side Chains

Alkaline potassium manganate (VII) solution oxidizes any hydrocarbon side chain attached to a benzene ring back to a single –COOH group. Prolonged heating is necessary. For example: as shown in the figure.



In case of the ethyl side chain, carbon dioxide is also produced but in each case, the main product is benzoic acid.

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

$KMnO_4$ is a strong oxidizing agent with intense dark purple colour. During reduction the purple permanganate ion changes into colourless Mn^{2+} ion.

Potassium manganate (VII) solution is used to find the concentration of all sorts of reducing agents. It is always used in acidic solution.

For example, it oxidizes

- Iron(II) ions to iron(III) ions

$$Fe^{2+} \xrightarrow{\text{acidic}} Fe^{3+} + e^-$$

- Hydrogen peroxide solution to oxygen

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$$

- Sulphite ions (IV) to sulphate ions (VI) ions

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

In each case, the half-equation for the manganate (VII) ions in acidic solution is:

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

14.3.4 Iron

Iron is the second most abundant metal in the Earth's crust. Concentrated deposits of iron ore are found in many localities, thus making it easy to mine. Iron is a transition metal with a symbol "Fe" and atomic number 26 and its atomic mass is 55.845 a.m.u.

14.3.4.1 Oxidation States

Most common oxidation states of iron are +2 and +3 but it can also exists in the form of Fe^{4+}, Fe^{5+} and Fe^{6+}. The +6 oxidation state of Fe is very rare. The Fe^{2+} and Fe^{3+} oxidation states are stable states.

- Iron in the +2 oxidation state is known as the ferrous ion. This ion is pale green in colour and is very easily oxidized to ferric ion. Even traces of dissolved oxygen in solution will complete this oxidation. Solution of ferrous ion is sometimes used as reducing agent.
- Most solutions containing ferric ions are usually yellow or yellow–brown due to formation of $[Fe(H_2O)_5(OH)]^{2+}$. $Fe^{3+}{}_{(aq)}$ yields a dark blue precipitate called ***Prussian blue***, $Fe_4[Fe(CN)_6]_3$ is formed, when treated with potassium ferrocyanide, $K_4[Fe(CN)_6]_{(aq)}$.

14.3.4.2 Iron as Catalyst in Haber's Process

In the Haber process, hydrogen reacts with nitrogen to produce ammonia. Without catalyst, the process would proceed too slowly to be economically viable. The reaction takes place according to the following steps:

$$N_2 + H_2 \longrightarrow N_2H_2$$

$$N_2H_2 + H_2 \longrightarrow N_2H_4$$

$$N_2H_4 + H_2 \longrightarrow 2NH_3$$

However, breaking the nitrogen triple bond to form N_2H_2 is very difficult and resulting compound is highly unstable and is likely to dissociate as soon as it is formed. The formation of N_2H_2 is highly endothermic. So the above reactions do not proceed easily without the use of catalyst.

The hydrogen and nitrogen are adsorbed on metallic iron surface.

$$N_{2(g)} \rightleftharpoons N_{2(ad)}$$

The hydrogen almost immediately splits into its component atoms by sharing or exchange of electrons with the catalyst surface

$$H_{2(g)} \rightleftharpoons 2H_{(ad)}$$

The nitrogen molecules split into their component atoms and they lock into the surface of the iron catalyst. This is the slowest step and so limits the rate of the entire process.

$$N_{2(ad)} \rightleftharpoons 2N_{(ad)}$$

The hydrogen atoms migrate across the surface of the catalyst and react with nitrogen and produce ammonia molecules that are still bound to the surface.

$$N_{(ad)} + H_{(ad)} \longrightarrow NH_{(ad)}$$

$$NH_{(ad)} + H_{(ad)} \longrightarrow NH_{2(ad)}$$

$$NH_{2(ad)} + H_{(ad)} \longrightarrow NH_{3(ad)}$$

The assembled ammonia molecules are desorbed from surface in the form of gas

$$NH_{3(ad)} \rightleftharpoons NH_{3(g)}$$

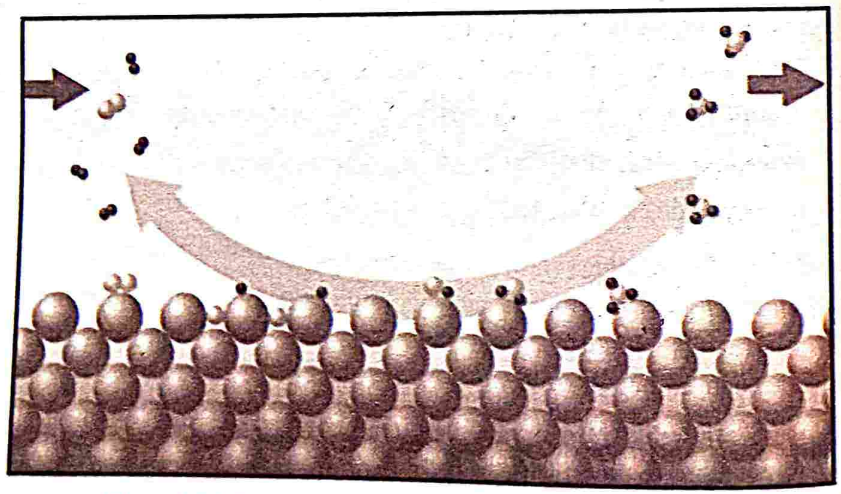


Figure 14.8 Catalytic action of iron surface in Haber process.

14.3.4.3 Iron as Catalyst in Reaction between Persulphate and Iodide Ions

The reaction between persulpahte ions (peroxodisulphate ions), $S_2O_8^{2-}$, and iodide ions in solution can be catalysed using either iron (II) or iron (III) ions.

The overall equation for the reaction is,

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

The catalyst used in this reaction is iron (II) ions. This reaction occurs in two steps.

$$S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$$

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

If you use iron (III) ions, the second of these reactions happens first.

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

Reactions of Hexaaquairon (II) with Water

Many hexaaqua complex ions can undergo acid base reactions with water to produce a solution of pH less than seven. These are not redox reactions because during the reaction no change in the oxidation state of central metal occurs e.g.

$$[Fe(H_2O)_6]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Fe(H_2O)_5(OH)]^{1+} + H_3O^+$$

Reactions of Hexaaquairon (II) with Ammonia

Ammonia can act as both a base and a ligand. In these cases, it simply acts as a base – removing hydrogen ions from the aqua complex.

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

Reactions of Hexaaquairon (III) with Water

In iron (III) case,

$$[Fe(H_2O)_6]^{3+} + H_2O_{(l)} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

Fe^{3+} (ferric) gives more acidic solution than Fe^{2+} (ferrous) ions.

Reactions of Hexaaquairon (III) with Ammonia

In Fe(III) case

$$[Fe(H_2O)_6]^{3+} + 3NH_3 \longrightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$$

14.3.4.5 Reactions of Iron (II) and (III) Ions with Carbonate and Thiocyanate Ions

There is an important difference between the behaviour of iron (II) and iron (III) ions.

Iron (II) Ions and Carbonate Ions

When iron (II) ion combines with carbonate ion, it produces precipitate of iron (II) carbonate.

$$Fe^{2+}_{(aq)} + CO^{2-}_{3\,(aq)} \longrightarrow FeCO_{3(s)}$$

Iron (III) Ions and Carbonate Ions

The hexaaquairon (III) ion is acidic to react with the weakly basic carbonate ion. If we add sodium carbonate solution to a solution of hexaaquairon (III) ions, it produces the precipitate of metal hydroxide.

In this reaction, the carbonate ions remove hydrogen ions from the hexaaqua ion and produce the neutral complex.

Depending on the properties of carbonates ions to hexaaqua ions, we will get either hydrogen carbonate ions or carbon dioxide gas which is formed by the reaction between the hydrogen ions and carbonate ions. The more usually used equation shows the formation of carbon dioxide.

$$2[Fe(H_2O)_6]^{3+} + 3CO^{2-}_3 \longrightarrow 2[Fe(H_2O)_3(OH)_3] + 3CO_2 + 3H_2O$$

Reaction of Iron (III) ions with Thiocyanate ions

Iron(III) ions reacts with thiocyanate ions, SCN^- (from sodium or potassium or ammonium thiocyanate solution) and an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$ is produced. This test confirms the presence of iron (III) ion in solution.

14.3.5 Copper

Copper (Cu), is brownish-red metallic element that is one of the most widely used metals. Copper is one of the two common yellow metals (the other being gold) although a thin coating of copper (I) oxide, Cu_2O, often makes copper look reddish.

The atomic number of copper is 29 and its atomic mass is 63.546 a.m.u.

14.3.5.1 Oxidation States

Copper shows a variety of oxidation states ranging from +1 to +4 in its compounds. The two principal oxidation states of copper are +1 and +2.

- *Copper (I) compounds are expected to be diamagnetic in nature and are usually colourless. Examples of these compounds are Cu_2O, CuCl, CuBr etc. In solid compounds copper (I) is often the more stable state at moderate temperatures. The compounds of this ion are called cuprous compounds.*

- The copper (II) ion is usually more stable in aqueous solutions. Compounds of this ion are called cupric compounds and are usually coloured. Examples are CuO, CuF_2, $CuCl_2$, $CuCO_3.CuSO_4$ etc.
- Copper (III) is most characteristically found in oxides. A simple example is potassium cuprate, $KCuO_2$, a blue–black solid. The best studied copper (III) compounds are the cuprate superconductors. Yttrium barium copper oxide ($YBa_2Cu_3O_7$) consists of both Cu (II) and Cu (III) centres.
- Like oxide, fluoride is a highly basic anion and is known to stabilize metal ions in high oxidation states. Indeed, both copper (III) and even copper (IV) fluorides are known, K_3CuF_6 and Cs_2CuF_6, respectively.

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

Reactions of Hexaaquacopper (II) Ions with Hydroxide Ions

Hydroxide ions (sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the copper ion.

The hydrogen ion has been removed from two of the water molecules, as a result a complex with no charge (a neutral complex) is produced. This complex is insoluble in water and so precipitation occurs.

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

Blue solution — Blue ppt

Reaction of Hexaaquacopper (II) Ions with Ammonia

The ammonia acts both a base and a ligand. When a small amount of ammonia is added to solution of hexaaquacopper (II) ions, it pulls out the H^+ ions from the complex ion and produce neutral complex.

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

Blue (solution) — Blue ppt

The precipitate dissolves in excess ammonia.

The ammonia replaces water as a ligand to give tetraamminediaquacopper (II) ions.

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

Blue ppt — Blue solution

Reaction of Hexaaquacopper (II) Ions with Carbonate Ions

The hexaaquacopper (II) ions are not acidic enough to release CO_2 from carbonates. In these cases precipitation of metal carbonate takes place and gives rise to the following reaction.

$$Cu^{2+}_{(aq)} + CO_3^{2-}(aq) \longrightarrow CuCO_{3(s)}$$

Society, Technology And Science

- Pigments give colour and opacity to paints. Amongst the organic pigments, particularly important are azo–, phthalocyanine and anthraquinone derivatives.
- Transition metals and their oxides when dissolved form coloured pigments.
- Different transition metals and their oxides pigments are known for their specific colour uses.
- The most common pigment is white titanium dioxide (titanium (IV) oxide) which provides over 70% of total pigments used. This pigment has a high refractive index and gives a gloss to the paint.
- Another widely used inorganic pigment is finely divided calcium carbonate. This has a low refractive index and is used, together with titanium dioxide, to produce 'matt' paints. *(Matt paint is defined by experts as dull. It does not shine at all and dries to a smooth finish that hides surface imperfection.)*
- Other pigments include iron oxides (black, yellow and red), zinc oxide, Co (II) nitrate (red), $K_2Cr_2O_7$ (orange), K_2CrO_4 (yellow), Ni (II) Chloride (green) and $KMnO_4$ (purple).

Key Points

- Transition elements are those elements, which have partially filled d or f orbitals either in their atomic state or in any common oxidation states.
- Binding energies, oxidation states and paramagnetism of transition metals increase with increasing number of unpaired electrons.
- Transition elements can exist in several oxidation states.
- Transition metal compounds are often coloured because of d – d orbital transition.
- When a complex ion absorbs a wavelength from visible light, it transmits a set of radiation that impart colour
- Those substances, which are attracted in magnetic field, are called paramagnetic substances and the phenomenon is known as paramagnetism.
- A ligand is an atom or ion or neutral molecule with one or more lone pairs of electrons available to donate to a transition metal ion.
- Transition elements form complexes by combining with ligands. Ligands bond to transition metal ions by one or more co-ordinate covalent bonds.
- Monodentate ligands possess only one donor site.
- Multidentate or polydentate ligands possess more than one donor sites
- Coordination sphere is the central atom along with the surrounding ligands enclosed in a square bracket.
- Transition metal atoms have similarity in their structure hence they are able to replace one another in the metallic lattice and form alloys.
- Coordination compounds have definite geometrical shapes because the bond formed between central metal atom and the ligands are directional in nature.
- Ionic and covalent compounds of transition metals are mostly coloured.
- All forms of Cr (VI) are powerful oxidizing agents.
- Many reactions involving transition elements are redox reactions. Some redox reactions are used in titrations to determine concentrations.
- Fe (II) compounds are octahedral in geometry.
- Permagnate (VII) ions are strong oxidizing agent, oxidize ethane to ethyl alcohol.

Exercise

Q 1. Choose the correct option from the given options.

1. The diamagnetic ion is
   a. Ni^{2+} b. Cr^{3+} c. Mn^{2+} d. Cu^{+}
2. Potassium ferrocyanide is a
   a. normal salt. b. mixed salt.
   c. double salt. d. complex salt.
3. The co-ordination compound $[CuCl_4]^{2-}$ exists in the shape of
   a. tetrahedral. b. octahedral.
   c. square planner. d. rhombic.
4. The oxidation state of chromium in CrO_2Cl_2 is
   a. 2 b. 3 c. 4 6d.
5. $[BeF_4]^{2-}$ is an example of
   a. square planar b. tetrahedral complex
   c. bent structure d. octahedral complex
6. Which of the following is a typical transition element
   a. Zn b. Cd c. Ra d. Co
7. The paramagnetic nature of a substance depends on
   a. the number of electron in the outer most orbit.
   b. the number of electron that are easily ejected.
   c. the number of un-paired electrons.
   d. the number of lone pair of electrons.
8. Ligands are
   a. electron pair donors. b. electron pair acceptors.
   c. neutral. d. donor and then acceptor.
9. Which one is not ferromagnetic?
   a. Fe b. Co c. Sb d. Ni
10. The co-ordination number of iron in $[Fe(CN)_6]^{4-}$ is
    a. 9 b. 3 c. 4 d. 6
11. Select ligand which is bidentate?
    a. H_2O b. NH_3 c. CO d. $C_2O_4^{2-}$
12. Cu^{2+} salt solution is blue in colour due to transition of electron from
    a. *s* to *p* orbital. b. *d* to *d* orbital.
    c. *p* to *d* orbital. d. *p* to *p* orbital.

13. Potassium dichromate acts as a strong
    a. oxidizing agent. b. reducing agent.
    c. bleaching agent. d. dehydrating agent.
14. One of the constituent of German silver is
    a. Ag b. Au c. Cu d. Al
15. The names which remains unchanged in naming co-ordination compounds are
    a. anionic ligands. b. cationic ligands.
    c. neutral ligands. d. none of these.

Q2. Write short answers of the following questions.

i. Give the reason that why Cu^{+} is diamagnetic but Cu^{2+} is paramagnetic.
ii. Write down the electronic configuration of the first transition series.
iii. Why the transition elements show the catalytic behaviour?
iv. Give the reason that transition elements form the co-ordination compounds.
v. Explain why transition metals have variable oxidation states.
vi. Justify the statement that "Scandium forms colourless and diamagnetic compounds".
vii. How do transition elements differ from *s* and *p*-block elements?
viii. What is the oxidation state of chromium in $[Cr(H_2O)_6]^{3+}$?
ix. Give the reason that Fe is a catalyst in Haber process but not in the preparation of sulphuric acid.
x. Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why?

Q3. Write detail answers of the following questions.

1. (a). Write down the electronic structure of 3d elements.
   (b). Explain why the electronic configuration for chromium and copper differ from those assigned using the Aufbau principle.
2. (a). Explain the origin of colour in coordination compounds
   (b). What are the general characteristics of transition elements?
   (c). Assess the catalytic nature of vanadium and iron.
3. Discuss in detail the nomenclature of co-ordination compounds with suitable examples.
4. (a). Explain and write the reactions of Potassium Manganate (VII) as an oxidizing agent in organic chemistry.
   (b). What are alloys? Describe some properties of an alloy that are different from the metals that compose it.

5. (a). Explain the oxidation states of copper.
(b). Write down some important reactions of hexaaquacopper (II) ions wi
hydroxide ions, ammonia and carbonate ions.

Project

Take a small amount of powder hydrated copper sulphate salt and heat in container. The colour of the hydrated copper sulphate is deep blue. During heating the deep blue colour fads and ultimately disappear. Record your observations.

1. Observe the colour change after heating and see what happened after heating.
2. Why the deep blue colour of the copper disappears.
3. Can you explain the reason of colour change?
4. Add some water to the heated copper sulphate and observe what happened.
5. Explain why the deep blue colour reappears.

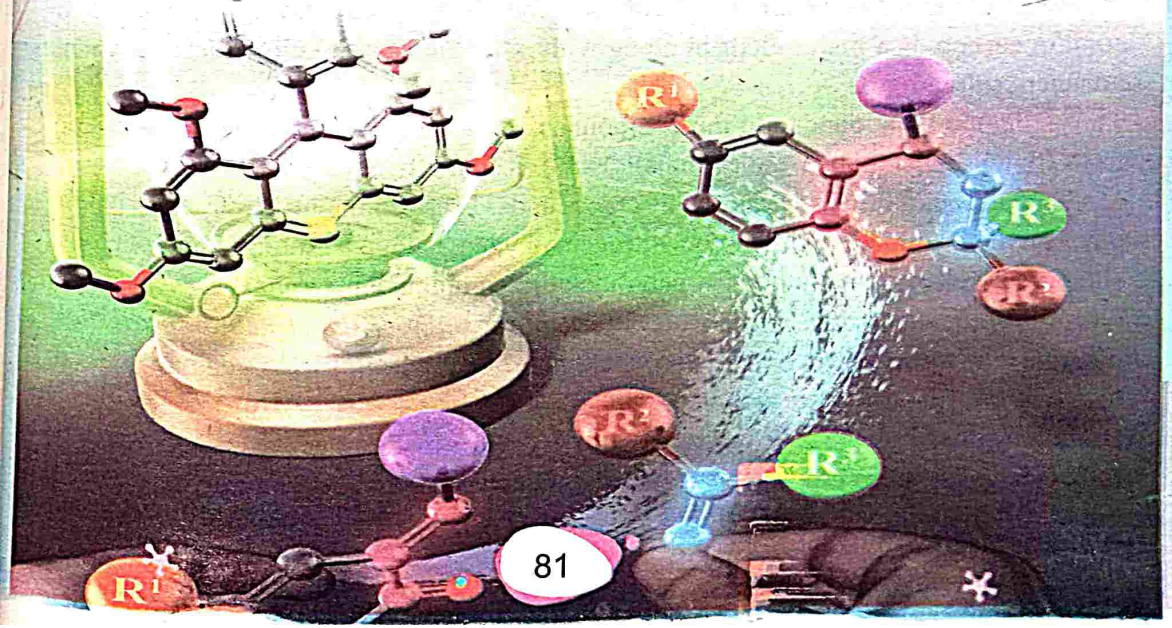
Unit
15

Organic Compounds

Teaching	Assessment	Weightage %
3	1	3

After studying this unit, 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 aromatic and aliphatic hydrocarbons. (Understanding)
- Explain the use of plants as a source of organic compounds. (Understanding)
- Explain that organic compounds are also synthesized in the laboratory. (Understanding)
- Define functional groups and homologous series. (Remembering)



Introduction

In our surrounding most of the things are made up of organic molecules. For example, the food we take is made up of carbohydrates, proteins, fats, and oil etc. medicines, colours, various polymers, CNG and petroleum products for our vehicles etc. all are organic compounds. Our life is totally dependent on organic compounds.

In early days, the chemical compounds were divided into two broad categories; organic and inorganic compounds based on their source of generation. Organic compounds were those obtained from living organism like animals and plants, inorganic compounds were those obtained from non-living (mineral) sources.

In 1815, Berzillius put forward a theory according to which the organic compounds could be produced only under the influence of some vital force existing in living organisms. This theory was called the vital force theory. Thus, according to this theory it was impossible to synthesize organic compounds in the laboratory. Later, in 1828, Friedrick Wohler prepared urea by heating ammonium cyanate (NH_4CNO) in the laboratory which was previously obtained from the living organisms.

$$\underset{\text{Ammanium cyanate}}{NH_4^+CNO^-} \xrightarrow{\Delta} \underset{\text{Urea (Carbamide)}}{NH_2-\overset{\overset{O}{\|}}{C}-NH_2}$$

Thus, the vital force theory was failed and methods of synthesis of new compounds were opened. Now many synthetic organic compounds of prime importance are synthesized in the laboratories.

When the composition of all the organic compounds was studied, they were found to contain carbon as a major element along with other elements like hydrogen, oxygen, nitrogen, sulphur etc.

Thus, organic compounds are the compounds containing carbon which are obtained from living things (plants and animals) as well as synthesized in the laboratory.

Methane is one of the simplest organic compounds. These compounds may also contain other elements, including hydrogen, nitrogen, oxygen, halogens, sulphur, phosphorous, silicon as well as metal atoms (organo-metallic compounds). *Organic chemistry is a branch of chemistry that deals with the scientific study of the structure, properties, composition, reactions and preparations of carbon-based compounds i.e. hydrocarbons and their derivatives.*

Hydrocarbons are those organic compounds which are made up of carbon and hydrogen only. The derivatives of hydrocarbons are organic compounds obtained by replacing at least one hydrogen from hydrocarbons especially saturated hydrocarbons and aromatic hydrocarbons, i.e benzene ring. They are alkyl halides, alcohols and phenol, ethers, ketones, aldehydes, carboxylic acids and their derivatives.

However, there is an exception to the above generalization. There are some compounds like carbon containing alloys (including steel), metal carbonates, bicarbonate, carbonyl, cyanides ($NaCN$), cyanates ($KOCN$, NH_4OCN), oxides and sulfides of carbon (CO, CO_2, CS_2) as well as the allotropes of carbon (diamond, graphite and amorphous forms), which although contain carbon but are not organic compounds. They are inorganic in nature either by their source or properties or nature of bonding.

15.1 Sources

The sources of organic compounds can be classified as (i) natural and (ii) artificial or man-made. Major natural sources of organic compounds are (plants, coal, petroleum and natural gas). Petroleum, coal, and natural gas are also called fossil fuel, a fuel formed under the earth surface from plants and animal remains. While artificial source includes man-made or synthesized organic compounds. Natural sources of organic compounds are given as follows.

15.1.1 Fossil Remains

Fossil fuels are formed by the anaerobic (without oxygen) decomposition of buried plants and animals.

1. Coal

Coal is an important solid fossil fuel of black or brownish–black colour normally occurring in rock strata in layers called coal beds.

Coal is mainly composed of carbon along with other elements like hydrogen, oxygen, sulphur and nitrogen. Coal is formed in nature from the decay of plant matter buried under the soil millions of years ago. Due to different bacterial and chemical reactions, it is first converted into a coal precursor called peat which under high pressure and temperature gets converted into coal.

Wood $\xrightarrow[\text{Chemical reaction}]{\text{Bacterial action}}$ Peat $\xrightarrow[\text{and pressure}]{\text{High Temperature}}$ Coal

Coal exist in different forms like lignite (low perecntage of carbon) sub–bituminous coal, bituminous coal and anthracite (highest rank coal due to presence of high percentage of carbon more than 91.5 %).

Coal is suitable fuel for power generation to minimize the use of petroleum and natural gas for heating homes. Coal is mainly used as a fuel to produce electricity and heat through combustion. It is the largest source of energy for the generation of electricity world wide. Coal is a major source of a large number of organic compounds, especially aromatic compounds.

2. Petroleum

The word petroleum is derived from Latin words: "Petra" means "rock" and "oleum" means "oil". Thus, the word petroleum means "rock oil" as it is present in underground porous rocks. It is also sometimes called "mineral oil" or "crude oil" or "liquid gold". Petroleum exists as a viscous liquid having dark brown colour with a strong unpleasant smell.

Composition: Petroleum is a mixture of hydrocarbons. The hydrocarbons in petroleum are mostly alkanes, cycloalkanes and aromatic hydrocarbons, while some other organic compounds in trace amount are found which contain nitrogen, oxygen, sulphur as well as trace amounts of metals such as nickel, copper and vanadium.

3. Natural Gas

Natural gas is a gaseous form of fossil fuel which is a mixture of low boiling hydrocarbons, methane, ethane, propane and butane.

Natural gas, a source of organic compounds, is also formed by the dead decay of animal matter and is usually found above the underground deposits of petroleum.

Under normal pressure and temperature, the lighter hydrocarbons methane, ethane, propane and butane occur as gases while the heavier ones from pentane and onwards are in the form of liquids. Usually natural gas and petroleum deposits, are found in association with each other.

15.1.2 Products of Plants and Animals (Natural Products)

Plants and animals are the major sources of organic compounds. Those compounds which are produced by plants and animals are called natural compounds or natural products. Plants have always been a rich source of a large number of organic compounds. Natural products may be extracted from tissues of plants. These compounds may be of medicinal importance. A large number of organic compounds are isolated from plants. Plants produce carbohydrates, oil, vitamins, dyes, natural fibre, (cotton and jute) etc.

15.1.3 Partial and Total Synthesis

According to modern concept, organic compounds can be isolated from living organisms as well as synthesized in the laboratory. The study of processes or chemical reactions by which organic compounds can be synthesized in the laboratory from a living or non-living source is called synthetic organic chemistry and the compounds are called synthetic organic compounds or simply synthetic compounds.

Organic compounds can be synthesized either through partial synthesis, or through total synthesis. Mostly, organic reactions occur in many steps. Sometimes, an intermediate product of a reaction is used to synthesize a targeted product. *The process in which the intermediate product or compounds, isolated from natural sources (e.g. coal, petroleum, natural gas, plants, animals, or microorganism, etc.) are used as a starting material to produce other organic molecules is called partial synthesis.* For example, for the formation of soap we use oil or fat from plants or animals and is reacted with the sodium or potassium hydroxide to get our target product i.e soap. Another example of partial synthesis is the production of alcohol from sugar (a compound obtained from plant) by fermentation using yeast.

On the other hand, *the process in which organic molecule is synthesized from small, cheap, and readily available molecules is called total synthesis.* In this synthesis the desired product is obtained by converting the starting material through many steps into targeted product. For example, we can produce urea from cheap and easily available material by chemical reaction through a number of chemical steps. For example, hydrogen is obtained from natural gas methane,

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

Nitrogen is obtained from air and reacted with H_2 to produce ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Ammonia and CO_2 are then reacted to produce urea in further two steps.

$$2NH_3 + CO_2 \longrightarrow NH_2COONH_4 \text{ (ammonium carbamate)}$$

$$NH_2COONH_4 \longrightarrow H_2O + NH_2CONH_2 \text{ (Urea)}$$

15.1.4 Products of Biotechnology

Biotechnology is a field of applied biology that involves the use of living organisms and bioprocesses in engineering, technology, medicine and other fields requiring bio-products. Most of products of biotechnology are organic compounds. One application of biotechnology is the direct use of living organisms e.g. fermenting bacteria for the manufacturing of organic products, like alcohol, milk products, citric acid, lactic acid and some amino acids. Other uses of biotechnology are production of biofuels, hormones/ enzymes, bio-degradable polymers and pharmaceutical chemicals.

15.2 Coal as a Source of Organic Compounds

Coal is a rich source of organic compounds. It can be converted into many organic compounds by the following ways.

15.2.1 Destructive Distillation of Coal

When coal is heated in the absence of air, it does not burn but produces many by-products. This process of heating coal in the absence of air is called destructive distillation of coal. The main products obtained by the destructive distillation of coal are:

i. Coke
ii. Coal Tar
iii. Ammoniacal Liquor
iv. Coal gas

i. Coke

Coke is a fuel which is used in homes and factories but it is mainly used in industries as reducing agent for the extraction of metals from their ores.

ii. Coal Tar

One of the products of coal is coal tar, which is a mixture of organic compounds. These can be separated by fractional distillation. The compounds, so obtained can be used for making soap, fats, dyes, plastics, perfume, drugs, pesticides, explosives. On fractional distillation, coal tar gives important organic compounds like benzene, toluene, xylene, phenol, cresol, naphthalene, anthracene etc.

iii. Ammoniacal liquor

The other by product is ammonia solution called ammoniacal liquor which is used for making fertilizers like ammonium sulphate, ammonium superphosphate etc.

iv. Coal gas

The coal gas is a mixture of hydrogen and carbon monoxide, which is combustible, making the coal gas an excellent fuel.

15.2.2 Conversion of Coal to Petroleum

Coal gas, obtained from the destructive distillation of coal can be converted into petroleum by a process known as Fischer–Tropsch (FT) process. *The Fischer – Tropsch process is a set of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons mainly alkanes.*

$$(2n+1)H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O$$

The conversion of CO to alkanes in presence of hydrogen involves hydrogenolysis of C–O bond and the formation of C–C bond. This process takes place in presence of transition metal catalysts (cobalt, iron, ruthenium or nickel etc.) at a temperature range 150–300°C.

15.3 Characteristics of Organic Compounds

The Following are some of the important characteristic features of organic compounds.

1. Unique Properties of Carbon

Carbon has the property of self linkage. It can link with hundreds and thousands of other carbon atoms to form long C – C chains or rings. This self–linkage of carbon atoms to form chains and ring compounds is called catenation.

Carbon can also form stable single and multiple bonds with each other and other atoms like hydrogen, oxygen, nitrogen, halogens, sulphur etc. As a result carbon forms a large number of organic compounds.

2. Isomerism

When two or more organic compounds have the same molecular formula but different structures, these are called isomers and this phenomenon is called isomerism.

3. Non –Ionic Character

Majority of organic compounds mainly involve covalent bond between C–C and C–H, therefore, they are generally non–polar and have non–ionic characters.

4. Solubility

Solubility depends upon the forces of attraction between the solute and solvent molecules. A general principle of solubility is, "like dissolve like" i.e. polar solute dissolves in polar solvent and non-polar solute dissolves in non-polar solvent. Since the organic compound are formed by covalent bonds and are mostly non-ionic and almost non-polar, so most of the organic compounds are insoluble in water, while some are partially soluble but they are readily soluble in non–polar solvents like ether, benzene, carbon tetrachloride etc.

5. Rates of Organic Reactions

Bonds between atoms in organic molecules are formed by mutual sharing of electrons and for a chemical reaction to occur the existing bonds must be broken and new bonds are formed. Therefore, the organic reactions are slow.

6. Similar Structural features and behaviour (Homologous Series)

Mostly organic compounds have similar structural features called functional group and similar physical and chemical properties. Therefore, they show similar behaviour to various chemical reactions. This similarity in behaviour has reduced the study of millions of organic compounds to a few classes of organic compounds or homologous series.

7. Polymerization

Some organic compounds exhibit the phenomena of polymerization. For example, ethylene polymerizes to polyethylene.

15.4 Uses of Organic Compounds

No field of science is so closely related to our daily life as is organic chemistry. Mo of the things that we come across in our daily life are organic substances. A fe examples of uses of organic compounds is given as follows:

- The food we eat (carbohydrates, proteins, vitamins, fats etc) is mostly constitu of organic things.
- The clothes we wear (cotton, silk, nylon) are organic compounds.
- Most of the medicines are organic in nature.
- Polymer is the most commonly used material today e.g. plastic, synthetic rubbe and leather, synthetic fibre etc. are all organic in nature.
  Ink, shoe polishes, pesticides, cosmetics, paints, dyes, preservatives, detergent and medicines etc, that we use in our daily life are all organic in nature.
- Our body is also made of thousands of complex organic molecules like protein nucleic acids, enzymes, fats, lipids etc. that are called life molecules.
- Almost all the chemical reactions that take place in living systems, includin our own body, are organic in nature.
- The fuels like petroleum products, petrol, diesel oil, compressed natural g (CNG), coal as well as natural gas (Sui gas) etc, are also mixtures of organi compounds that run our cars and industries.

Society, Technology And Science

The chemists use plants and animal compounds to make new compounds that are not found in nature. Many farmers in USA grow maize for the production of ethanol rather than food. There are hundreds of chemical substances, that have been derived from plants for use as medicines e.g. quinine (antimalarial drug), asprine (used for cardiac diseases, pain killer), borneol (anti-inflammatory), benzyl benzoate (scabicide) and galantamine hydrobromide (Alzheimer's disease)

15.5 New Allotrope of Carbon: Bucky Ball

Diamond and graphite are two main, well known allotropes of carbon but fullerene constitute another form of carbon allotrope. Fullerenes are molecules of varying siz consisting entirely of carbon atoms. The first fullerene was discovered in 1985 an named as Buckminster fullerene or in short fullerene. It was a hollow spherical shape cage made of 60 carbon atoms (C_{60}). It was named as bucky ball.

In Bucky balls, the smallest member is C_{20} which is made of 20 carbon atoms while the most common one is C_{60}. Apart from spherical shaped fullerenes, ellipsoidal and tubular fullerenes are also found.

Bucky balls and other fullerenes are similar in structure to graphite, which consists of hexagonal rings made of carbon, but also pentagonal or sometimes heptagonal rings are also found. The existence of fullerenes is very rare in nature. Negligible amounts of C_{60}, C_{70}, C_{76} and C_{80} are found in nature.

15.6 Functional Groups and Homologous Series

There are millions of organic compounds known so far and thousands are discovered and synthesized every year. As mentioned, this diversity and such a large number of organic compounds are due to some peculiar behaviour of carbon. It is difficult to study the chemistry of each individual compound. Therefore, the organic compounds are classified into different groups, in order to make their study easy. One such classification is on the basis of structure of organic molecules and the other on the basis of functional groups.

a. Classification on the Basis of Structure (Old Classification)

This classification of organic compounds is based on the arrangement of carbon atoms in molecules. According to this classification organic compounds are broadly divided into the following groups.

i. Open Chain or Acyclic Organic Compounds (Aliphatic compounds)

In these compounds carbon atoms are linked to each other in open chains, which may be a straight chain or a branched chain.

$$CH_3 - CH_2 - CH_2 - CH_3$$

n-butane (a straight chain compound)

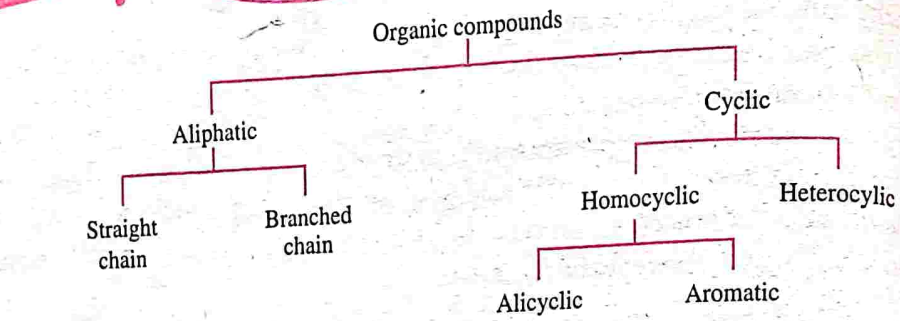
$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - CH_3$$

isobutane (a branched chain compound)

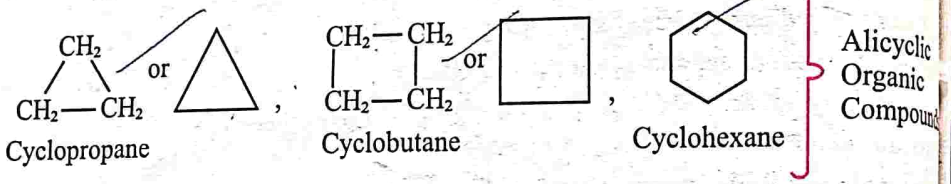
ii. Closed chain or cyclic Organic Compounds (Alicyclic compounds)

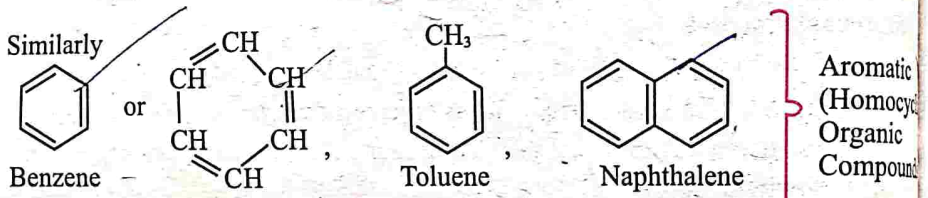
In closed chain compounds carbon atoms are arranged in closed chain forms. They may be homocyclic or heterocyclic organic compounds.

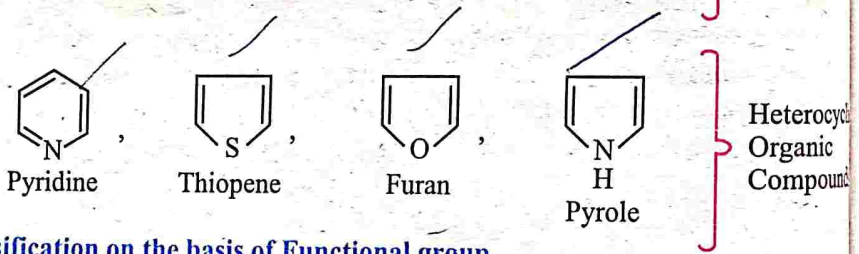
Homocyclic, which are also known as carbocyclic organic compounds, are those in which cycle or ring is made only of carbon atoms. They are further divided into alicyclic having properties similar to open chain compounds and aromatic in which benzene ring is present.



On the other hand, heterocyclic organic compounds are those cyclic compounds in which ring contain at least one atom other than carbon.







b. Classification on the basis of Functional group

An atom or a group of atoms that gives certain characteristic properties to an organic compound is called a functional group because it is the chemically active or functional part of a molecule. Each functional group represents a different class of organic compounds.

Tidbit

Alkanes contain only single bonds and having general formula is C_nH_{2n+2} where $n = 1, 2, 3, \ldots$ shows number of carbon atoms e.g. methane (CH_4), ethane (C_2H_6) etc.

Different classes of organic compounds, their functional groups and general formulae are summarized in the following table along with example.

Table: 15.1 Classification of Organic Compounds Based on Functional Groups

Class of Compounds	Functional Group	Name of Functional group	General Formula	Example
Alkane	–	–	C_nH_{2n+2}	CH_4 methane
Alkene	$>C=C<$	Double bond	C_nH_{2n}	C_2H_4 or $CH_2=CH_2$ ethene
Alkyne	$-C\equiv C-$	Triple bond	C_nH_{2n-2}	$HC\equiv CH$ or C_2H_2 ethyne
Alkyl halide	–X(F, Cℓ, Br, I)	Halo (Flouro, Chloro, Bromo)	R–X or $C_nH_{2n+1}X$	$CH_3-C\ell$ methyl chloride C_2H_5-I ethyl iodide
Alcohol or alkanol	–OH	Hydroxyl	R–OH or $C_nH_{2n+1}OH$	CH_3-OH methyl alcohol (methanol)
Amine	$-NH_2$	Amino	$R-NH_2$ or $C_nH_{2n+1}NH_2$	CH_3-NH_2 methyl amine
Ether	–O–	Oxygen (oxa)	R–O–R or $(C_nH_{2n+1})_2O$	CH_3-O-CH_3 dimethyl ether
Ketone	$-\overset{O}{\overset{\|}{C}}-$	Carbonyl (Keto group)	$(C_nH_{2n+1})_2CO$	$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ dimethyl ketone (acetone)
Aldehyde	$-\overset{O}{\overset{\|}{C}}-H$ or –CHO	Formyl	$R-\overset{O}{\overset{\|}{C}}-H$ or $C_nH_{2n+1}CHO$	$CH_3-\overset{O}{\overset{\|}{C}}-H$ acetaldehyde (ethanal)

Carboxylic acid	$-\overset{\overset{O}{\|}}{C}-OH$ or $-COOH$	Carboxyl	$R-\overset{\overset{O}{\|}}{C}-OH$ or $C_nH_{2n+1}COOH$	$CH_3-\overset{\overset{O}{\|}}{C}-OH$ acetic acid (ethanoic acid)
Acid halide	$-\overset{\overset{O}{\|}}{C}-X$ or $-COX$	Halo carbonyl	$R-\overset{\overset{O}{\|}}{C}-X$ or $C_nH_{2n+1}COX$	$CH_3-\overset{\overset{O}{\|}}{C}-Cl$ acetyl chloride
Acid amide	$-\overset{\overset{O}{\|}}{C}-NH_2$ or $-CONH_2$	Amide	$R-\overset{\overset{O}{\|}}{C}-NH_2$ or $C_nH_{2n+1}CONH_2$	$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ acetamide
Ester	$-\overset{\overset{O}{\|}}{C}-OR'$ or $-COOR$	Ester (alkoxy carbonyl)	$R-\overset{\overset{O}{\|}}{C}-O-R$ or $C_nH_{2n+1}COOC_nH_{2n+1}$	$CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$ methyl acetate
Alkyl cyanide or Nitrile	$-C\equiv N$	Cyano	$R-CN$ or $C_nH_{2n+1}CN$	CH_3CN methyl cyanide

Homologous Series

A series of organic compounds in which all members possess similar structural features and similar chemical characteristics, but each member is different from the next member by a methylene ($-CH_2-$) group is called homologous series. All the members that differ from each other by methylene group, $-CH_2-$, are called homologues. Each class of organic compounds has its own homologous series which can be represented by a general formula. For example, alkanes (saturated hydrocarbons) form a series of compounds. It can be represented by a general formula C_nH_{2n+2} where '*n*' shows the number of carbon atoms in the corresponding alkane.

Table 15.2 Alkane Homologous Series

No. of C atoms	Molecular formula (C_nH_{2n+2})	Name with suffix (–ane)	Structural formula
1	CH_4	Methane	CH_4
2	C_2H_6	Ethane	CH_3CH_3
3	C_3H_8	Propane	$CH_3CH_2CH_3$
4	C_4H_{10}	Butane	$CH_3CH_2CH_2CH_3$
5	C_5H_{12}	Pentane	$CH_3CH_2CH_2CH_2CH_3$
6	C_6H_{14}	Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
7	C_7H_{16}	Heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
8	C_8H_{18}	Octane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	C_9H_{20}	Nonane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	$C_{10}H_{22}$	Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

As it is clear from alkane homologous series that each member is different from the adjacent member by CH_2. Similarly, this series can be expanded beyond C_{10} to higher alkanes. Similar homologous series can be developed for alkenes, alkynes, alcohols, ethers, amines, carboxylic acids, carbonyl compounds etc.

Characteristics of homologous Series

- As mentioned, each class of organic compounds has its own homologous series having general formula.
- All the members of homologous series have similar chemical properties and same general methods of preparation similar structural features and same functional group.
- The physical properties like melting point, boiling points, densities etc, increase down the series due to increase in their molecular masses.

15.7 Detection of elements in Organic Compounds

The main elements present in organic compounds are carbon and hydrogen as well as oxygen, nitrogen, sulphur and halogens. Following methods can be used to detect these elements, in the organic compound.

Detection of Carbon

As carbon is always present in all the organic compounds, there is no need to test for it. The test is performed only to establish whether a given compound is organic or not. The organic substance is mixed with dry cupric oxide in 1:3 ratio and heated in a test tube fitted with a delivery tube. The other end of which is dipping into lime water (solution of $Ca(OH)_2$). Carbon converts to carbon dioxide which reacts with lime water to turn it milky due to formation of calcium carbonate.

$$Ca(OH)_{2(aq)} + CO_{2(g)} \longrightarrow CaCO_{3(s)} \downarrow + H_2O_{(\ell)}$$

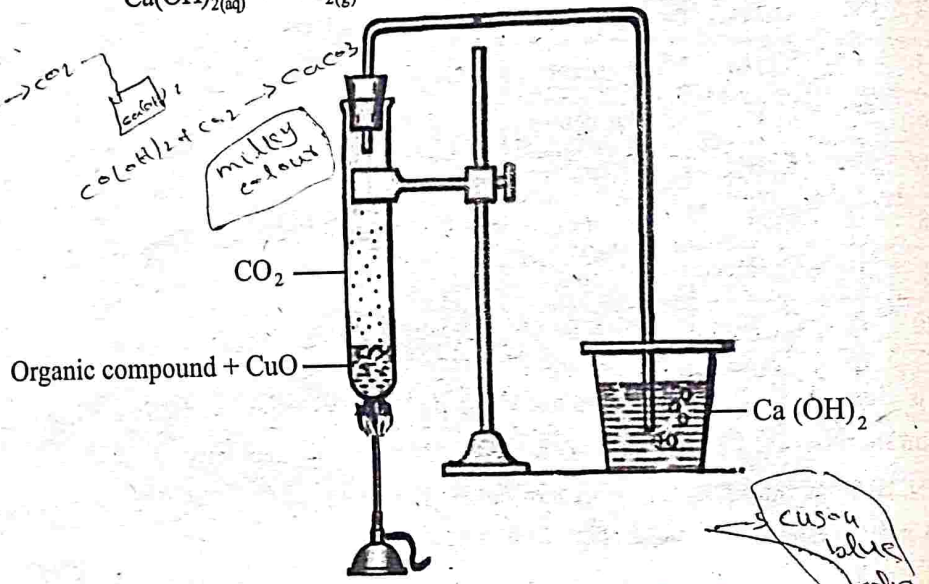


Figure 15.1 Production and detection of carbon dioxide gas.

Detection of Hydrogen

If hydrogen is present in the compound, it is oxidized to water vapours which condenses in small droplets on the cooler end of the test tube. The water formation is further confirmed by passing the issuing gases (water vapours) from anhydrous copper sulphate (white) that is turned blue as copper sulphate converts to hydrated form ($CuSO_4 \cdot 5H_2O$).

Detection of Nitrogen, Sulphur and Halogens

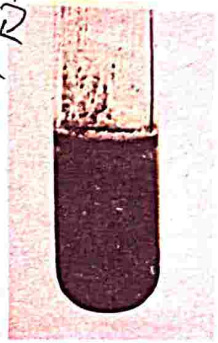
Nitrogen, sulphur and halogens can be detected in organic compounds by sodium extract test or Lassaigne's test. For this purpose, sodium extract or Lassaigne's solution is prepared first. The substance is heated strongly with sodium metal in a fusion tube till the tube becomes red hot which is plunged into the distilled water in a china dish and filtered after boiling the contents of china dish. The filtrate is called Lassaigne's solution or sodium extract.

Detection of Nitrogen

Take a part of Lassaigne's solution in a test tube and add to it few drops of sodium hydroxide and then few millilitres of freshly prepared ferrous sulphate ($FeSO_4$) solution and boil it. After cooling, add few drops of ferric chloride ($FeCl_3$) solution and excess of concentrated HCl solution. The formation of Prussian blue or green colouration confirms the presence of nitrogen.

Detection of Sulphur

To another portion of sodium extract add some acetic acid first and then lead acetate solution. Black precipitate of lead sulphide will be formed which confirms the presence of sulphur.



black precipitate formed

Detection of Halogens

Boil a portion of sodium extract with concentrated nitric acid and then add to it silver nitrate solution. The formation of white precipitate soluble in ammonium hydroxide solution indicates chlorine, pale yellow precipitate slightly soluble in NH_4OH indicates bromine and deep yellow precipitates insoluble in NH_4OH solution shows the presence of iodine in the organic compound.

Detection of Oxygen

Oxygen can be detected by following methods.

i. The substance is heated alone in a dry test tube usually in nitrogen atmosphere. Formation of water droplets on the cooler part of the test tube obviously show the presence of oxygen.

ii. Different tests are applied for oxygen containing functional groups like alcohol (–OH), carbonyl compounds like ketone (–CO–), aldehyde (–CHO) and carboxylic acid (–COOH). If any one is detected, the presence of oxygen is confirmed.

Key Points

- Generally, all the compounds were classified on the basis of their origin. Th compounds that were having living source (plants and animals) were called organi and those coming from non living sources (minerals) were called inorganic.
- According to vital force theory, organic compounds can only be obtained fro living organisms and could not be synthesized in the laboratory from inorgani sources.
- The study of the chemistry of the carbon containing compounds (organi compounds) is called organic chemistry.
- The major sources of organic compounds are plants and animals as well as fossi fuels.
- The abundance of organic compounds is due to unique behaviour of carbon as wel as due to some special characteristics of these compounds themselves.
- Organic chemistry has applications in almost all fields and the importance o organic compounds can hardly be neglected.
- The discovery of fullerenes (bucky balls) has significantly expanded the number o known allotropes of carbon.
- Functional group is the active part of organic compounds which greatly affects th chemistry of organic compounds.
- Organic compounds can be classified on the basis of structure as well as on th basis of functional group.
- Each class of organic compounds have their own homologous series that can b represented by a general formula.

Exercise

Q I. Choose the correct one from the given options.

1. The first organic compound prepared in the laboratory was
   a. peat b. urea c. sugar d. alcohol
2. All the substances are organic except
   a. graphite b. urea c. methane d. acetic acid
3. The type of coal containing highest percentage of carbon is
   a. Anthracite b. Lignite c. Peat d. Bituminous
4. Petroleum is mainly a mixture of
   a. heterocyclic compounds. b. aromatic Hydrocarbons.
   c. saturated hydrocarbons. d. unsaturated hydrocarbons.
5. The major component of natural gas is
   a. butane b. ethane c. propane d. methane
6. All of the following fractions are obtained by destructive distillation of coal except
   a. coal tar. b. refinery gas. c. coal gas. d. coke.
7. Coal can be converted to petroleum by
   a. Haber process. b. Destructive distillation.
   c. Fischer –Tropsch process. d. Fractional distillation.
8. Pyridine belongs to which class of organic compounds
   a. heterocyclic b. hydrocarbon
   c. alicyclic d. homocyclic
9. Which of the following represents the functional group of amides?
   a. –COOR b. $-NH_2$ c. $-C \equiv N$ d. $-CONH_2$
10. Which of the following elements can not be detected in a given organic compound, directly?
    a. Chlorine b. Phosphorous c. Nitrogen d. Oxygen
11. Lassaigne's solution is used to test the presence of
    a. nitrogen. b. halogen. c. sulphur. d. all of these.
12. Lassigne's solution plus silver nitrate gives yellow precipitate which is insoluble in ammonium hydroxide. This shows the presence of
    a. nitrogen b. sulphur c. iodine d. carbon
13. Fischer-Tropsch synthesis involve the formation of alkanes by the combination of
    a. CO and H_2 b. CO_2 and H_2 c. C and H_2 d. All of these
14. Bucky balls consists of ..... carbon rings
    a. tetragonal b. pentagonal c. hexagonal d. b and c both

15. Pyridine

a. is homocyclic compound.
b. contains nitrogen.
c. is heterocyclic compound.
d. both b and c.

Q2. Write short answers of the following questions.

i. What is meant by organic compounds and organic chemistry?
ii. Write down the procedure for the test of presence of nitrogen in organic compound.
iii. What is homologous series? Give the characteristics of homologous series.
iv. Although bucky ball is an allotropic form of carbon, but it is included in organic chemistry.
v. Mention those compounds which although contain carbon but are not considered organic.
vi. Differentiate between partial and total synthesis?
vii. How coal can be converted into petroleum?
viii. Discuss the reasons for the presence of large number of organic compounds?
ix. Differentiate between acyclic and cyclic organic compounds.

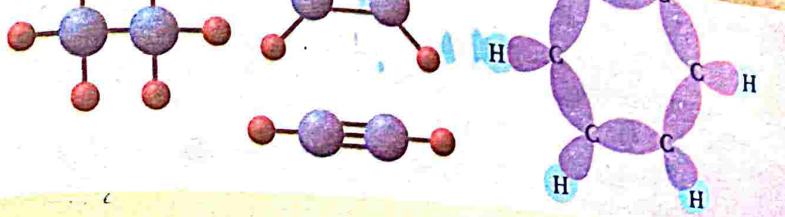
Q3. Write detail answers of the following questions.

1. What are fossil fuels? Discuss different types of fossil fuels.
2. Elaborate the detection of various elements in organic compound.
3. Write the different fractions obtained by the destructive distillation of coal. Give their importance.
4. Explain some of the important characteristics of organic compounds.
5. Define functional group. How organic compounds are classified on the basis of functional group?
6. Give old classification of organic compounds based on arrangement of carbon atoms in the molecule.

Project

Perform tests for detection of carbon, hydrogen and nitrogen in Urea (or any other available organic compound containing C, H and N) by following the procedure discussed in **section 15.7.**

Unit 16



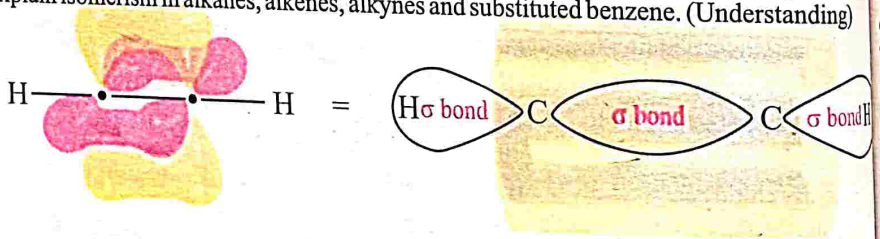
Hydrocarbons

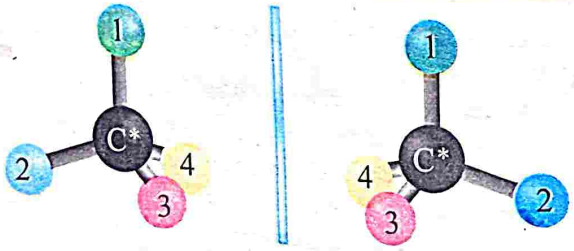
Teaching	Assessment	Weightage %
18	2	14

After studying this unit, 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 unreactive 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 center gives rise to optical isomerism. (Understanding)
- Identify chiral centres in given structural formula of a molecule. (Analyzing)
- Explain the nomenclature of alkenes. (Understanding)
- Explain the shape of ethene molecule in terms of sigma and pi carbon-carbon bonds. (Understanding)
- Use the IUPAC naming system for alkenes. (Applying)
- 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 i.e. hydrogenation, hydrohalogenation, hydration, halogenation, halohydration, epoxidation, ozonolysis and polymerization. (Understanding)
- Explain the concept of conjugation in alkenes, having alternate double bonds. (Understanding)
- 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 term delocalized electrons in the context of benzene ring. (Understanding)
- Describe addition reactions of benzene and methyl benzene. (Applying)
- Describe the mechanism of electrophilic substitution in benzene. (Understanding)
- Discuss the chemistry of benzene and toluene by nitration, sulphonation, halogenations, Friedel–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 of alkynes. (Applying)
- Compare the reactivity of alkynes with alkanes, alkenes and arenes. (Analyzing)
- Discuss the shape of alkynes in terms of sigma and pi carbon-carbon bonds. (Applying)
- Describe the preparation of alkynes, using elimination reactions. (Applying)
- Describe acidity of alkynes. (Understanding)
- Discuss the chemistry of alkynes by hydrogenation, hydrohalogenation, hydration, bromination, ozonlysis 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 organic compounds which contain carbon and hydrogen only. For example methane (CH_4), ethylene (C_2H_4), acetylene (C_2H_2) benzene (C_6H_6) etc. These compounds are thought to serve as basis for all other organic compounds. That is, all other organic compounds are considered as the derivatives of hydrocarbons where one or more hydrogen atoms have been replaced by another atom or group of atoms.

Petroleum, natural gas and coal are the main natural sources of hydrocarbons. These sources are frequently found in underground deposits. The significance of hydrocarbons can be realized by their uses in daily life and in industries and power generation as fuel and as raw materials for synthesis of many other organic compounds.

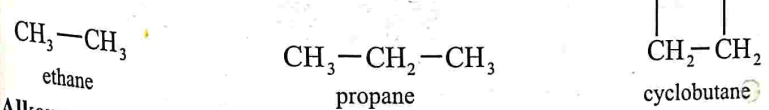
16.1 Types of Hydrocarbons

Hydrocarbons are divided into two major categories i.e. Aliphatic hydrocarbons and Aromatic hydrocarbons. This classification dates from the nineteenth century, when organic chemistry was almost exclusively devoted to the study of materials from natural sources and these terms were coined that reflected a substance's origin.

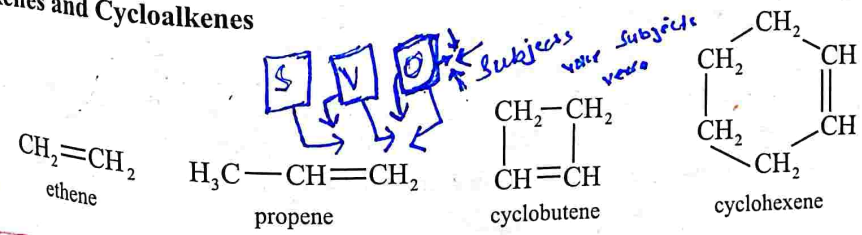
1. Aliphatic Hydrocarbons

The word aliphatic was derived from the Greek word *aleiphar* (fat), as these compounds were mostly derived from fats and oils. Aliphatic hydrocarbons are further classified into saturated and unsaturated hydrocarbons. In saturated hydrocarbons, the carbon atoms are joined to each other only by single bond. They include alkanes and cycloalkanes. Unsaturated hydrocarbons must contain a carbon-carbon multiple bond. They include, alkenes having carbon-carbon double bond and alkynes having carbon-carbon triple bond. These aliphatic hydrocarbons may be cyclic and open chain (acyclic). Examples of some aliphatic hydrocarbons are given below.

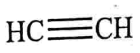
Alkanes and Cycloalkanes



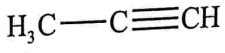
Alkenes and Cycloalkenes



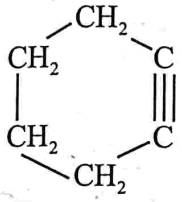
Alkynes and Cycloalkynes



ethyne



propyne



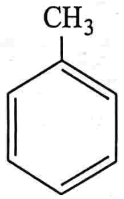
cyclohexyne

2. Aromatic Hydrocarbons

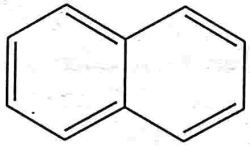
The term aromatic was derived from the Greek word aroma (fragrant), because of their pleasant smell. Aromatic hydrocarbons, were typically obtained by treatment of pleasant-smelling plant extracts. Another name for aromatic hydrocarbons is arenes. Benzene (C_6H_6) is the parent member of this class and hence aromatic is the term used for benzene and all those compounds that resemble benzene in their chemical properties. Over time, chemists discovered that many derivatives of benzene are, in fact, odorless. Nevertheless, the term aromatic is still used to describe all derivatives of benzene, regardless of whether they are fragrant or odourless. Examples of some aromatic hydrocarbons are given below.



benzene



toluene



naphthalene

16.2 Alkanes and Cycloalkanes

Alkanes are open chain saturated hydrocarbons, which can be represented by the general formula C_nH_{2n+2} (where "n" is the number of carbon atoms), while cycloalkanes are cyclic saturated hydrocarbons represented by the general formula C_nH_{2n} ($n > 2$). It is to be noted from the general formula of cycloalkanes, that there are two hydrogen atoms less than the corresponding alkanes. In cycloalkanes, two carbon atoms of the molecule utilize one of their valency in forming bonds with other carbon atoms for formation of cyclic ring.

Tidbit

An aromatic organic compound is cyclic, planar, fully conjugated compound containing (4n+2) pi electrons; where n should be 0, 1, 2, 3 ...

16.2.1 Nomenclature

The naming of organic compounds is called Organic Nomenclature. Nomenclature in organic chemistry is of two types: common (or trivial) and systematic (or IUPAC system). At the beginning of organic chemistry, each new compound was given an individual name, which was based on its source, some property or other trivial reason. For example, the compound HCOOH was given the name formic acid. The name formic acid was derived from Latin word *formica* meaning ant, because it was obtained from red ants. Such names, which are based on the source of the compounds are called common names or trivial names.

With the increase in the number of organic compounds it became impossible to give names to such a large number of organic compounds. Moreover, trivial names do not give any information about the structure of the compounds. Need was, therefore, felt to name organic compounds in a systematic way. Thus, the "International Union of pure and Applied chemistry" (IUPAC) in 1957, set rules for giving systematic names to organic compounds on the basis of structure. This is known as the IUPAC system of nomenclature.

16.2.1.1 Nomenclature of Alkanes

Alkanes are named by both common and IUPAC systems.

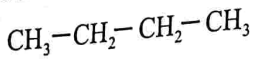
(a) Common System

The first four members of the series are named as methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_1H_4) while the rest are named by using the Greek prefixes that indicate number of carbon atoms in the molecule. Thus the prefix pent (5) is used for the compound having five carbon atoms, hex (6) for six, hept (7) for seven, oct (8) for eight, non (9) for nine and dec (10) for ten carbon atoms. (see table 16.1). The suffix "–ane" should be added with above prefixes for complete name.

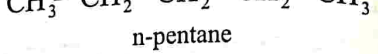
Table 16.1 Name and Formulae of First 10 Alkanes

No. of Carbon Atoms	Name	Molecular Formula	No. of Carbon Atoms	Name	Molecular Formula
1	methane	CH_4	6	hexane	C_6H_{14}
2	ethane	C_2H_6	7	heptane	C_7H_{16}
3	propane	C_3H_8	8	octane	C_8H_{18}
4	butane	C_4H_{10}	9	nonane	C_9H_{20}
5	pentane	C_5H_{12}	10	decane	$C_{10}H_{22}$

i. The prefix n– (from normal) is used for those alkanes in which all the carbon atoms are in one continuous straight chain.

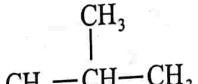


n-butane

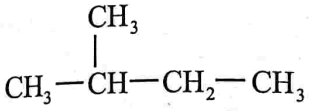


n-pentane

ii. The prefix iso– is used for those alkanes which have a methyl group (CH_3–) attached to the second last carbon atom of the continuous chain.

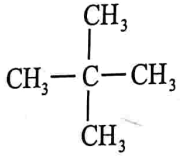


isobutane

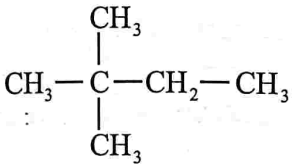


isopentane

iii. The prefix neo– is used for those alkanes which have two methyl groups attached to the second last carbon atom of the continuous chain.



neopentane



neohexane

Alkyl group (R–)

Alkyl group contain a hydrogen atom less than alkane and represented by R– having general formula C_nH_{2n+1}. The name of alkyl group is derived by replacing the *–ane* suffix of the corresponding alkane with *–yl*. Methane becomes methyl (CH_3–); ethane becomes ethyl (CH_3CH_2–) and so on. The dash at the end of the chain represents a potential point of attachment for some other atom or group of atoms. Some of the alkyl groups are shown below.

One carbon

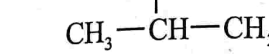
methyl group

Two carbon

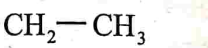


ethyl group

Three carbon



propyl group (or "n-propyl group")



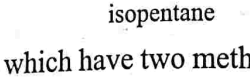
isopropyl group

Four carbon



butyl group (or "n-butyl group")

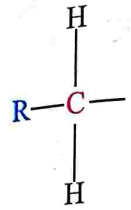
isobutyl group



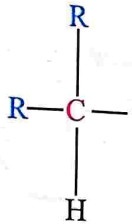
sec-butyl group

tert-butyl group (or "t-butyl group")

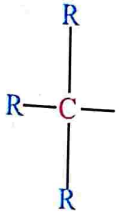
The names of the secondary–butyl (sec–butyl) and tertiary–butyl (tert–butyl or t–butyl) groups are based on the degree of alkyl substitution of the carbon atom attached to the main chain. In the sec–butyl group, the carbon atom bonded to the main chain is secondary (2°) or bonded to two other carbon atoms. In the tert–butyl group, it is tertiary (3°) or bonded to three other carbon atoms.



a *primary* (1°)carbon



a *secondary* (2°)carbon



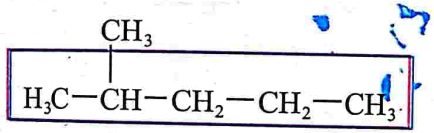
a *tertiary* (3°)carbon

(b) IUPAC System

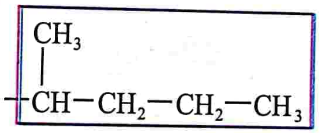
In this system the parent names of the alkanes are retained such as methane, ethane, propane, butane, pentane, hexane and so on while the branching (if any) is treated as substituent, attached to the main continuous carbon chain.

Rules for naming of alkanes:

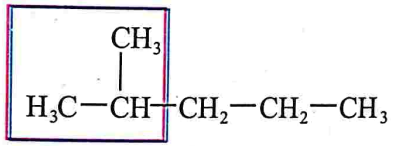
1. Find the longest continuous chain of carbon atoms and use this chain as the base name or parent or stem name.



(correct)

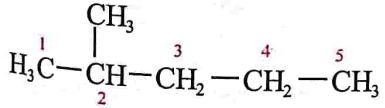


(correct)

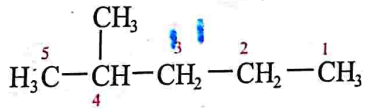


(incorrect)

2. Number the longest chain, beginning with the end nearest a branch.

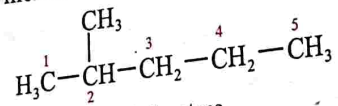


(correct)



(incorrect)

3. Name the substituents on the longest chain (as alkyl groups), before the stem name. Give the location of each substituent by the number of the main chain carbon atom to which it is attached.

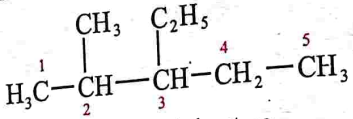


2-methylpentane

Tidbit

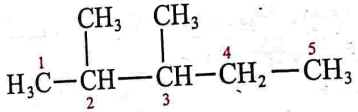
Except carboxylic acids and its some derivatives, the names of all other organic compounds are written as single word without any space.

4. When two or more different substituents are present, list them in alphabetical order.



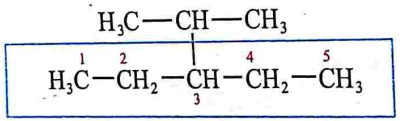
3-ethyl-2-methylpentane

5. When two or more of the same alkyl substituent are present, use the prefixes di–, tri– tetra–, and so on (ignored in alphabetizing).



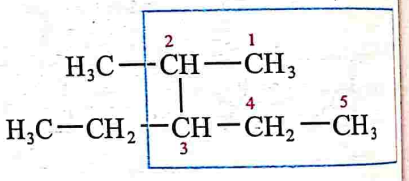
2,3-dimethylpentane

6. When there are more than one longest chains, select the chain which carries more substituents.



3-isopropylpentane

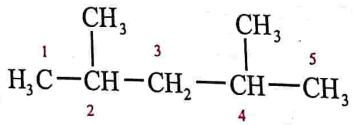
(incorrect)



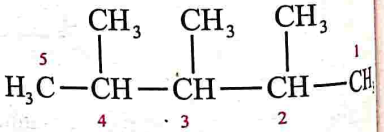
3-ethyl-2-methylpentane

(correct)

Other examples



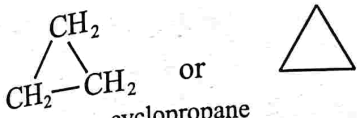
2,4-dimethylpentane



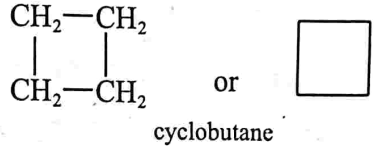
2,3,4-trimethylpentane

16.2.1.2 Nomenclature of Cycloalkanes

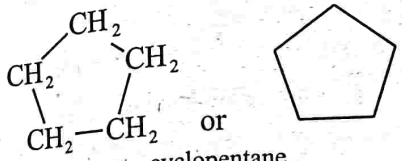
Cycloalkanes are alkanes that contain a ring of three or more carbons. Cycloalkanes are named by placing the prefix "*cyclo*–" to the name of alkane having the same number of carbon atoms as in the ring. For convenience, cycloalkanes are represented by geometric figures e.g. cyclopropane is represented by a triangle, cyclobutane by a square, cyclopentane by a pentagon, cyclohexane by a hexagon and so on. Each corner of these geometric figures represent a $-CH_2-$ group.



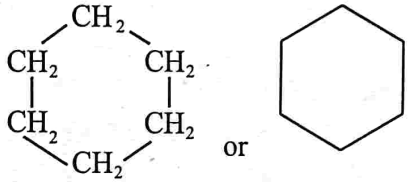
cyclopropane



cyclobutane

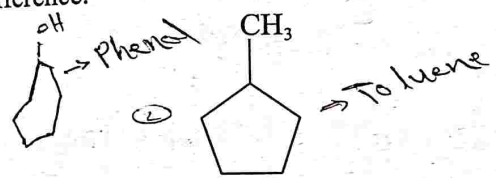


cyclopentane

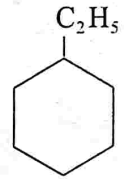


cyclohexane

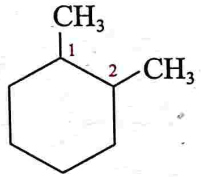
Monosubstituted cycloalkanes are named as alkylcycloalkanes. For polysubstituted cycloalkanes, the prefixes *di–*, *tri–* etc. should be used to represent the number of identical substituents. Their positions are specified by numbering the carbon atoms of the ring in the direction that gives the lowest number to the substituents at the first point of difference.



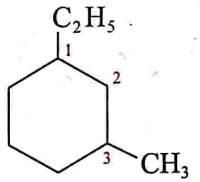
methylcyclopentane



ethylcyclohexane



1,2-dimethylcyclohexane

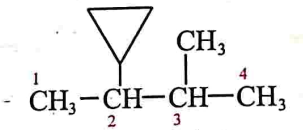


1-ethyl-3-methylcyclohexane

When the ring contains fewer carbon atoms than an alkyl group attached to it, the compound is named as an alkane and the ring is treated as a *cycloalkyl* substituent.



3-cyclopropylpentane



2-cyclopropyl-3-methylbutane

16.2.2 Physical Properties

16.2.2.1 Physical Properties of Alkanes

- First four members (C_1–C_4) are colorless gases at room temperature. Straight chain alkanes upto seventeen carbons (C_5–C_{17}) are colorless liquids at room temperature. Higher unbranched alkanes having eighteen or more carbon atoms are wax like colorless solids.
- The boiling points of normal alkanes increase with the increase in molecular mass. Straight chain alkanes have higher boiling points than isomeric branched alkanes. For example, the boiling points of n-pentane and isopentane are 36°C and 28°C respectively.
- The melting points of normal alkanes also increase with increasing molecular mass. However, there is no regularity in the change in melting point with the number of carbon atoms in a molecule.
- Alkanes, being non-polar are soluble in non-polar solvents like ether, benzene etc. but they are insoluble in polar solvents such as water.
- The density of alkanes also generally increases with increase in molecular weight, till it reaches a maximum value of 0.81 g/mL. Alkanes are therefore, lighter than water and this is the reason why petroleum floats on water surface.

Table 16.2 Boiling and Melting Points of some Alkanes

Alkane	Melting Point (°C)	Boiling Point (°C)
methane	–182.5	–161.5
ethane	–172	–88.6
propane	– 188	–42.1
n-butane	– 138	0
n-pentane	– 130	36.0
n-hexane	–95.3	68.7
isobutane	–159	–12
isopentane	–160	28
isohexane	–154	60

16.2.2.2 Physical Properties of Cycloalkanes

- Cyclopropane and cyclobutane are gases at room temperature and atmospheric pressure, while remaining cycloalkanes are mostly liquids.
- The boiling points of cycloalkanes show a gradual increase with increase in the molecular mass. The boiling point of cycloalkanes are higher than corresponding open chain alkanes.
- The increase in melting points of cycloalkanes is also not regular with increase in molecular mass. The alternating behavior of melting points of cycloalkanes with odd and even numbers of carbon atoms is more pronounced here than in open-chain alkanes. The observed differences again can be attributed to the differences in the packing density of both series.
- They are insoluble in water but dissolve in ether, benzene, carbon tetrachloride etc. due to non-polar nature.
- Density of cycloalkanes also increases with molecular mass. Their densities are less than 1 g/mL.

Table 16.3 Boiling and Melting points of some Cycloalkanes

Cycloalkane	Melting Points (°C)	Boiling Points (°C)
cyclopropane	–127	–33
cyclobutane	–50	13
cyclopentane	–94	49.2
cyclohexane	6.7	81
cycloheptane	–12	119

16.2.3 Structure

16.2.3.1 Structure of Ethane

In ethane (C_2H_6) each carbon atom is bonded to four other atoms, so it uses sp^3–hybrid orbitals to form these bonds. There are six C–H covalent bonds and one C–C covalent bond. Each of the C–H bonds, is the result of linear overlap of sp^3–hybrid orbital of carbon and *1s* orbital of hydrogen. The C–C sigma bond is formed due to the overlap of sp^3–hybrid orbitals, one from each carbon atom (Fig. 16.1). All the C–H and C–C bonds are sigma (δ) bonds. All the bond angles are 109.5°(tetrahedral geometry). The C–C bond length is 154 pm and each C–H bond length is 109.5 pm.

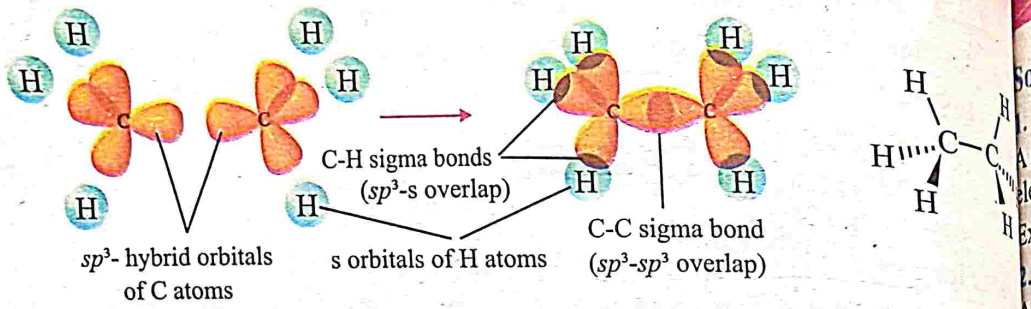


Figure 16.1 Orbitals overlap description in formation of C–C and C–H sigma bonds of ethane

Self-assessment

Draw orbital hybridization model of propane and show different types of overlaps in formation of carbon-carbon and carbon–hydrogen sigma bonds.

16.2.3.2 Structure of Cyclopropane

In cyclopropane (C_3H_6), each carbon atom, like alkanes, is bonded to four other atoms so it uses sp^3-hybrid orbitals to form sigma bonds. However, in this case, the sp^3–sp^3 overlap of C–C bond is not maximum as in the case of alkanes. This is due to the fact that in cyclopropane the C–C–C bond angle is 60° and not 109.5° (tetrahedral angle) due to which orbitals do not overlap exactly along their axes **(Figure.16.2)**, but overlap outside of inter-nuclear axes, and form bent bonds. The C–C bond of cyclopropane is therefore weaker than C–C bond of alkane, due to less effective overlap of sp^3–hybrid orbitals of carbon in cycopropane. The C–H bonds are formed by overlap of sp^3–hybrid orbital of carbon and *1s* orbital of hydrogen.

In cyclopropane, the three carbon atoms occupy the corners of an equilateral triangle which results in the C–C–C bond angles to be of 60°. Since the hybridization of carbon is sp^3, these C–C–C bond angles should be 109.5°.This deviation from the normal tetrahedral angle of 109.5° to 60° causes a strain in molecule, called Angle strain. The H–C–H bond angle is approximately 115° and the C–C and C–H bond lengths are 151 pm and 108 pm respectively.

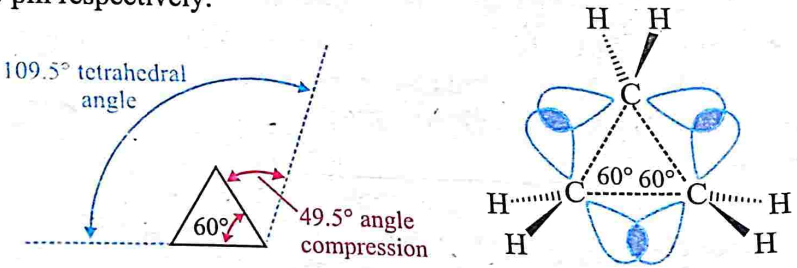


Figure 16.2 Overlap between sp^3–hybrid orbitals of carbon atoms in cyclopropane.

Some important terms

1. Electrophile (Electron loving) → chemical A specie that attract/love towards electron.

A reagent which can accept an electron pair in a reaction is called an electrophile. An electrophile may be positive ion or neutral molecule with an electron-deficient center. Examples are; H^+, Cl^+, CH_3^+, NO_2^+, $AlCl_3$, BF_3, SO_3 etc.

2. Nucleophile (Nucleus loving) A chemical specie that attract/love positive charge

A reagent which can donate an electron-pair to an electrophilic center, in a reaction is called a nucleophile. A nucleophile may be negative ion or neutral molecule with lone pair of electrons. Examples are; Cl^-, $\bar{O}H$, $\bar{C}H_3$, $\bar{N}H_2$, $\ddot{N}H_3$, $H_2\ddot{O}$ etc.

Nucleus, shell, e⁻, p⁺, N

3. Free Radicals

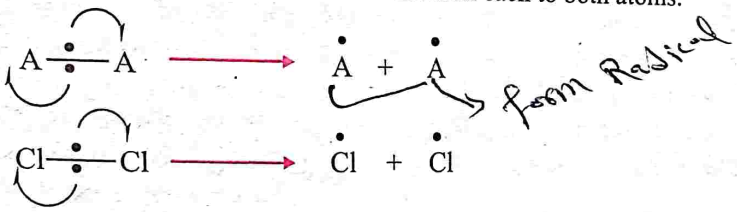
A free radical is an atom or group of atoms having unpaired electron(s). Free radicals are produced during the homolytic fission of a covalent bond. They are very reactive as they have strong tendency to pair up their unpaired electron with another electron from wherever available. Examples are; $H^\bullet$, $Cl^\bullet$, $^\bullet CH_3$ etc.

A:A → A· + ·A Radical

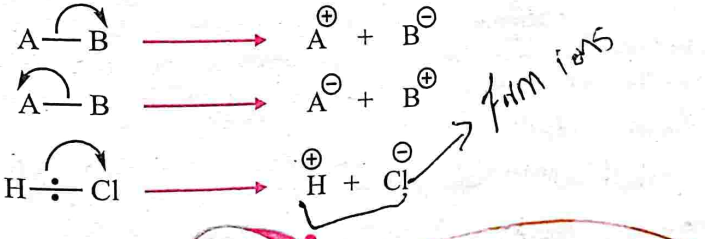
4. Homolytic and Heterolytic bond fission

Bond breaking (fission) is an endothermic process. If sufficient amount of energy is available, a covalent bond can undergo fission in two ways.

i) **Homolytic Bond Fission or Homolysis:** In Homolytic fission, a chemical bond breaks in such a way that each of the two bonded atoms acquires one of the bonding electrons. Homolysis results in the formation of free radicals. The arrows in the following general example shows the movement of one electron each to both atoms.



ii) **Heterolytic Bond Fission or Heterolysis:** In Heterolytic fission the chemical bond breaks in such a way that one of the bonded atoms acquires both of the bonded electrons. The atom with high electronegativity, usually, acquires both the bonding electrons. Heterolysis results in the formation of ions (electrophile and nucleophile). The arrow in the following general example indicates the movement of sigma electrons towards a single atom.



16.2.4 Relative Stability and Reactivity

(a) Alkanes

Alkanes are quite inert and unreactive towards most of the reagents under ordinary conditions. That is why they are also called *paraffins*. The word paraffin is derived from Latin words *parum affinis* (little affinity or little reactivity) and testifies to the low reactivity of alkanes. The little reactivity of alkanes is attributed to saturated nature and presence of non-polar C–C and C–H sigma bonds. Consequently polar reagents do not react with alkanes under normal conditions. Furthermore, the C–H and C–C bonds are strong bonds and hence alkanes are relatively stable to common reagents such as acids, alkalies, reducing and oxidizing agents etc. at ordinary conditions. However, they can react with several reagents, if the right conditions are used. The characteristic reactions of alkanes are free-radical substitution reactions.

(b) Cycloalkanes

Cycloalkanes resemble alkanes in their chemical behaviour except for cyclopropane and cyclobutane. The strength of bond and hence the stability, depends on the extent of overlap of orbitals. In the case of cyclopropane and cyclobutane, the extent of overlap of orbitals is not maximum due to greater angle strains and are unstable (Section 16.2.3.2). Cyclopropane undergoes ring opening reactions with several reagents to give open chain addition product. Cyclobutane, having less angle strain than that of cyclopropane, is more stable and hence it undergoes ring opening reaction only under severe conditions. For example, hydrogenation of cyclopropane and cyclobutane to corresponding open chain alkanes in the presence of nickel catalyst, occurs at 80°C and 200°C respectively. Higher members are even more stable and do not undergo ring opening reactions. Instead, they resemble open chain alkanes in reactivity and undergo only radical substitution reactions.

16.3 Radical Substitution Reactions

16.3.1 Overview

Substitution reactions are those reactions in which an atom or group of atoms, attached to the carbon in a molecule is replaced by another atom or group of atoms. The substitution reaction may be initiated by free radical, nucleophile or electrophile. Substitution reactions which involve free radical intermediates are called radical substitution reactions. One of the examples of free radical substitution reaction is the chlorination of methane in the presence of ultraviolet light, shown below.

$$\underset{\text{methane}}{CH_4} + Cl_2 \xrightarrow[\text{light}]{\text{U.V.}} \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

In above reaction, hydrogen atom of the methane molecule is replaced by a chlorine atom (a free radical).

16.3.2 Mechanism of Free Radical Substitution Reactions

We will discuss the mechanism of chlorination of methane to methyl chloride. The mechanism involve the following steps:

Step-1: Initiation: A chlorine molecule undergoes homolytic fission in the presence of ultraviolet light to give chlorine free radicals.

$$:\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}: \xrightarrow[\text{light}]{\text{U.V.}} 2[:\ddot{\underset{\cdot\cdot}{Cl}}\cdot]$$

Step-2: Propagation: (a) A chlorine free radical attacks the methane molecule to give methyl free radical and HCl.

$$:\ddot{\underset{\cdot\cdot}{Cl}}\cdot + H:CH_3 \longrightarrow :\ddot{\underset{\cdot\cdot}{Cl}}:H + \cdot CH_3$$

chlorine atom — methane — hydrogen chloride — methyl radical

(b) The methyl free radical, thus produced attacks a chlorine molecule to form methyl chloride and chlorine free radical.

$$:\ddot{\underset{\cdot\cdot}{Cl}}:\ddot{\underset{\cdot\cdot}{Cl}}: + \cdot CH_3 \longrightarrow :\ddot{\underset{\cdot\cdot}{Cl}}\cdot + :\ddot{\underset{\cdot\cdot}{Cl}}:CH_3$$

chlorine molecule — methyl radical — chlorine atom — chloromethane

These propagation steps are repeated again and again.

Step-3: Termination: The above chain reaction comes to an end, when any two free radicals combine to form stable products.

$$\dot{C}l + \dot{C}l \longrightarrow Cl-Cl$$
$$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3-Cl$$
$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$$

In actual practice the above reaction does not stop at methyl chloride stage. The remaining three hydrogen atoms of methyl chloride can be successively replaced by chlorine atoms.

$$CH_3-Cl + Cl_2 \longrightarrow \underset{\substack{\text{methylene chloride}\\ \text{(dichloromethane)}}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow \underset{\text{chloroform (trichloromethane)}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \longrightarrow \underset{\text{carbon tetrachloride (tetrachloromethane)}}{CCl_4} + HCl$$

Thus, a mixture of all the four substitution products i.e. methyl chloride, methylene chloride, chloroform and carbon tetrachloride are obtained. The extent of their concentration in the mixture depends on the relative amounts of chlorine and methane. If chlorine is taken in excess, the reaction goes to the final substitution product and carbon tetrachloride is the major product. On the contrary, when chlorine is limited and methane is in excess, the major product of the reaction is methyl chloride.

Tidbit

Mechanism is the step-wise description of a chemical reaction.

16.4 Oxidation of Organic Compounds

Oxidation generally refers to the increase in oxidation state of an atom. Oxidation of organic compounds corresponds to an increase in the oxidation state of carbon. Oxidation of carbon occurs when a bond between carbon and an atom which is less electronegative than carbon is replaced by a bond to an atom that is more electronegative than carbon (in substitution reactions). Oxidation state of carbon increases with increase in the number of bonds between carbon and oxygen and decreases the number of carbon–hydrogen bonds, as shown in **Table 16.4**. We can extend the generalization that any element more electronegative than carbon will have the same effect on oxidation number as oxygen. Thus, the oxidation numbers of carbon in CH_3Cl and in CH_3OH are the same (–2).

Table 16.4 Oxidation Number of Carbon in One-Carbon Compounds

Compound	Formula	Oxidation state
methane	CH_4	–4
methyl alcohol	CH_3OH	–2
formaldehyde	HCHO	0
formic acid	HCOOH	+2
carbon dioxide	CO_2	+4

Combustion of alkanes is an important reaction, which is also a type of oxidation reaction. Alkanes (and also other hydrocarbons), burn in air to produce carbon dioxide and water. The reaction is highly exothermic and large quantity of heat is evolved. The heat released on complete combustion of a substance is called its heat of combustion. For example,

$$CH_4 + 2O_2 \xrightarrow{\text{ignition}} CO_2 + 2H_2O + 890.95\ kJ/mol$$

The reaction is of high significance, as it provides basis for their use as fuels to get heat and power. When there is an insufficient supply of oxygen, alkanes on combustion, form carbon monoxide and water or carbon soot and water.

$$\underset{\text{(limited)}}{2CH_4 + 3O_2} \xrightarrow{\text{ignition}} 2CO + 4H_2O + \text{heat}$$

$$\underset{\text{(very limited)}}{CH_4 + O_2} \xrightarrow{\text{ignition}} C + 2H_2O + \text{heat}$$

Methane on heating at high pressure, with a regulated supply of oxygen and in the presence of a suitable catalyst, provides a variety of products like methyl alcohol etc. For example, when a mixture of methane and air is passed over copper catalyst at a temperature 250°C and pressure of 100 atm, as a result, by controlled oxidation process, methane is converted to methanol. Later on this methyl alcohol by controlled oxidation, can be further converted to formaldehyde.

$$2CH_4 + O_2 \xrightarrow{Cu/250°C/100atm} 2CH_3OH$$

16.5 Alkenes

Alkenes are the unsaturated hydrocarbons which contain a carbon–carbon double bond. They can be represented by the general formula C_nH_{2n}. They are also known as **olefins**, derived from Latin *oleum* meaning 'oil' and *ficare* meaning 'to form', because their lower members form oily derivatives on treatment with chlorine or bromine.

16.5.1 Nomenclature

There are two systems for naming alkenes i.e. Common and IUPAC system.

(a) Common System

The common names of fist four members are derived from those of the corresponding alkanes by replacing the ending "ane" with "–ylene".

$CH_2 = CH_2$ ethylene

$CH_3 - CH = CH_2$ propylene

Greek letters, α, β, γ etc. are used to distinguish isomers having double bond different positions.

$$\overset{\alpha}{C}H_2=\overset{\beta}{C}H-\overset{\gamma}{C}H_2-\overset{\delta}{C}H_3$$
α - butylene

$$\overset{\alpha}{C}H_3-\overset{\beta}{C}H=\overset{\gamma}{C}H-\overset{\delta}{C}H_3$$
β - butylene

(b) IUPAC System

Tidbit

Now α, β, γ are replaced numbers 1, 2, 3 in IUPAC.

The IUPAC rules for naming alkenes are;

i. Select the longest continuous carbon chain that include the maximum number of double bonds.

ii. The name given to the longest chain will act as parent name, whereby the suf *-ane* of the corresponding alkane is replaced by suffix *-ene*.

iii. If there are two double bonds, the suffix is *-diene*; for three, *-triene*; for fo *-tetraene*; and so on, are used.

iv. Number the chain from the end that gives lower number to the doubly bonded carbo

v. Since double bond appears between two carbon atoms, therefore its positio indicated by the number of that carbon atom, bearing lower number and t number is written before suffix *–ene, -diene etc.*

vi. Carbon–carbon double bonds take precedence over alkyl groups in determin the main carbon chain and the direction in which it is numbered.

vii. Name substituent groups as in alkanes, indicating their locations by the num of the main-chain carbon to which they are attached.

viii. For compounds that show geometric isomerism, add the appropriate prefix: *c* or *trans*-.(see section 16.6)

Examples

$CH_2=CH_2$
ethene

$CH_3-CH=CH_2$
propene

$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$
but–1–ene

$\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$
but–2–ene

$\overset{5}{C}H_3-\overset{4}{C}H(\overset{CH_3}{\vert})-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$
4–methylpent–1–ene

$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_3$
penta–1,3–diene

16.5.2 Structure

Tidbit

In 1993, the IUPAC recommended a logical change in the positions of the numbers used in names. Instead of placing the numbers before the root name (1-butene), they recommended placing them immediately before the part of the name they locate (but-1-ene).

Consider ethene (C_2H_4) to illustrate the structure of alkenes. In ethene, each carbon atom has three sp^2–hybridized orbitals which are coplanar. One of the sp^2-hybrid orbitals of one carbon atom overlaps linearly with that of another carbon atom to form a *sigma* (δ) bond. The other two sp^2-hybrid orbitals of each carbon atom overlap with *1s* orbital of hydrogen atoms to form C-H *sigma* bonds. The unhybridized *p*-orbitals of the two carbon atoms, which remain perpendicular to the plane of hybridized orbitals, overlap in a side-wise (parallel) fashion to form a *pi* (π) bond between the two carbon atoms. **(Figure.16.3).**

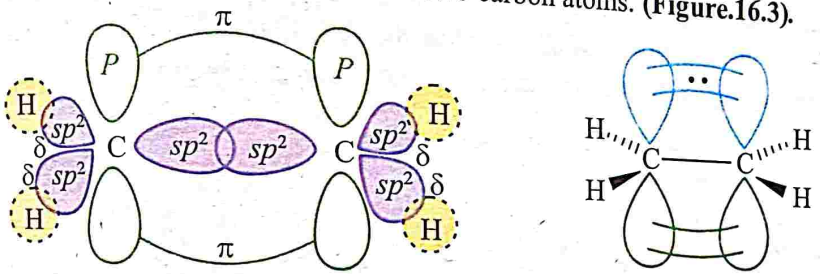


Figure 16.3 Orbital overlap discription in formation of sigma and pi bonds in ethene.

The overall structure of ethene is planar in which H–C–C and H–C–H bond angles are approximately equal to 120°. The carbon-carbon double bond length is 134 pm and C–H bond lengths are 108 pm.

16.5.3 Conjugation

If an alkene has two double bonds, it is called a diene (or alkadiene), if three double bonds, then triene (or alkatriene) and so on. When two double bonds in an alkene (diene, triene etc) are separated by just one single bond, the two double bonds are said to be conjugated and the alkene is a conjugated alkene. The interaction between the two double bonds in a conjugated dienes (or triene etc.) delocalizes the electron density and increases the stability of the molecule, and termed as conjugation. The simplest diene that can have two conjugated *pi* bonds is buta–1,3–diene. Similarly hexa–1,3,5–triene is a triene with three conjugated double bonds and so on.

$CH_2=CH-CH=CH_2$
buta–1,3–diene

$CH_2=CH-CH=CH-CH=CH_2$
hexa–1,3,5–triene

Let us consider buta–1,3–diene to illustrate the phenomenon of conjugation. All the four carbon atoms in buta–1,3–diene are sp^2-hybridized. The C–C and C–H sigma bonds are the result of the overlap of sp^2-hybrid orbitals with each other and with *1s* orbitals of the hydrogen atoms respectively. All the carbon and hydrogen atoms lie in the same plane. Additionally, each of the four carbon atom also possess a unhybridized *p* orbital, which are perpendicular to the plane of sigma bonds. These four *p* orbitals overlap to form delocalized *pi* molecular orbitals (**Figure.16.4**). These delocalized *pi* electrons are thus attracted by all four carbon atoms. The delocalization of *pi* electrons is responsible for greater stability of buta–1,3–diene. As a consequence of conjugation, the C–C single bond in buta–1,3–diene is 148 pm (1.48 Å) which is shorter than the normal C–C single bonds (154 pm) of alkane while the C–C double bond are 137 pm (1.37 Å) which are longer than normal isolated C–C double bonds (134 pm).

Tidbit

When the double bonds in a diene are separated from each other by two or more single bonds, they are called isolated double bonds. Adjacent double bonds in a diene are referred as comulated double bonds.

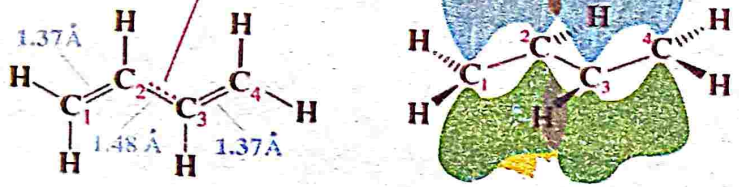


Figure 16.4 Overlap of four p orbitals in buta-1,3-diene.

16.5.4 Relative Stability of Alkenes

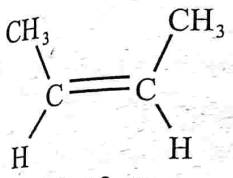
Various alkenes have different stability which depends upon the position of the double bond in the molecule and the number, nature and relative position of substituents on double bonded carbon atoms. In general, the greater the number of alkyl groups attached to the double bonded carbons, the greater is the stability of alkene. For geometric isomers of an alkene, *trans*-isomer is always more stable than *cis*-isomer **(Section 16.6.2.1)**. For isomeric dienes, conjugated dienes are more stable than non-conjugated.

Measurement and comparison of the heats of hydrogenation or heats of combustion of different isomeric alkenes, give us a clue about the relative stability of these alkenes. Stable alkenes evolve small amount of heat upon combustion and hydrogenation and vice versa.

Consider the heats of combustion of the four isomeric butylenes of molecular formula C_4H_8, as given below. Comparison of the heats of combustion of butylenes shows that but–1–ene evolves the largest amount of heat on combustion. In other words, but–1–ene possess the highest energy and is thus the least stable of the four butylenes. Similarly isobutylene (2-methylpropene) has lowest value of enthalpy of combustion, and the most stable of the four isomers.

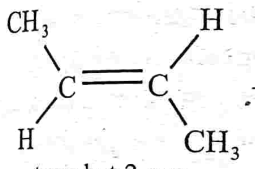
$CH_3-CH_2-CH=CH_2 + 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2719\,kJ/mol$

but-1-ene



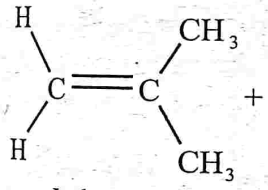
$+ 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2712\,kJ/mol$

cis-but-2-ene



$+ 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2707\,kJ/mol$

trans-but-2-ene



$+ 6O_2 \longrightarrow 4CO_2 + 4H_2O + 2703\,kJ/mol$

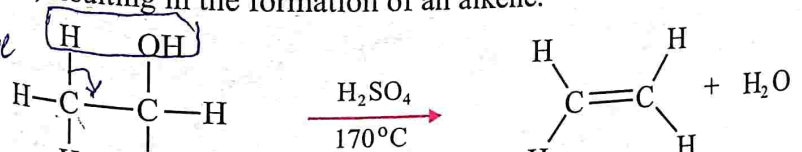
Isobutylene
(2-methylpropene)

16.5.5 Preparation of Alkenes

Alkenes can be prepared by the following methods.

16.5.5.1 Dehydration of Alcohols

When an alcohol is heated at 170°C, in the presence of sulfuric acid, a water molecule is eliminated, resulting in the formation of an alkene.

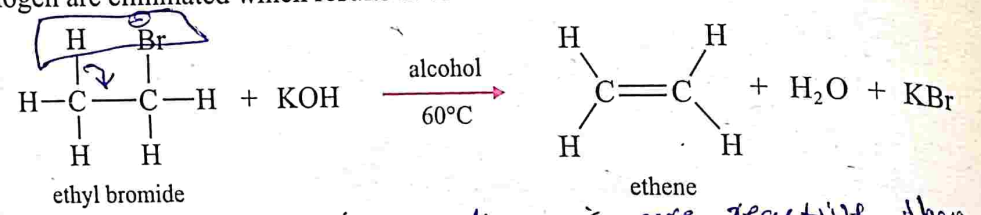


ethyl alcohol — ethene

ıdustrially dehydration of alcohol is carried out by passing vapours of alcohol over lumina (Al_2O_3) at 400°C.

6.5.5.2 Dehydrohalogenation of Alkyl Halides

When an alkyl halide is heated with alcoholic solution of KOH or NaOH, hydrogen and ıalogen are eliminated which results in the formation of an alkene.



ethyl bromide — ethene

16.5.6 Reactivity of Alkenes

Alkenes are more reactive than alkanes due the presence of *pi* (π) bond in the alkene molecules. The overlap of atomic orbitals forming the *pi* bond is not as effective as that in *sigma* (δ) bonds. Thus, *pi* bond is weaker than a *sigma* bond and more easily broken. The electron density of *pi* bond lies above and below the bond axis. It is therefore, more exposed and easily accessible to an external electrophilic (electron seeking) reagent, commonly known as electrophile. It is, therefore, favorable for alkenes to add an electrophile across the double bond by breaking the weak *pi* bond to form strong *sigma* bonds and to produce a saturated compound. Such reactions in which unsaturated compounds are converted into saturated compounds, are called addition reactions. When addition reaction of alkenes is initiated by electrophile, this addition is specifically called electrophilic addition.

16.5.7 Reactions of Alkenes

16.5.7.1 Hydrogenation (Addition of Hydrogen)

Alkenes readily add hydrogen to form alkanes in the presence of finely divided catalyst such as nickel, platinum or palladium at a temperature of 200–250°C and under moderate pressure (1–5 atm). This is called catalytic hydrogenation and reaction occurs on the surface of catalyst. The reaction is exothermic and the heat released during hydrogenation of an alkene is called heat of hydrogenation.

$$\underset{\text{ethene}}{H_2C=CH_2} + H_2 \xrightarrow[\text{or Pt or Pd/25°C}]{\text{Ni/200–250°C}} \underset{\text{ethane}}{CH_3-CH_3}$$

$$\underset{\text{propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow[\text{Pt or Pd/25°C}]{\text{Ni/200–250°C}} \underset{\text{propane}}{CH_3-CH_2-CH_3}$$

Preparation of vegetable ghee from vegetable oil is an example of catalytic hydrogenation at industrial scale. The catalyst used in this process is Raney Nickel after the name of M. Raney, who developed this catalyst.

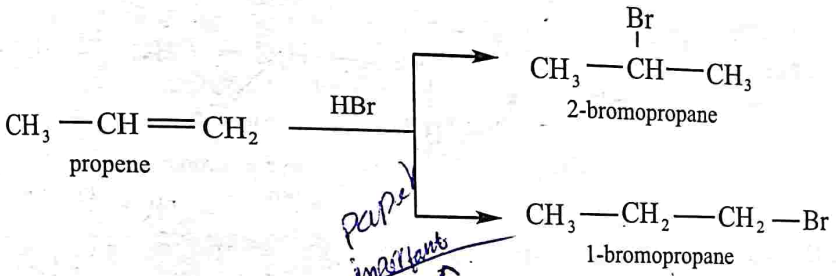
$$\text{Vegetable oil} + H_2 \xrightarrow[\text{Raney Ni}]{\text{150–250°C}} \text{Vegetable ghee}$$

16.5.7.2 Hydrohalogenation

Alkenes react with hydrogen halide (halogen acids: HCl, HBr or HI) to form an addition product, the alkyl halides (or haloalkanes). The order of reactivity of halogen acids increases down the group.

$$\underset{\text{ethene}}{CH_2=CH_2} + H-Br \longrightarrow \underset{\text{ethyl bromide}}{CH_3-CH_2-Br}$$

When the alkene is symmetric (as in the case of ethene), only single product is formed. However if the alkene is asymmetric, two different isomeric products are possible. For example, propene can react with HBr in the following two ways.



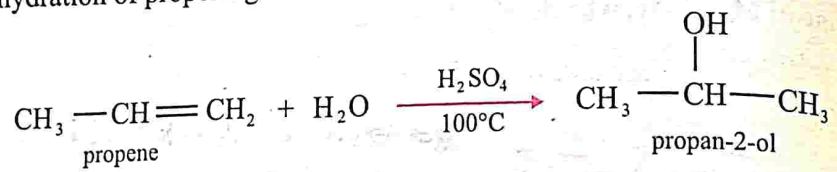
However, experimentally it has been found that 2–bromopropane is the major product. In fact this is in accordance with the Markovnikov's rule, which states that; *when an asymmetric reagent is added to an asymmetric alkene, the positive part of the molecule attaches itself to that carbon atom involved in the double bond, holding greater number of hydrogen atoms.*

16.5.7.3 Hydration

Alkenes can add a molecule of water across the double bond to form alcohols. This process is known as hydration. Direct hydration of alkene can be accomplished by acid-catalyzed addition of water at 100°C. The most commonly used acids to catalyze this reaction are sulfuric acid and phosphoric acid.

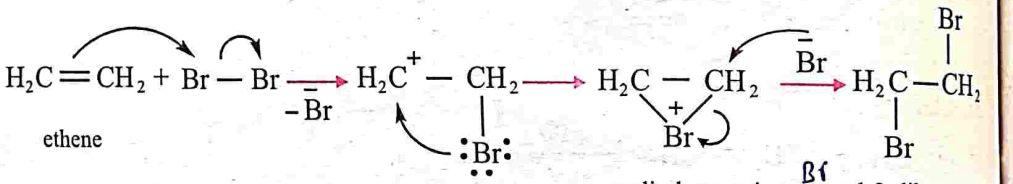
$$\underset{\text{ethene}}{H_2C=CH_2} + H_2O \xrightarrow[100°C]{H_2SO_4} \underset{\text{ethyl alcohol}}{CH_3-CH_2-OH}$$

In case of asymmetric alkenes, the reaction follows the Markovnikov's rule. For example hydration of propene gives mainly isopropyl alcohol (propane–2–ol).



16.5.7.4 Halogenation

Alkenes readily add halogen (chlorine and bromine) in an inert solvent such as carbon tetrachloride or carbon disulfide to form vicinal dihalides (or *vic*-dihalides). Vicinal dichlorides and dibromides are unstable at high temperature, while vicinal diiodides are unstable even at room temperature. The reactivity of various halogens with alkenes decrease down the group. Reaction involves in the formation of a cyclic halonium ion. For example ethene upon reaction with bromine in inert solvent, form 1, 2 dibromoethane (ethylene dibromide).



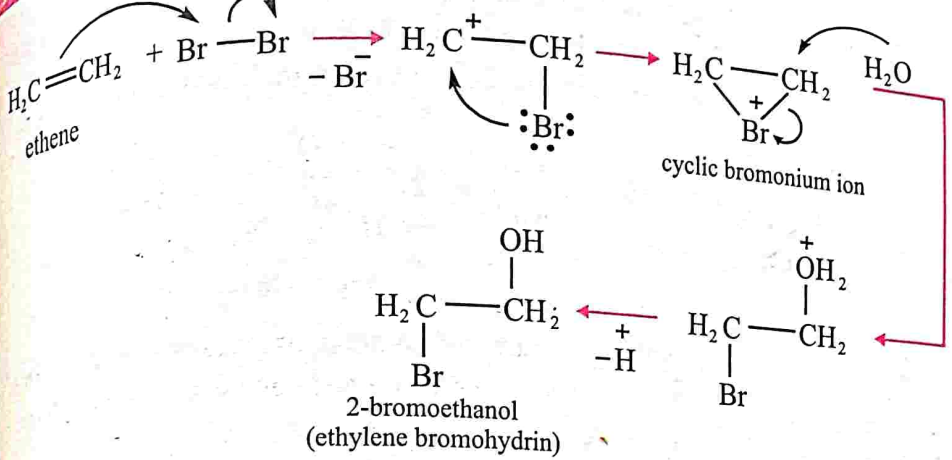
The bromination of alkenes provides a useful test for the presence of a double bond in the molecules. When dilute solution of bromine is added to a compound containing carbon-carbon double bond, the colour of bromine rapidly discharges as the colorless dibromo compound is formed. This is called bromine water test.

Tidbit

Geminal dihalides (or gem-dihalide) have both halogen atoms attached to the same carbon atom whereas vicinal dihalides (or vic-dihalides) have their two halogen atoms attached to two adjacent carbon atoms.

16.5.7.5 Halohydration

When alkene is reacted with halogen in an inert solvent, *vic*-dihalides are formed, because halide ion is the only nucleophile available for reaction with the intermediate cyclic halonium ion. However if the reaction is performed in aqueous solution, water can also act as nucleophile and attack on cyclic halonium ion to form halo-alcohols, commonly known as halohydrin. For example; ethene when reacted with aqueous bromine, forms 2-bromoethanol, commonly called ethylene bromohydrin.

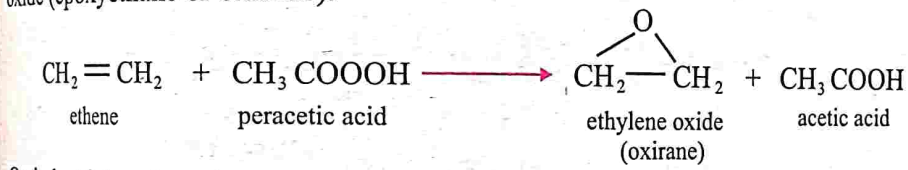


Self-assessmnet

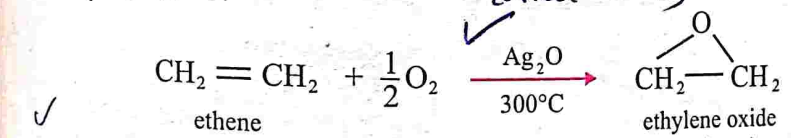
Predict the product of bromohydration of but-2-ene and write the complete reaction.

16.5.7.6 Epoxidation

Alkenes on reaction with peroxyacids (or peracid) yield cyclic ethers called epoxides (or oxiranes). This process in known as epoxidation. The most commonly used peracid, is peracetic acid. For example ethylene when treated with peracetic acid form ethylene oxide (epoxyethane or oxirane).

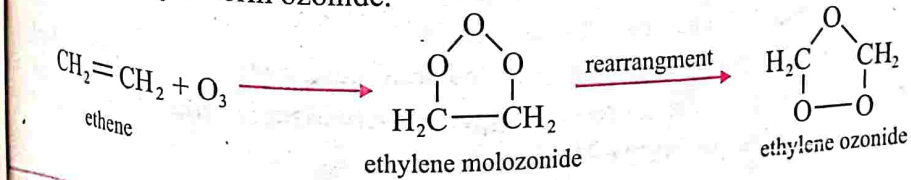


On industrial scale, ethylene oxide is prepared, by air oxidation of ethene with silver oxide catalyst at 300°C.

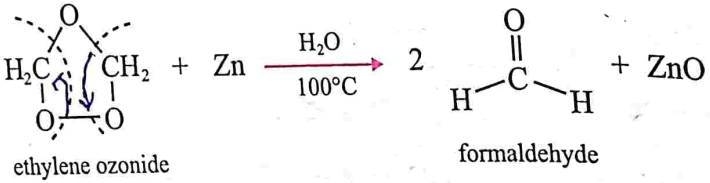


16.5.7.7 Ozonolysis

When ozone (O_3) gas is passed through a solution of alkene in an inert solvent, at low temperature (–80°C), an addition product molozonide is formed. This molozonide rearranges rapidly to form ozonide.



ozonides are highly unstable and explosive and cannot be isolated. Ozonides are decomposed using reducing agents like zinc dust, to form carbonyl compounds. For example, cleavage of ethylene ozonide with zinc, yield two molecules of formaldehyde.

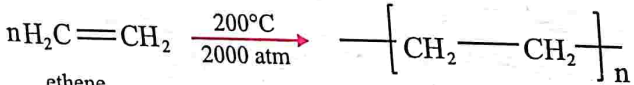


ethylene ozonide — formaldehyde

This conversion process of an alkene to carbonyl compounds is called ozonolysis. This reaction can be used for locating the position of the double bond in an unknown alkene.

16.5.7.8 Polymerization

Polymerization is a process in which small molecules (monomers) chemically join together to form large molecules (polymers). Simple alkenes when subjected to high temperature and pressure in the presence of a catalyst, form long chain addition polymers. Polymerization of alkenes is essentially the conversion of *pi* bonds to *sigma* bonds, which is a thermodynamically favorable process. For example ethene polymerizes to form polyethene in different ways. One approach involves relatively high pressure (2000 atm) and high temperature (200 °C) and the use of a free radical initiator catalyst such as peroxides.



ethene — polyethene (polyethylene)

Polyethylene is used as plastic material in the industries. It is used in the manufacture of shopping bags, sport nets, dustbins, water pipes, packing materials and cable insulation.

16.6 Isomerism

Many of the organic compounds have the same molecular formula but they are different from each other in their structure and properties. Such compounds are called isomers and this phenomenon is called isomerism.

There are two main types of isomerism i.e. Constitutional or Structural isomerism and Stereoisomerism. Each of these two main types of isomerism is further classified into different types as shown in **Figure 16.5**.

Tidbit

The prefix *iso-* is derived from Greek word *isos*, "the same". The suffix *–mer* in the word "isomer" is derived from the Greek word *meros*, meaning "part". Thus isomers are different molecules that have the same parts (elemental composition).

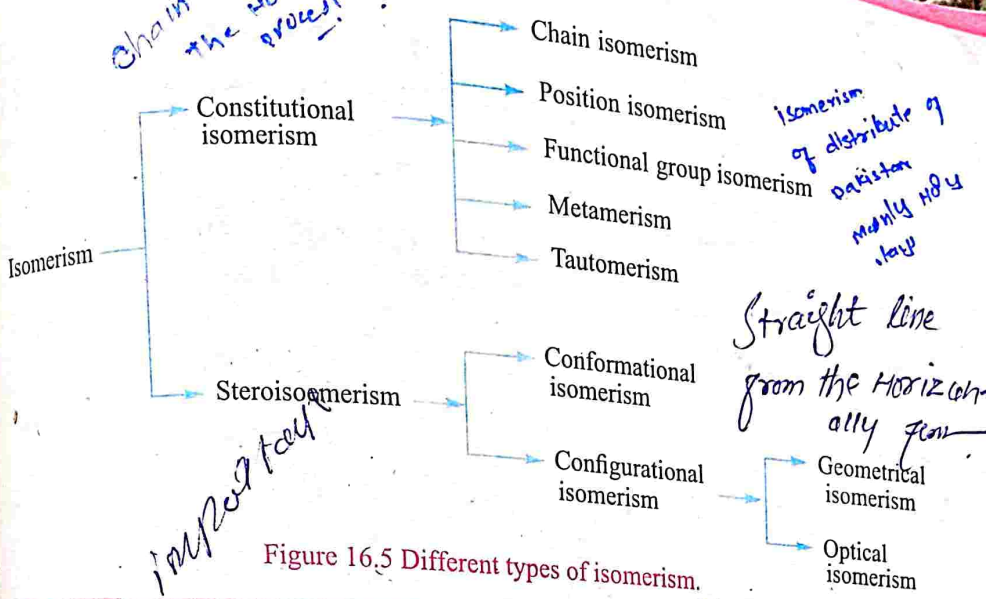


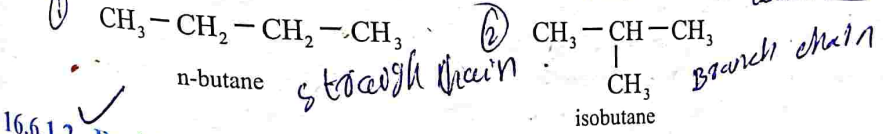
Figure 16.5 Different types of isomerism.

16.6.1 Constitutional isomerism

In this type of isomerism, the isomers have the same molecular formula but different connectivity in structure. It is also called structural isomerism. Structural isomerism is of five types.

16.6.1.1 Chain Isomerism or Skeletal Isomerism

Chain isomerism occurs when there is a difference in arrangement of the carbon atoms in main chain of a molecule. If two or more compounds having the same molecular formula with different carbon chains, then they are said to exhibit the property of Chain isomerism. This phenomenon is also called as skeletal isomerism. The number of possible chain isomers increases with number of carbon atoms. For example; butane has two isomers, pentane has three, hexane has five isomers and so on. The two chain isomers of butane (C_4H_{10}) are given below.



n-butane — isobutane

16.6.1.2 Position Isomerism

Position isomerism arises when there is a difference in the position of functional group. When the position of the functional groups with respect to main chain changes, the phenomenon is called as position isomerism. For example; position isomers of propyl alcohols and butylenes are given below.

$CH_3-CH_2-CH_2-OH$ — propan-1-ol (n-propyl alcohol)

$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$ — propan-2-ol (isopropyl alcohol)

$CH_3-CH_2-CH=CH_2$ — but–1–ene

$CH_3-CH=CH-CH_3$ — but–2–ene

16.6.1.3 Functional group Isomerism

Functional group isomerism involves in compounds ethyl alcohol and dimethyl ether position isomers, having the same molecular formula but different functional groups. For example, ethyl alcohol and dimethyl ether are functional group isomers.

$CH_3-CH_2-\boxed{OH}$ ethyl alcohol ⇌ $CH_3-\boxed{O}-CH_3$ dimethyl ether

Similarly, Propionaldehyde and acetone are also functional group isomers.

CH_3-CH_2-CHO propionaldehyde ⇌ $CH_3-CO-CH_3$ acetone

16.6.1.4 Metamerism

This type of isomerism is exhibited due to the unequal distribution of carbon atoms (or alkyl groups) on either side of the functional group. Isomers belong to the same homologous series. For example, diethyl ether and methyl n-propyl ether are metamers.

$CH_3-CH_2-\boxed{O}-CH_2-CH_3$ diethyl ether ⇌ $CH_3-O-CH_2-CH_2-CH_3$ methyl n-propyl ether

16.6.1.5 Tautomerism

Tautomers are constitutional isomers that differ from each other by position of a proton (and may also a pi bond). It is a special type of functional group isomerism, in which the isomers are in dynamic equilibrium with each other. Tautomerization is the process of inter-conversion of tautomers, and an equilibrium process, which means that the equilibrium will establish with specific concentrations of tautomers of a compound. One of the important example of tautomerism is keto-enol tautomerism. The keto and enol tautomers of acetone are given below.

$H-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$ propanone (*keto* form) ⇌ $CH_2=\underset{\displaystyle OH}{\underset{|}{C}}-CH_3$ propen-2-ol (*enol* form)

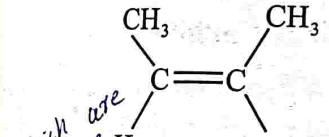
The result of this keto-enol tautomerization, is the migration of a proton from one location to another, accompanied by a change in location of the *pi* bond.

16.6.2 Stereoisomerism

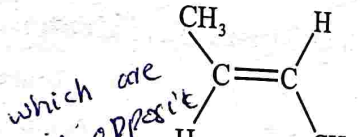
When isomerism is caused by different arrangement of atoms or groups in space, the phenomenon is called stereoisomerism. Thus, *the stereoisomers have the same molecular formula and connectivity of atoms, but differ in the arrangement of atoms or groups in space.* In other words, the isomers that have the same constitution but differ in the spatial arrangement of their atoms are called stereoisomers. Some stereoisomers which are inter-convertible by rotation of single bond are called conformational isomers. But the stereoisomers which are not inter-convertible without breaking and making of some bonds, are called configurational isomers. Conformational isomerism is beyond the scope of this book, so we will discuss only the configurational isomerism in stereoisomers, which is of two types i.e, geometric and optical isomerism.

16.6.2.1 Geometrical Isomerism

Geometric isomers have different arrangement of atoms or groups when the rotation is restricted in a molecule. For example, but–2–ene have two stereoisomeric forms, *cis*–but–2–ene and *trans*–but–2–ene, as shown below.



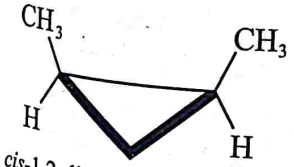
cis-but-2-ene



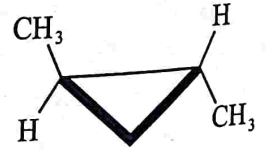
trans-but-2-ene

The isomers in which the two methyl groups are on the same side of the double bond is called the *cis* (a Latin word meaning "on this side") isomer, while *trans* (a Latin word meaning "across") isomer has got them on the opposite sides of the double bond. Consequently this type of isomerism is also called *cis–trans* isomerism. Due to restricted rotation of carbon-carbon double bond, the *cis* and *trans* isomers are not inter-convertible without breaking of *pi* bond. These are two different compounds and have different properties.

Geometric isomerism in alkenes is possible only when each double bonded carbon atom is attached to two different atoms or groups, thus propene does not have geometric isomers. Geometric isomerism is also possible in substituted cycloalkanes. For example 1,2–dimethylcyclopropane also has two geometric isomers.



cis-1,2-dimethylcyclopropane



trans-1,2-dimethylcyclopropane

16.6.2.2 Optical Isomerism

Optical isomerism is a type of isomerism in which the isomers have different interaction towards plane polarized light. If a stereoisomer rotates plane of polarization in clockwise direction, it is called dextrorotatory isomer, and if it rotates the plane of polarization in counter-clockwise direction, it is levorotatory isomer.

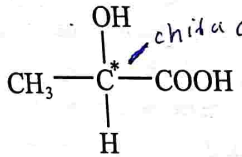
Lactic acid (2–hydroxypropanoic acid) is an example of a compound which shows optical isomerism and has two optical isomers. The isomer which is dextrorotatory is called (+)–lactic acid, while the levorotatory isomers is called (–)–lactic acid **(Section 16.6.5).**

16.6.3 Chiral Centres

A chiral center is an atom that has four different atoms or groups bonded to it. A chiral atom may have one lone pair and three different atoms or groups attached. It is also called chirality center or stereogenic center. Interchange of two groups at stereogenic center (or stereocenter) in a molecule gives another stereoisomer.

16.6.4 Carbon based Chiral Center - Chiral Carbon

A tetrahedral carbon atom in a molecule that bears four different substituents is referred to as a chiral carbon atom, stereogenic carbon or asymmetric carbon atom, and is often designated by an *asterisk* (*). For example, lactic acid has a chiral carbon which is bonded to four different groups (–H, –OH, $–CH_3$, –COOH).



2-hydroxypropanoic acid
(Lactic acid)

16.6.5 Chirality

A molecule is chiral if its two mirror-image forms are not superimposable in three dimensions. The mirror image of chiral molecules is actually another stereoisomer. The word "chiral" is derived from the Greek word *cheir*, meaning "hand," and it is entirely appropriate to speak of the "handedness" of molecules. All chiral molecules are also asymmetric. The opposite of chiral is achiral. A molecule that is superimposable on its mirror image is achiral. Achiral molecules must have a plane of symmetry. Lactic acid has a chiral carbon and is also a chiral molecule. The non-superimposable mirror images of lactic acid are shown in **(Figure 16.6).**

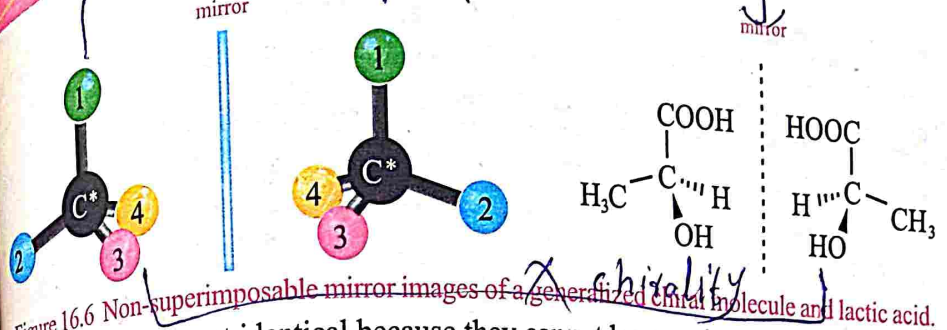


Figure 16.6 Non-superimposable mirror images of a generalized chiral molecule and lactic acid.

These structures are not identical because they cannot be superimposed on each other. They are the mirror images of each other. Such non superimposable mirror images constitute optical isomers and are called *enantiomers* of each other.

16.6.6 Optical Activity

Ordinary light is composed of electromagnetic radiations vibrating in many different planes and is unpolarized. The oscillating waves are of different wave lengths (polychromatic) in all possible planes perpendicular to the direction of propagation. It becomes monochromatic (light of a single wave length) when it is passed through a monochromator but it still has waves in all the planes. When this unpolarized light passes through a polarizing filter, the randomly vibrating light waves are filtered so that most of the light passing through is vibrating in one direction, and is now plane-polarized light **(Figure 16.7)** also.

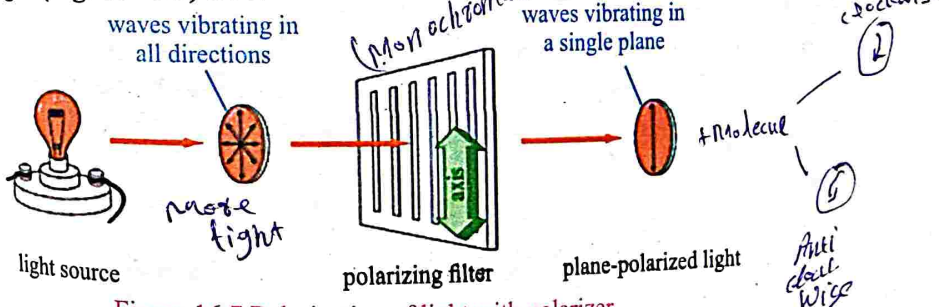


Figure 16.7 Polarization of light with polarizer.

Solutions of some organic compounds have the ability to rotate the plane of polarized light. These compounds are said to be optically active, and this property of a compound is called optical activity. Optical activity of a compound is measured by an instrument called polarimeter. An optically active compound can exist in two enantiomeric forms, which rotate the plane of polarized light in opposite directions. These enantiomers are therefore optical isomers. The isomer which rotates the plane of polarized light to the right (clockwise direction) is said to be dextrorotatory isomer or (+)-isomer and the isomer which rotates the plane of polarized light to the left (anticlockwise direction) is

said to be levorotatory isomer or (–)-isomer (**Figure 16.8**). Polarimetry is a conv
method used to distinguish between enantiomers, based on their ability to rotate
plane of polarized light in opposite directions.

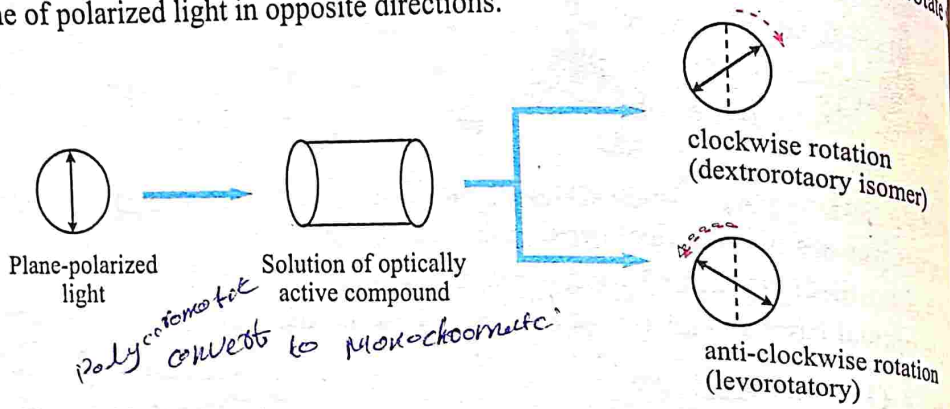


Figure 16.8 Rotation of plane-polarized light in different direction by two enantiomers

16.7 Alkynes

Alkynes are unsaturated hydrocarbons which contain a carbon –carbon triple bo
They can be represented by the general formula C_nH_{2n-2}. The first and most import
member of this series is acetylene ($HC \equiv CH$) and hence these are generally ca
acetylenes. The carbon-carbon triple bond is therefore called acetylenic bond.

16.7.1 Nomenclature

There are two systems for naming alkynes i.e. common and IUPAC systems.

(a) Common System

The first member of the alkyne series is named as acetylene.

$$H-C\equiv C-H$$
acetylene

The higher alkynes are regarded as the alkyl derivatives of acetylene. For example:

$$CH_3-C\equiv CH \quad , \quad CH_3-C\equiv C-CH_3$$
methyl acetylene, dimethyl acetylene

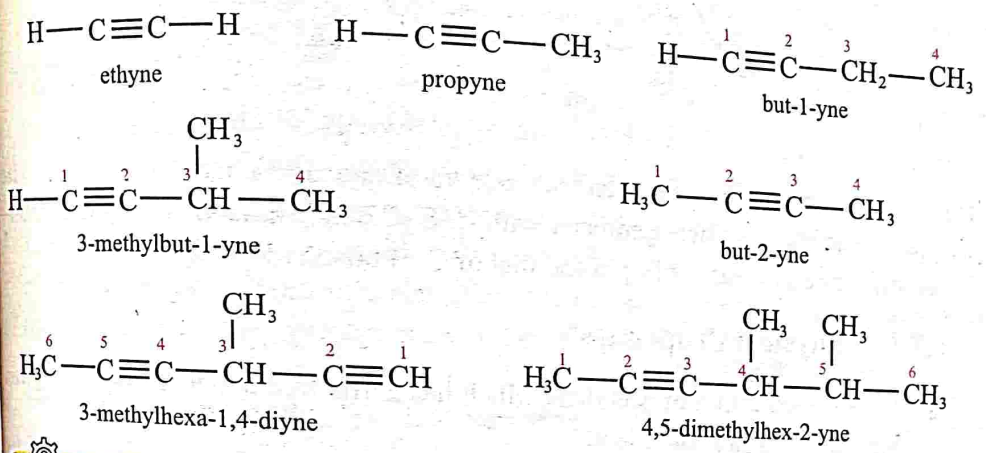
(b) IUPAC System

The IUPAC rules for naming akynes are the same as those for alkanes, except
following.

i. The longest continuous carbon chain must include maximum number of triple bo
ii. The name given to the longest chain acts as parent name, whereby the end
"–ane" of the corresponding alkane is replaced by suffix "–yne".

iii. Number the chain in such a way that triply bonded carbon atom gets (–C≡C–) the smallest number.
iv. The position of the triple bond is indicated by the number of that triply bonded carbon atom which bears lower number and this number is written before "–yne".
v. For more than one triple bonds in the molecule, the prefix di, tri, tetra etc are used before "–yne".
vi. Name substituent groups as in alkanes, indicating their locations by the number of the main-chain carbon to which they are attached.

The following examples will illustrate the above rules.



Self-assessmnet

Draw the structures of the following alkynes
- 3,3,4–trimethylpent–1–yne
- 3–methylhexa–1,4–diyne
- 4–ethyl–3,5–dimethylhex–1–yne

16.7.2 Structure

To illustrate the structure of alkynes, we would consider the structure of acetylene as an example. In acetylene each carbon atom has two *sp*-hybrid orbitals which lie on the same line. Each carbon atom also has two unhybridized *p* orbitals, which are perpendicular to each other and to the plane of *sp*-hybrid orbitals. One *sp*-hybrid orbital of one carbon atom linearly overlaps with the *sp*-hybrid orbital of the other carbon atom to form *sigma* bond between the two carbon atoms. The other *sp*-hybrid orbital of both the carbon atoms overlap with 1*s* orbitals of the two hydrogen atom to form two C–H sigma bonds. The two unhybridized *p* orbitals of both the carbon atoms approach each other in a sidewise manner to form two *pi* bonds. **(Figure 16.9)**

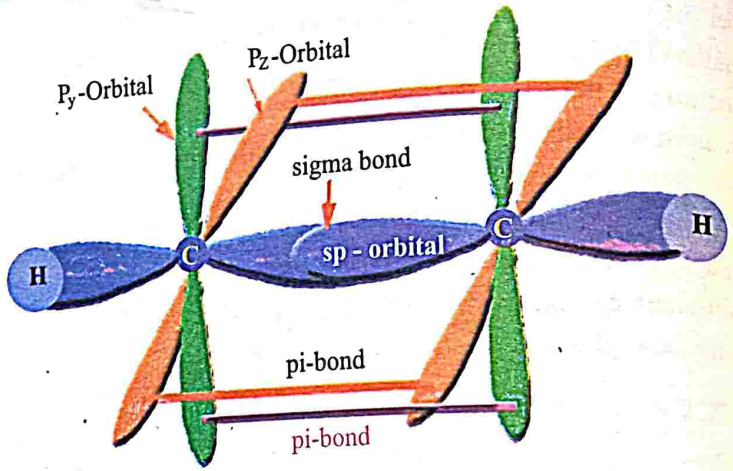


Figure 16.9 Orbital hybridization model of acetylene.

Thus, the carbon –carbon triple bond is made up of one *sigma* and two *pi* bonds. acetylene molecule has linear geometry with H–C–C bond angle of 180°. The carb carbon triple bond length is 119 pm and that of C–H bond is 106 pm.

16.7.3 Physical Properties

- With the exception of acetylene which has garlic like odour, all other alky are odourless and colourless.
- The first three members (ethyne, propyne and butynes) are gases, next e straight chain alkynes (C_5–C_{12}) are liquids and higher alkynes are solids at ro temperature and pressure.
- The boiling points of alkynes are slightly higher than the corresponding alka and alkenes and increase regularly with increase in the number of carbon at in the alkynes. However, their melting points do not follow a regular sequ Instead, they change irregularly with increase in the number of carbon at **(Table 16.4)**. Boiling points of terminal alkynes are lower than isomeric terminal alkynes.
- Alkynes like alkanes and alkenes are non-polar; therefore, they are insoluble water but readily dissolve in organic solvents such as ether, ethanol, acet carbon tetrachloride, benzene etc.
- The density of alkynes increases with molecular mass. They are slig denser than the corresponding alkanes and alkenes. All alkynes are lig than water.

Table 16.4 Boiling and Melting Points of Some Alkynes

Alkyne	Melting Points (°C)	Boiling Points (°C)
acetylene	–82	–84
propyne	–101	–23
but–1–yne	–126	8
but–2–yne	–32	27
pent–1–yne	–101	40
pent–2–yne	–90	55

16.7.4 Relative Stabilities of alkynes

Like alkenes, the alkynes also exhibit stability to varying degree. The stability of alkynes, also depends on factors like position of the triple bond in the molecule and number and nature of the substituents attached to triple bonded carbon atoms. Generally non-terminal alkynes are relatively more stable than terminal alkynes.

The stabilities of various isomeric alkynes can be compared, by measuring their heats of hydrogenation or heats of combustion. Stable alkynes evolve small amount of heat upon combustion and hydrogenation and vice versa. For example butyne has two isomers i.e. but-1-yne and but-2-yne. Upon hydrogenation but-1-yne releases large amount of heat than but-2-yne, therefore but-1-yne is less stable than but-2-yne.

$$\underset{\text{but-1-yne}}{HC{\equiv}C{-}CH_2{-}CH_3} + 2H_2 \longrightarrow \underset{\text{butane}}{CH_3{-}CH_2{-}CH_2{-}CH_3} + 292\ \text{kJ/mol}$$

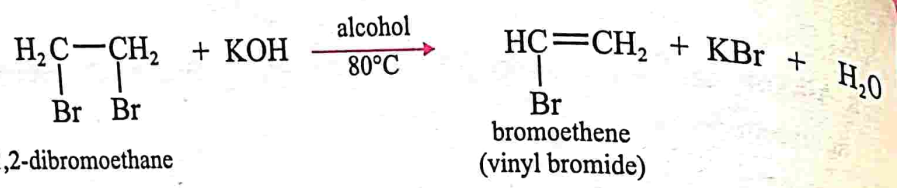
$$\underset{\text{but-2-yne}}{CH_3{-}C{\equiv}C{-}CH_3} + 2H_2 \longrightarrow \underset{\text{butane}}{CH_3{-}CH_2{-}CH_2{-}CH_3} + 275\ \text{kJ/mol}$$

16.7.5 Preparation of Alkynes by Elimination Reactions

Elimination reactions involve the removal of atoms or groups from two adjacent carbon atoms to form *pi* bond. This is also called 1,2-elimination or *β*-elimination **(Section 17.1.7)**. These reactions result in the formation of unsaturated compounds. Alkyne can be prepared by the following elimination reactions.

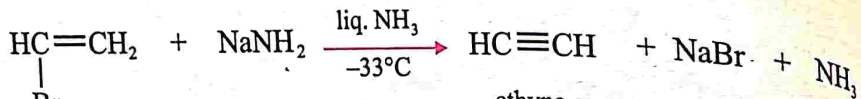
16.7.5.1 Dehydrohalogenation of Vicinal Dihalides

Vicinal and geminal dihalides, when treated with alcoholic potassium hydroxide or sodium amide in liquid ammonia, form alkynes. It is a two step reaction. The elimination product of the first step (vinyl halide), is treated with stronger base such as sodium amide to remove another molecule of HX.



1,2-dibromoethane

bromoethene
(vinyl bromide)

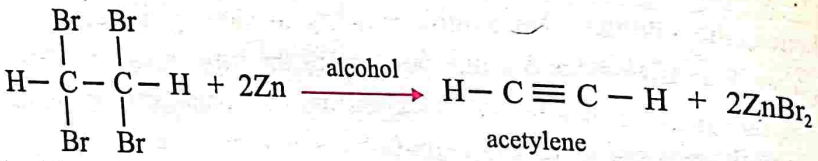


bromoethene

ethyne

16.7.5.2 Dehalogenation of Tetrahalides

When tetrahalides having two halogen atoms on each of the two adjacent carbons, are heated with zinc dust in alcohol, alkynes are formed.



1,1,2,2-tetrabromoethane

acetylene

16.7.6 Reactivity of Alkynes

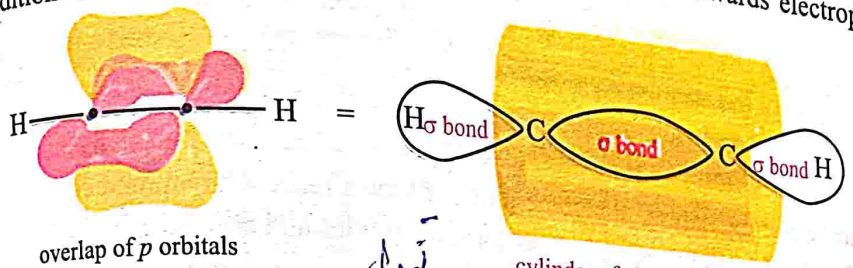
Alkynes are unsaturated hydrocarbons like alkenes. Thus they resemble alkenes in most of their reactions. For example, alkyne add hydrogen, halogens and halogen acids much like the addition of these reagents to alkenes. However, unlike alkenes which add one molecules of these reagents, alkynes add two molecules in a step-wise manner. Characteristic reaction of alkyne are also electrophilic addition reactions.

It is to be noted that a carbon–carbon triple bond of alkynes, in general, is less reactive than a carbon–carbon double bond of alkenes, towards electrophilic reagents. This is due to the following reasons.

i. The triple bonded carbon atoms in alkynes are *sp*-hybridized while double bonded c-atoms in alkenes are sp^2-hybridized. Greater the *s* character of an orbital, the more highly the electrons in that orbital are held by the nucleus. Thus, *pi* electrons in alkynes (50% s-character) are more strongly held by the carbon atom than in case of alkenes (33.33% s-character) and are less easily available for reactions with electrophile. This makes alkynes, less reactive than alkenes in electrophilic reactions.

ii. In alkynes, there are two pi bonds, the four lobes of which merge to form a single electron cloud. This cloud is cylindrically symmetrical about the inter-nuclear axis and occupies large volume **(Figure 16.10)**. Thus, the *pi* electron–density per unit

volume becomes low. Due to decrease in the electron density, *pi* electrons are not easily available to an electrophile and hence less reactive towards electrophilic addition reactions.



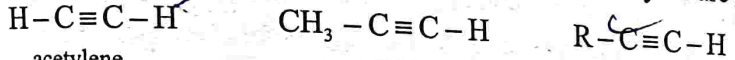
overlap of *p* orbitals

cylinder of electron density

Figure 16.10 Formation of cylindrical pi electronic cloud of triple bond.

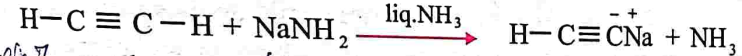
16.7.7 Acidity of Terminal Alkynes

Alkynes in which the triple bond is at the end of the chain, are referred to as terminal or 1-alkynes. Some examples and general formula of terminal alkynes are given below.



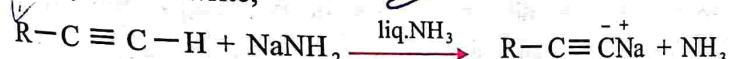
acetylene propyne terminal alkyne

Terminal alkynes and acetylene are slightly acidic in nature. They readily donate proton to a strong base. Thus if acetylene or a terminal alkyne is treated with a solution of sodium amide ($NaNH_2$) in liquid ammonia, sodium acetylide or generally sodium alkynide is obtained.



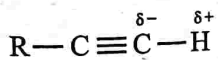
acetylene sodium acetylide

Or more generally we can write;



1–alkyne sodium alkynide

Acetylene and other terminal alkynes are more acidic than alkanes and alkenes, as clear from pKa values given in **Table 16.5**. The acidity of an acetylenic hydrogen is due to *sp*-hybridization of triple bonded carbon atom. A *sp*-hybrid orbital has 50% *s* character in it and renders the carbon atom more electronegative than sp^2 and sp^3-hybridized carbons. As a result, the *sp*-hybridized carbon atoms of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.



terminal alkyne

Table 16.5 pKa values of Ethane, Ethene and Ethyne

Compounds	Hybridization	*s* Character (%)	pKa
ethane	sp^3	25	50
ethene	sp^2	33.33	44
ethyne	sp	50	25

Because of acidic nature, acetylene and 1-alkynes react with ammonical solutions of cuprous chloride and silver nitrate to form acetylides and alkynides of these metals.

$$\underset{\text{acetylene}}{CH\equiv CH} + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\substack{\text{dicopper acetylide}\\(\text{red ppt})}}{CuC\equiv CCu} + 2NH_4Cl + 2H_2O$$

$$\underset{\text{acetylane}}{HC\equiv CH} + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\substack{\text{disilver acetylide}\\(\text{white ppt})}}{AgC\equiv CAg} + 2NH_4NO_3 + 2H_2O$$

Copper and silver acetylides are highly explosive in dry condition. They can, however, be decomposed by acids such as nitric acid to regenerate acetylene. Since non-terminal alkynes do not form alkynides, this reaction can be used as a test to distinguish terminal alkynes from non-terminal alkynes.

16.7.8 Addition Reactions of Alkynes

16.7.8.1 Hydrogenation

The conditions for hydrogenation of alkynes are similar to those employed for alkenes. In the presence of finely divided platinum, palladium or nickel, two molecules of hydrogen add to the triple bond of an alkyne to yield an alkane. Addition of two molecules of hydrogen to alkynes occurs in two steps, initially forming the corresponding alkenes and finally alkanes.

$$\underset{\text{ethyne}}{HC\equiv CH} + H_2 \xrightarrow[\text{or Pt or Pd/25°C}]{\text{Ni/ 230-250°C}} \underset{\text{ethene}}{CH_2=CH_2}$$

$$\underset{\text{ethene}}{CH_2=CH_2} + H_2 \xrightarrow[\text{or Pt or Pd/25°C}]{\text{Ni/ 230-250°C}} \underset{\text{ethane}}{CH_3-CH_3}$$

With efficient catalysts such as platinum, palladium, or nickel, it is usually impossible to stop the reaction at the alkene stage. However, hydrogenation of an alkyne can be stopped at the alkene stage by using a "poisoned" (partially deactivated) catalyst made by treating a good catalyst with a compound that makes the catalyst less effective. Lindlar's catalyst

is a poisoned palladium catalyst; composed of powdered barium sulfate coated with palladium, poisoned with quinoline. In an internal alkyne, *syn* addition gives a *cis*-alkene product (if cis/trans-isomerism is possible in product alkene).

Tidbit

Syn addition is the addition of two substituents to the same side of a double or triple bond.

16.7.8.2 Reduction by Dissolving Metal

Terminal alkynes and acetylene, react with metals such as sodium in liquid ammonia to form salts called alkynides or acetylides **(Section 16.7.7)**. However, reduction of non-terminal alkynes to *trans*-alkene (*anti* addition), can be carried by reduction of alkynes with sodium metal in liquid ammonia.

$$\underset{\substack{\text{Non-terminal}\\\text{alkyne}}}{R-C\equiv C-R} + 2Na \xrightarrow[-33°C]{\text{liq. } NH_3} \underset{\text{trans-alkene}}{\begin{matrix} R & & H \\ & C=C & \\ H & & R \end{matrix}} + 2NaNH_2$$

16.7.8.3 Hydrohalogenation

Two molecules of halogen acids are added to alkynes in two steps, to form geminal dihalides. In case of symmetric alkyne, the second step follows the Markovnikov's rule. However, addition of halogen acids to asymmetric alkynes follows Markovnikov's rule in both the steps.

For a symmetrical alkyne:

$$\underset{\text{ethyne}}{H-C\equiv C-H} + \overset{\delta+}{H}-\overset{\delta-}{Br} \longrightarrow \underset{\substack{\text{vinyl bromide}\\(\text{bromoethene})}}{\begin{matrix} Br \\ | \\ CH_2=CH \end{matrix}}$$

$$\underset{\substack{\text{vinyl bromide}\\(\text{bromoethene})}}{\begin{matrix} Br \\ | \\ CH_2=CH \end{matrix}} + \overset{\delta+}{H}-\overset{\delta-}{Br} \xrightarrow{\text{(Markovnikov's rule)}} \underset{\substack{\text{1,1-dibromoethane}\\(\text{a } gem\text{-dibromide})}}{\begin{matrix} Br \\ | \\ CH_3-CH \\ | \\ Br \end{matrix}}$$

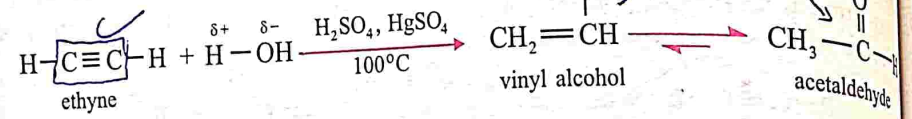
For an asymmetric alkyne;

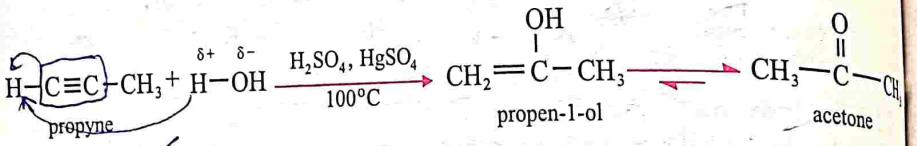
$$\underset{\text{propyne}}{H-C\equiv C-CH_3} + \overset{\delta+}{H}-\overset{\delta-}{Br} \xrightarrow{\text{(Markovnikov's rule)}} \underset{\text{2-bromopropene}}{\begin{matrix} Br \\ | \\ CH_2=C-CH_3 \end{matrix}}$$

$$\underset{\text{2-bromopropene}}{\begin{matrix} Br \\ | \\ CH_2=C-CH_3 \end{matrix}} + \overset{\delta+}{H}-\overset{\delta-}{Br} \xrightarrow{\text{(Markovnikov's rule)}} \underset{\text{2,2-dibromopropane}}{\begin{matrix} Br \\ | \\ CH_3-C-CH_3 \\ | \\ Br \end{matrix}}$$

16.7.8.4 Hydration

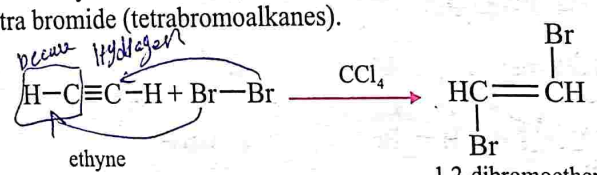
Alkynes undergo acid-catalyzed addition of water across the triple bond in the presence of mercuric ion as a catalyst. A mixture of mercuric sulfate in aqueous sulfuric acid is commonly used as the reagent. The hydration of alkynes is similar to the hydration of alkenes, and it also goes with Markovnikov orientation. The enol formed on tautomerization give corresponding aldehyde or ketone. The product is an aldehydes in case of acetylene, and ketone in case of higher alkynes.

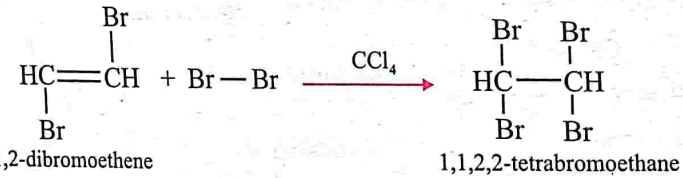




16.7.8.5 Halogenation (Bromination)

Bromine adds to alkynes in two steps, initially forming dibromoalkene (mainly *trans*) and then a tetra bromide (tetrabromoalkanes).

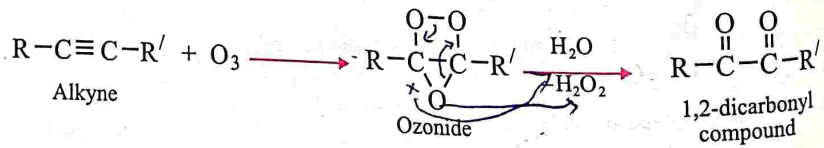


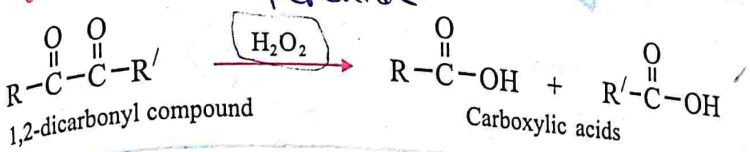


Chlorine also react in similar way.

16.7.8.6 Ozonolysis

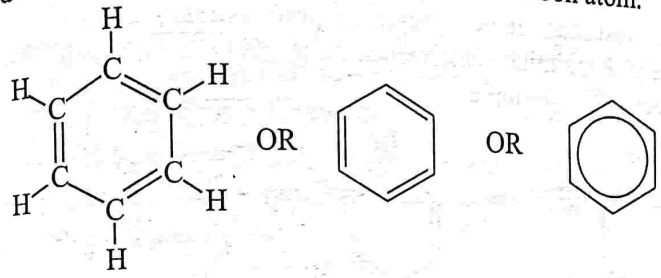
Alkynes react with ozone to form ozonides. The ozonides may be decomposed with water to give a 1,2-dicarbonyl compound, which is finally oxidized to an acid by hydrogen peroxide produced in the reaction, resulting in formation of carboxylic acids.





16.8 Benzene and Substituted Benzenes

Benzene is an aromatic hydrocarbon. Its molecular formula is C_6H_6. The following ring structure is usually written for benzene, where each corner represents a carbon atom. It is understood that one hydrogen atom is bonded to each carbon atom.

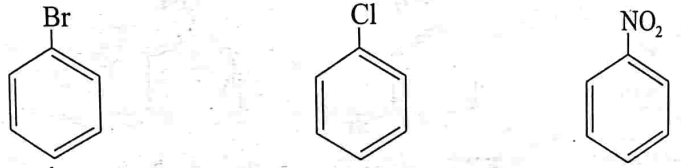


Monosubstituted and polysubstituted benzene derivatives are formed by the replacement of one or more hydrogen atoms respectively.

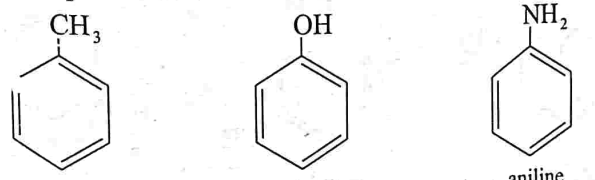
16.8.1 Nomenclature

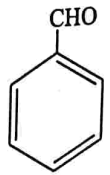
Benzene and its substituted compounds are named by common names which are also accepted by the IUPAC System.

i. **Monosubstituted benzene derivatives** are named by putting the name of the substituent before the word benzene. For example;

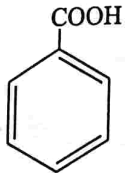


Some Monosubstituted benzene derivatives have been given "Special names". They must be remembered as such. Some of the examples are given below. Their systematic names are also given in parenthesis.



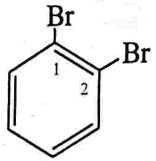


benzaldehyde
(benzenecarbaldehyde)

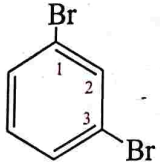


benzoic acid
(benzenecarboxylic acid)

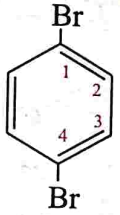
ii. In disubstituted benzene derivatives, the relative position of substituents in 1,2-, 1,3- and 1,4-disubsituted can be represented prefixes *ortho (o-), meta (m-) and para (p-)* respectively. For similar substituents, the prefix *di-* is also used before the name of the substituents. For example



o-dibromobenzene
(1,2-dibromobenzene)

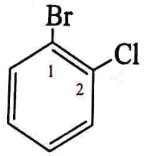


m-dibromobenzene
(1,3-dibromobenzene)



p-dibromobenzene
(1,4-dibromobenzene)

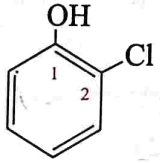
If the substituents are different, they are named in alphabatical order. If one of the substituent is such that it gives special name to the molecule then the special name is used as the parent name. The other substituent, along with its position, is named before the parent name.



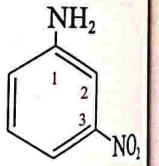
o-bromochlorobenzene
(1-bromo-2-chlorobenzene)



m-bromonitrobenzene
(1-bromo-3-nitrobenzene)

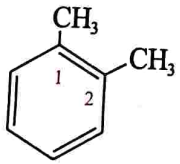


o-chlorophenol
(2-chlorophenol)

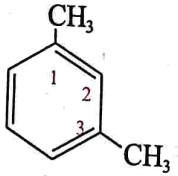


m-nitroaniline
(3-nitroaniline)

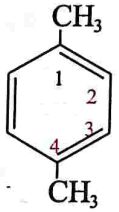
Some disubstituted benzene derivatives are given special names. For example;



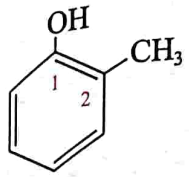
o-xylene
(1,2-dimethylbenzene)



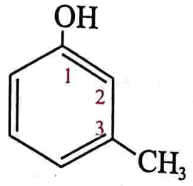
m-xylene
(1,3-dimethylbenzene)



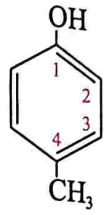
p-xylene
(1,4-dimethylbenzene)



o-cresol
(2-methylphenol)



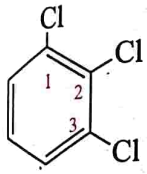
m-cresol
(3-methylphenol)



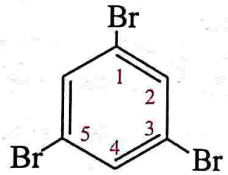
p-cresol
(4-methylphenol)

iii. Polysubstituted benzene derivatives, are named similarly to disubsituted derivatives.

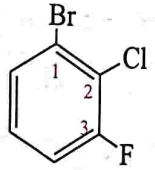
- For similar atoms/groups the prefix *tri-, tetra-* etc. are used before the substituents.
- If different groups attached, they are named in alphabetical order.
- To indicate the position of the substituents, the ring is numbered in such a way that all the numbers used in the name give the lowest sum. If a substituent gives special name, it should be considered at position-1, and the special name is the parent name of molecule. For example;



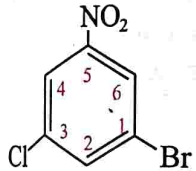
1,2,3-trichlorobenzene



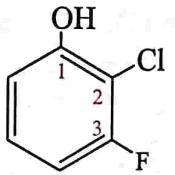
1,3,5-tribromobenzene



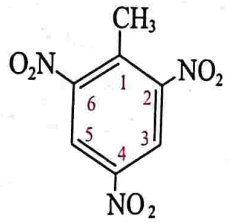
1-bromo-2-chloro-3-fluorobenzene



1-bromo-3-chloro-5-nitrobenzene

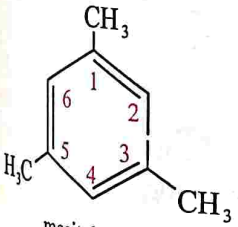


2-chloro-3-fluorophenol

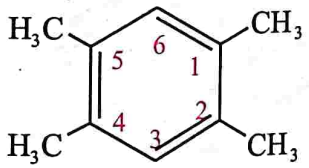


2,4,6-trinitrotoluene (TNT)

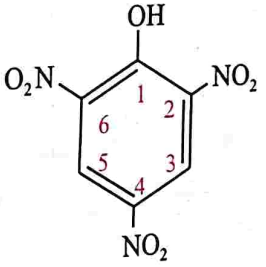
Some polysubstituted benzene derivatives have been assigned special names. Few examples are given below. Their systematic names are given in parenthesis.



mesitylene
(1,3,5-trimethylbenzene)

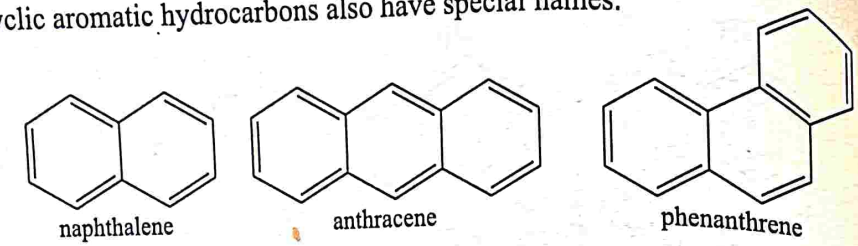


durene
(1,2,4,5-tetramethylbenzene)



picric acid
(2,4,6-trinitrophenol)

Polycyclic aromatic hydrocarbons also have special names.



16.8.2 Physical Properties of Benzene

Benzene is a colourless liquid at room temperature and atmospheric pressure. It has a peculiar smell and burning taste. The density of benzene is 0.88 g/mL. Benzene melts at 6°C and boils at 80°C. Benzene is more symmetrical than similar aliphatic compounds, so it packs better into crystals and has high melting point than corresponding aliphatic hydrocarbons. For example, benzene melts at 6°C, while hexane melts at –95°C. It is highly inflammable. Benzene is insoluble in water but soluble in ether, carbon tetrachloride etc.

16.8.3 Structure: Molecular Orbital Aspects

The structure of benzene can best be described in terms of molecular orbital hybridization model. Each carbon atom of the ring is linked to others by sp^2–hybrid orbitals and with *s* orbitals of the six hydrogen atoms, forming six C–C and six C–H sigma bonds respectively **(Figure 16.11)**. Since, the sigma bond results from the overlap of planar sp^2-hybrid orbitals, all carbon and hydrogen atoms in benzene lie in the same plane and all the bond angles are 120°.

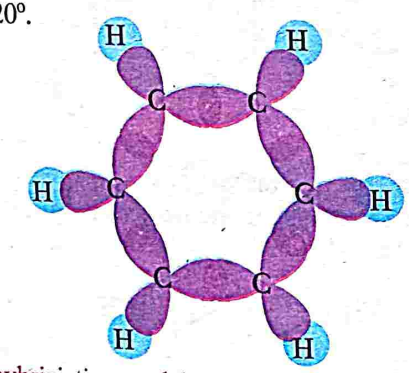


Figure 16.11 Orbital hybriziation model of benzene and formation of sigma bonds.

Each carbon atom also possesses a half-filled unhybridized *p* orbital, which are perpendicular to the plane of sigma bonds. The side-wise overlap of these *p* orbitals produces delocalized *pi* molecular orbitals containing six electrons, which are associated with all six carbon atoms. It is this extensive *pi* electron delocalization which is responsible

or the greater stability of benzene. The electron cloud of these delocalized *pi* electron lies alf below and half above the ring **(Figure 16.12)**. The carbon-carbon and carbon-ydrogen bond lengths are 139 pm (1.39 Å) and 108 pm (1.08 Å) respectively.

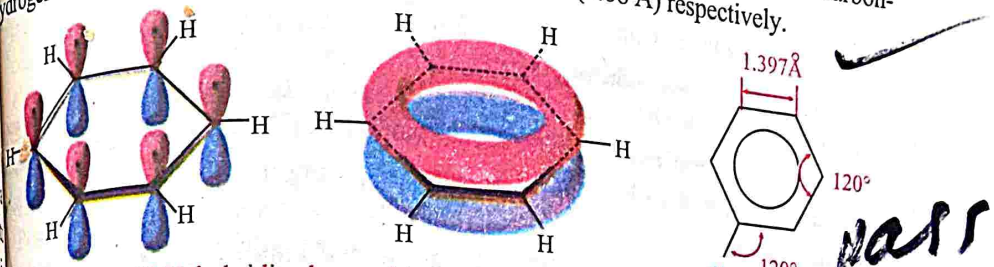


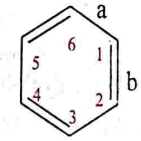
Figure 16.12 Unhybridized p-p orbitals overlap to form delocalized *pi* bonds.

16.8.4 Resonance, Resonance Energy and Stabilization

esonance

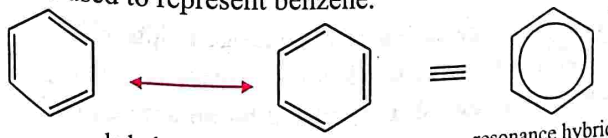
ome molecules (or ions) are not adequately represented by a single Lewis structure. wo or more valence-bond structures are drawn for such molecules, differing only in placement of electrons. These different structures are called resonance structures or sonance forms or canonical form because they are not different molecules, just fferent ways of drawing the same molecule. The actual molecule is said to be a sonance hybrid of its resonating forms.

r example, the structure (which is cyclohexa-1,3,5-ene) is used to represent benzene. It is not the real ucture of benzene because if this is the real structure of nzene, it is expected that benzene should add three olecules of Br_2 (in absence of light), but in actual practice it does not do so. Benzene dergoes electrophilic substitution reaction rather than addition. The bond length of nds "a" and "b" should be 154 pm and 134 pm respectively. However, all carbon-rbon bonds in benzene are equal and having bond lengths of 139 pm.



cyclohexa–1,3,5–triene

us, the above structure is not the actual structure of benzene. In such case we write ore than one structure to represent the actual structure of a molecule i.e. benzene. *This presentation of a real structure as a weighted average of two or more contributing uctures is called resonance.* The following resonance structures, commonly called kule structures, are used to represent benzene.



kekule structures

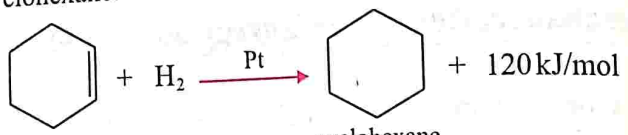
resonance hybrid

It should be noted that the concept of resonance does not mean that these struc rapidly shifts between canonical forms. In fact, all the molecules of a substance the same structure all the time, in which all the electrons are delocalized over the w system involved in resonance.

Resonance Energy and Stability of Benzene

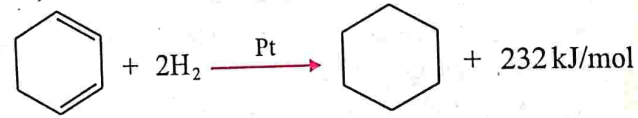
The resonance energy of a molecules is the difference between the energy of the stable canonical form and that of the actual molecule. For benzene it can be calcu by measuring its heat of hydrogenation and comparing it with that of the most s canonical from.

Hydrogenation of cyclohexene (having one double bond) evolves 120 kJ/mol energy to form cyclohexane.



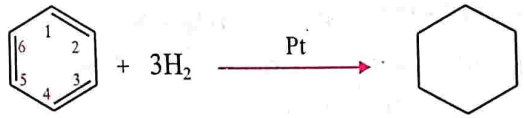
cyclohexene — cyclohexane

Hydrogenation of cyclohexa–1,3–diene (having two double bonds) evolves 232 kJ to form cyclohexane, which is almost double of the value 120 kJ/mol for cyclohe



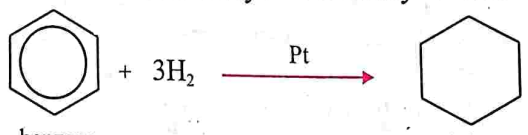
cyclohexa-1,3-diene — cyclohexane

The molecule cyclohexa-1,3,5-triene (Kekule structure) normally written for be and having three double bonds, should release energy three time to that of cyclohe (i.e. 120×3 = 360 kJ/mol), upon hydrogenation.



cyclohexa-1,3,5-triene — cyclohexane

But hydrogenation of benzene actually evolves only 208 kJ/mol.



benzene — cyclohexane

Thus, the measured (experimental) heat of hydrogenation of benzene is less th expected value of the most stable canonical form by an amount of 152 kJ/mol. Be is, therefore, is said to be resonance stabilized by an amount of 152 kJ/mol w known as its resonance energy.

16.8.5 Reactivity and Reactions

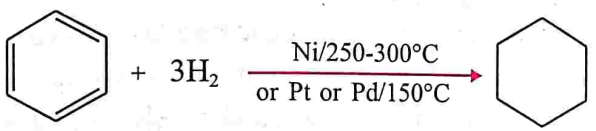
Due to unusual stability (resonance stabilization), benzene and its derivatives do not give addition reactions like those of alkenes. In alkenes the *pi* electronic cloud is localized between the two carbon atoms and thus they readily undergo addition reactions. In benzene the *pi* electronic cloud makes a continuous sheet above and below all the six nuclei and the *pi* electrons are, thus delocalized, which give benzene more stability. Benzene, therefore, prefers to undergo electrophilic substitution reactions rather than addition reactions, to retain its aromatic character.

16.8.5.1 Addition Reactions

Benzene is very resistant to addition reaction and requires much more vigorous conditions than generally required for alkenes and alkynes. It does not undergo electrophilic addition reaction, but may give free-radical type addition and catalytic addition reactions in proper conditions.

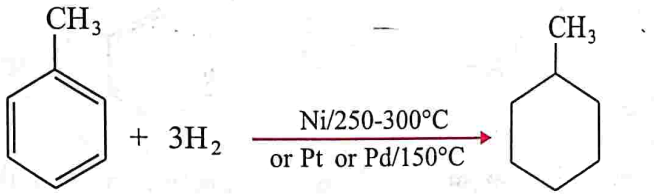
16.8.5.1.1 Addition of Hydrogen

Benzene reacts with hydrogen in the presence of Ni, Pt or Pd catalyst at elevated temperature and high pressure to form cyclohexane. The reaction is also called catalytic hydrogenation.



benzene — cyclohexane

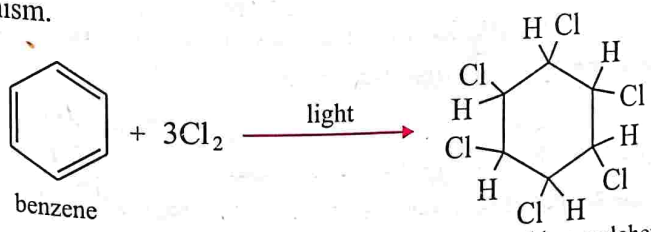
Similarly toluene (a benzene derivative) upon catalytic hydrogenation yield methylcyclohexane.



toluene — methylcyclohexane

16.8.5.1.2 Addition of Halogens

Benzene reacts with chlorine or bromine in the presence of light to form benzene hexachloride and benzene hexabromide respectively. The reaction follow free radical addition mechanism.

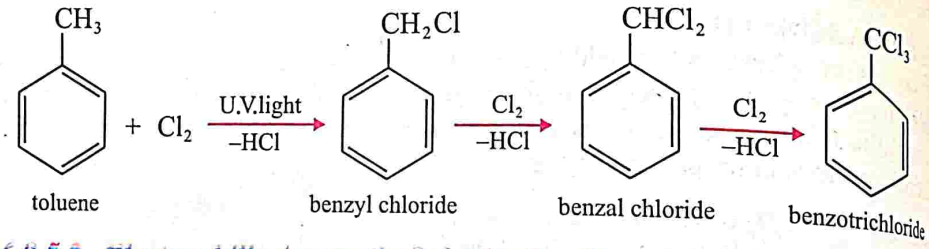


benzene — 1,2,3,4,5,6-hexachlorocyclohexane

However, when halogen is treated with toluene in the presence of ultraviolet light, halogenation occurs at aliphatic side chain (methyl group) to yield successively, benzyl chloride, benzal chloride and benzo trichloride. The reaction follow free radical substitution mechanism **(Section 16.3)**, instead of addition.

Tidbit

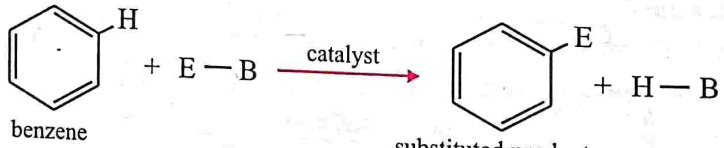
The name Benzene hexachloride (BHC) is incorrectly used for 1,2,3,4,5,6-hexachlorocyclohexane. The most important isomer for commercial purposes is the Lindane, which is used in shampoos to kill head lice.



16.8.5.2 Electrophilic Aromatic Substitution Reactions

16.8.5.2.1 General Introduction

Reaction in which hydrogen atom of the aromatic ring is replaced by an electrophile is called electrophilic aromatic substitution reaction. Benzene ring with its delocalized π electrons is an electron rich system. It is attacked by electrophiles giving substituted products. A generalized electrophilic substitution reaction is shown below. The catalysts most commonly used are acids.

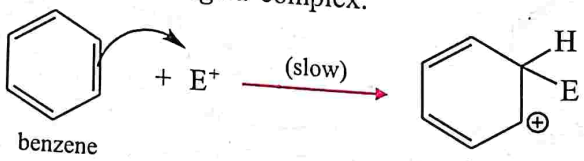


Mechanism of electrophilic aromatic substitution reaction involves the following three steps.

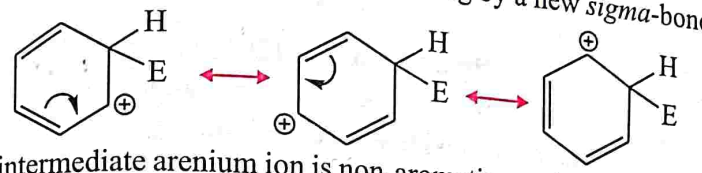
Step–1: Formation of an electrophile



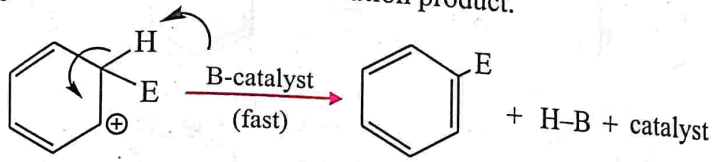
Step–2: The electrophile attacks the aromatic ring to produce a non-aromatic carbocation called arenium ion or *sigma*-complex.



The intermediate arenium ion is resonance stabilized and is a hybrid of the following three structures. This resonance-stabilized carbocation is called a *sigma*-complex because the electrophile is joined to the benzene ring by a new *sigma*-bond.



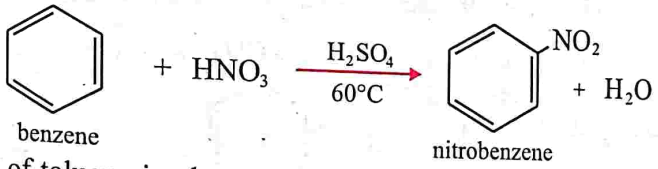
Step–3: The intermediate arenium ion is non-aromatic species and is unstable. It loses a proton to form a stable aromatic substitution product.



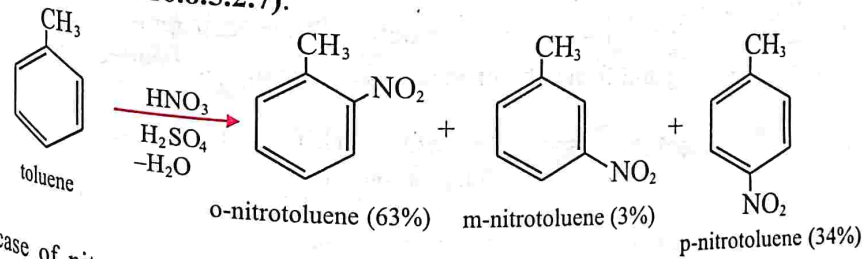
The overall reaction is the substitution of a proton by an electrophile on the aromatic ring: electrophilic aromatic substitution.

16.8.5.2.2 Nitration

Benzene reacts with concentrated nitric acid in the presence of concentrated sulphuric acid at 60°C to form nitrobenzene.



While nitration of toluene in above conditions yield a mixture of isomeric *o*,-*m*- and *p*-nitrotoluene, in unequal proportions. The *ortho* and *para* products predominate, while very little *meta* product is obtained due to *ortho/para* orienting effect of methyl group **(see Section 16.8.5.2.7)**.



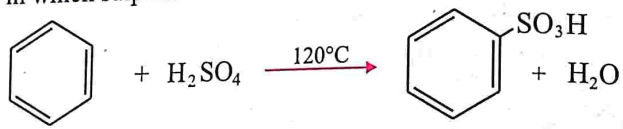
In case of nitration, the electrophile is nitronium ion, produced by reaction of concentrated nitric and sulfuric acid. The electrophile nitronium ion attacks on benzene ring and forms substitution products via arenium ion intermediate **(Section 16.8.5.2.1)**.

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{+}{N}O_2 + 2H\overset{-}{S}O_4 + H_3O^+$$

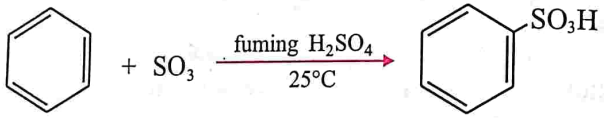
nitronium ion
(Electrophile)

16.8.5.2.3 Sulphonation

Benzene reacts with concentrated sulfuric acid at 120°C or fuming sulfuric acid at room temperature, to give benzenesulphonic acid. Fuming sulphuric acid is concentrated sulphuric acid in which sulphur trioxide has been dissolved.

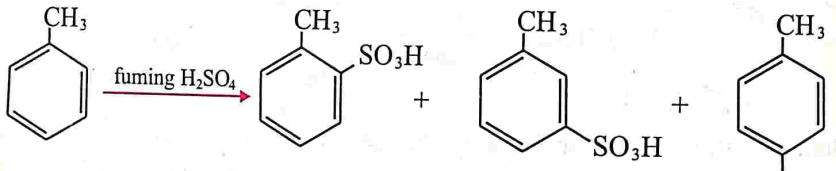


benzene — benzenesulphonic acid



benzene — benzenesulphonic acid

Sulphonation of toluene also yield a mixture of isomeric *o–*, *m–* and *p-* methylbenzenesuphonic acid, in different percentages. The ortho and para products again predominate, while meta product is obtained in small amount.



toluene — o-methylbenzenesulphonic acid (43%) — m-methylbenzenesulphonic acid (4%) — p-methylbenzenesulphonic acid (53%)

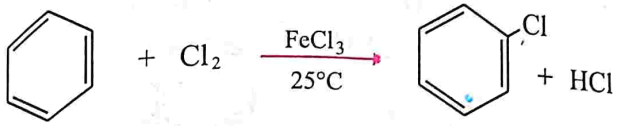
The electrophile is sulphur trioxide in this reaction. The electrophile sulphur trioxide attacks on benzene ring and forms the products via arenium ion intermediate.

$$2H_2SO_4 \longrightarrow SO_3 + H\overset{-}{S}O_4 + \overset{+}{H}_3O$$

sulphur trioxide
(Electrophile)

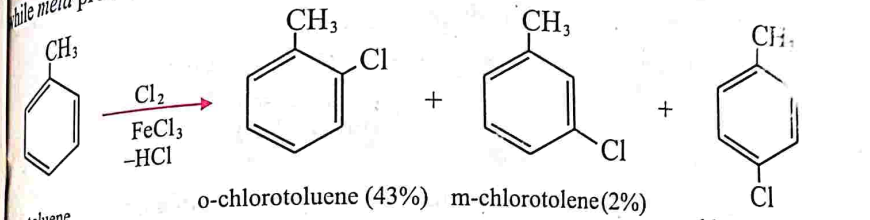
16.8.5.2.4 Halogenation

Benzene reacts with molecular halogen at room temperature, in the presence of Lewis acid catalyst to form halobenzene. For example reaction of chlorine with benzene in the presence ferric chloride is given below.



benzene — chlorobenzene

Chlorination of toluene in presence of $FeCl_3$ results in a mixture of isomeric *o-, m- and p-*chlorotoluenes, in different percentages. The *ortho* and *para* products predominate, while *meta* product is obtained in small amount.



toluene — o-chlorotoluene (43%) — m-chlorotolene(2%) — p-chlorotoluene (55%)

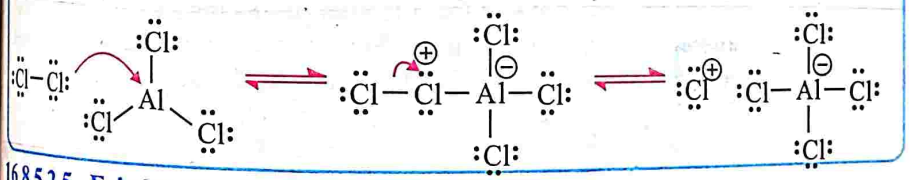
The electrophile is chloronium ions formed by reaction with ferric chloride and chlorine molecules. The electrophile chloronium ion attacks on benzene ring and form products via arenium ion intermediate.

$$Cl_2 + FeCl_3 \longrightarrow \overset{+}{Cl} + \overset{-}{F}eCl_4$$

chloronium ion
(Electrophile)

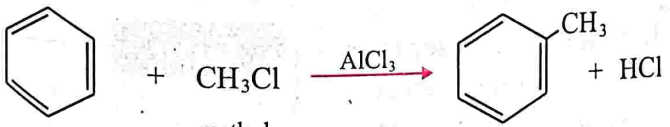
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Chlorine reacts with $AlCl_3$ to form a complex, which reacts as if it were Cl^-.



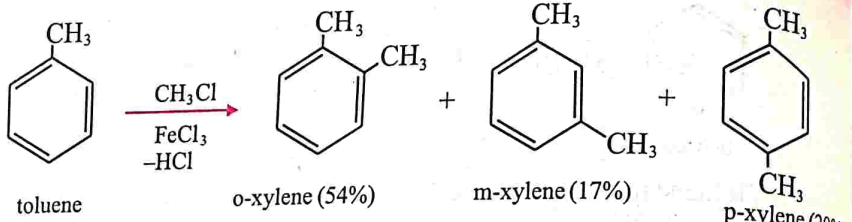
16.8.5.2.5 Friedel-Crafts Alkylation

Benzene reacts with alkyl halides in the presence of Lewis acid catalyst to form alkyl benzenes. For example, reaction of benzene with methyl chloride in the presence of aluminum chloride yields toluene.



benzene — methyl chloride — toluene

Substituting methyl groups into toluene, via Friedel-Craft's alkylation results in formation of three isomeric xylenes. Mainly the *o- and p-*xylene are formed.



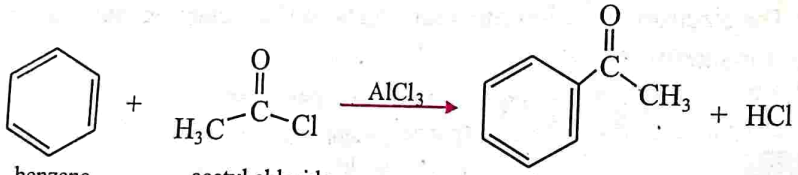
The electrophile in this reaction is a methyl cation (a carbocation) formed by reacti methyl chloride with aluminum chloride. The electrophile carbocation then attacks benzene ring and forms substitution products.

$$CH_3Cl + AlCl_3 \longrightarrow \overset{+}{C}H_3 + \overset{-}{A}lCl_4$$

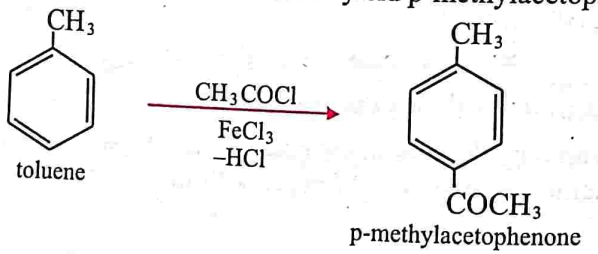
methyl cation (Electrophile)

16.8.5.2.6 Fridel-Crafts Acylation

Benzene reacts with acid halides (or anhydrides) in the presence of a Lewis acid catalys to give aromatic ketones. For example, benzene reacts with acetyl chloride in th presence of aluminum chloride catalyst to form acetophenone.



In acylation of toluene, virtually all the substitution occurs at 4-position (p-position) The reason that you get virtually none of the o-isomer in this instance is because of th size of the incoming acyl group is very large. For example, reaction of toluene wit acetyl chloride in the presence of ferric chloride yield p-methylacetophenone.

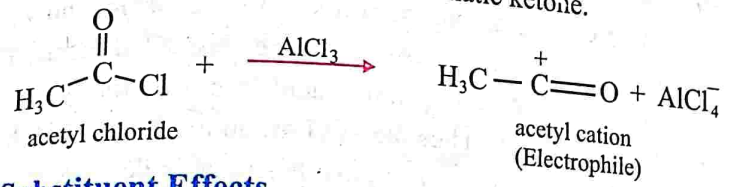


The electrophile in Friedel-Crafts acylation is a carbocation, generally called an acylium ion (RCO^+). Acetyl cation (an acylium ion) is formed by reaction of acetyl chloride with aluminum chloride catalyst. The electrophile

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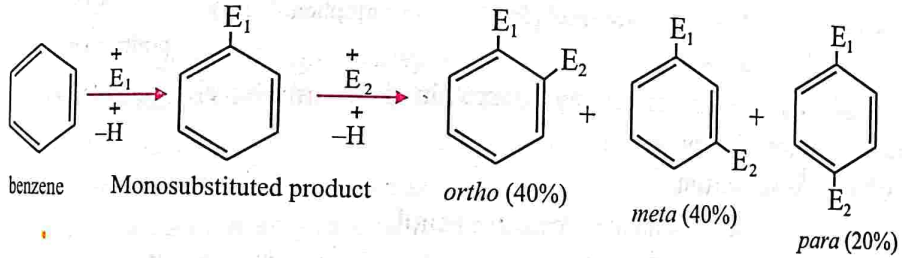
Acylation can only be used to give aromatic ketones, but not aldehydes. This is because the formyl chloride (HCOCl) decomposes to CO and HCl under the reaction conditions.

acylium ion attack on benzene ring and form aromatic ketone.



16.8.5.2.7 Substituent Effects

An electrophilic substitution reaction of benzene results only in the formation of one monosubstituted product because all hydrogen atoms of benzene ring are equivalent. However, second substituent can occupy any of the three remaining position to form three isomeric (*ortho, meta* and *para*) disubstituted products. It is expected that *ortho, meta* and *para* disubstituted products should be formed with ratio of 2:2:1, as given below.



However, in actual practice the disubstituted products are not formed with the above expected percentages. This is because the first substituent ($-E_1$) effect the ring making the *ortho*, *meta* and *para* position non-equivalent for electrophilic attack. Similarly the first substituent may also increase or decrease the reactivity of ring for second substitution. These effects are called substitution effects.

Types of effects of Substituents

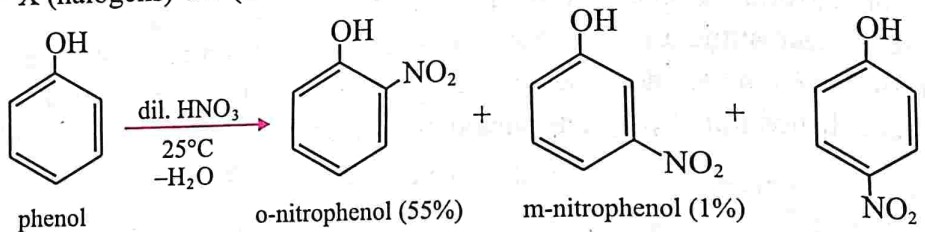
Effect of a substituent already present on the benzene ring on further substitution can be divided into two categories i.e. Orientation Effect and Reactivity Effect.

(A) Directing or Orientation Effect

The first substitutent may direct the incoming electrophile to *ortho, meta or para* position, depending on the nature of the first substituent. This is called the directing or orientation effect. It has been experimentally observed that some groups, when attached to the benzene ring, direct the second incoming substituent to either *ortho* and *para* positions or to the *meta* position. Thus, the substituents (groups) can be divided into two classes.

i. *Ortho/Para* Directing substituents

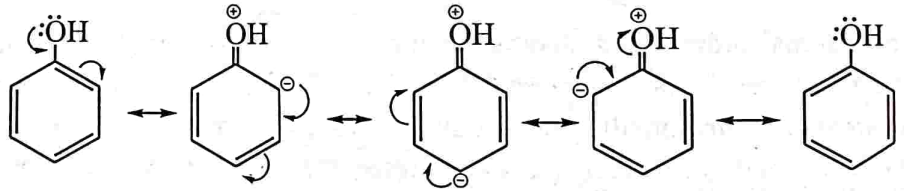
Substituents which direct the second substituent to the *ortho* and *para* positions simultaneously are called the *ortho/para (o/p)* directing substituents. For example, when phenol is nitrated, with dilute nitric acid, the reaction yields mainly the *o*–nitrophenol and *p*–nitrophenol. Thus the –OH group of phenol, which has directed the second substituent $-NO_2$ to *ortho* and *para* positions is designated as *ortho/para* directing. Some common *ortho/para* directing groups are, –OH, $-NH_2$, –NHR, $-NR_2$, –R, –X (halogens) etc. **(Table 16.6)**.



The ortho/para directing effect can be explained in terms of charge distribution and relative stability of arenium ion.

a. Charge Distribution

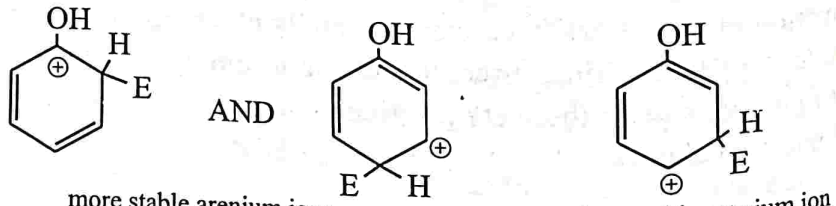
Consider, the various resonance forms of phenol.



As can be seen that one of the non–bonding electron pairs of oxygen of the –OH group is delocalized over the ring, making the *ortho* and *para* positions more electron rich than the *meta* position. The electrophile would naturally prefer to attack at these electron rich centers, to give mainly ortho and para disubstituted products.

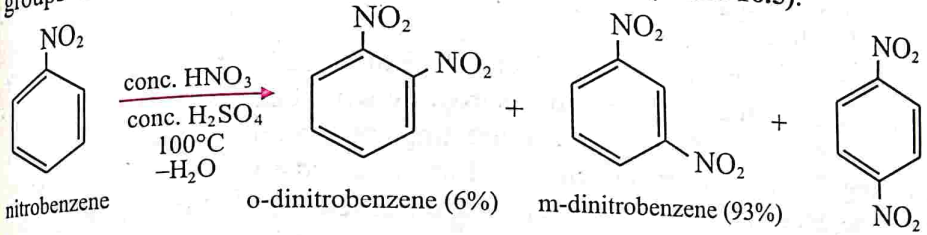
b. Relative Stability of Arenium ion

The intermediate arenium ion in the presence of *ortho/para* directing groups is more stable when the second substituent is at *ortho/para* positions than when it is at meta position as shown below.



ii. *Meta* Directing substituents

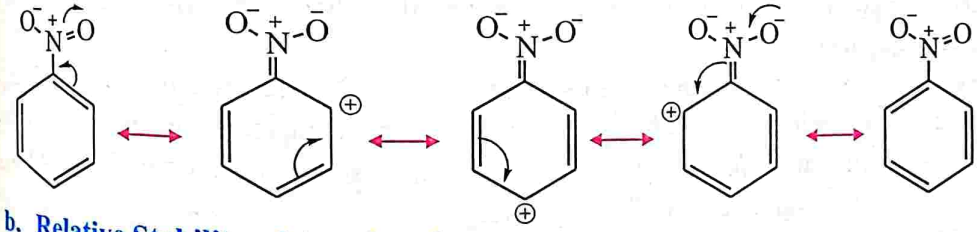
The substituents which direct the second incoming substituent to *meta* position, are called *meta*–directing substituents. For example, nitration of nitrobenzene in the presence of concentrated nitric acid and sulfuric acid at 100°C gives mainly *m*–dinitrobenzene. Thus the substituent $-NO_2$ group, which has directed the second $-NO_2$ group to the *meta* position is meta directing. Some common meta directing groups are $-NO_2$, –CN, –CHO, –COR, –COOH etc. **(Table 16.5)**.



The *meta*–directing effect of a group may also be due to the following two reasons i.e. charge distribution and relative stability by arenium ion.

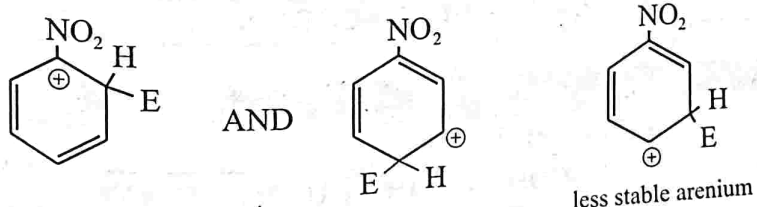
a. Charge Distribution

These groups withdraw electron density from *ortho* and para positions. Thus, *meta* position of the ring has relatively more electronic density than *ortho* and *para* positions, and becomes an attractive target for electrophile. It is clear from the resonance structures of nitrobenzene that *ortho* and *para* positions have small electron density compared to *meta* position.



b. Relative Stability of Arenium ion

Secondly, the arenium ion formed in the presence of *meta* orienting groups is more stable when the second substituent is at *meta* position than when it is at *ortho* or *para* positions, as shown below.



Self-assessmnet

Draw the possible resonance structures for chlorobenzene and benzaldehyde.

(B) Effect of Substituent on the Reactivity of the Benzene Ring

The substituent attached to the benzene ring also affects the reactivity of benzene ring in comparison with the unsubstituted benzene, this is called reactivity effect. Reactivity effect may be ring activating or deactivating.

i. Ring activating effect

The *ortho/para* directing groups release electrons to the ring by resonance making it electron rich. Thus, the attack of a second electrophile would be faster as compared to the benzene ring itself. Thus, the *ortho/para* directing species increase the reactivity of the benzene ring. They are ring activators and are referred to as activating groups. Halogens are the exceptions to this. It has been observed that halogens, though are *ortho/para* directing, are ring deactivators.

For example, the nitration of benzene **(Section 16.8.5.2.2)** requires concentrated nitric acid and sulfuric acid at 60°C, while nitration of phenol can easily occur with dilute nitric acid at 25°C as discussed earlier in this section. This is due to activating effect of –OH group.

ii. Ring deactivating effect

All *meta* directing groups and halogens (F, Cl, Br, I) withdraw electrons from the ring making it electron deficient. Thus in the presence of *meta* directing species, the attack of a second electrophile would be slower as compared to the benzene ring. Hence, these groups are ring deactivators.

For example, the nitration of benzene **(Section 16.8.5.2.2)** requires concentrated nitric acid and sulfuric acid at 60°C, while nitration of nitrobenzene can be even slower with concentrated nitric acid and sulfuric acid at 100°C as discussed earlier in this section. This is due to deactivating effect of $-NO_2$ group.

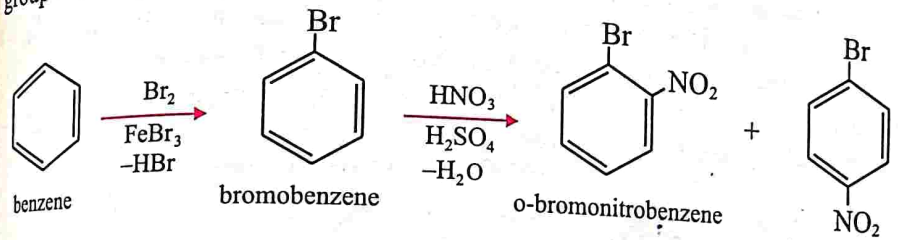
Table 16.5 Orientation and Reactivity Effect of Some Common Groups

Activators		
Strong	**–OH, $-NH_2$, –NHR, $-NR_2$**	***ortho/para* directors**
Moderate	**–OCOR, –NHCOR, –NRCOR**	
Weak	**R–**	
Deactivators		
Weak	**–X (F, Cl, Br, I)**	
Moderate	**–CHO, –COR, –COOH, $-CONH_2$, –COOR**	***meta* directors**
Strong	**$-NO_2$, $-{}^+NH_3$, $-{}^+NR_3$**	

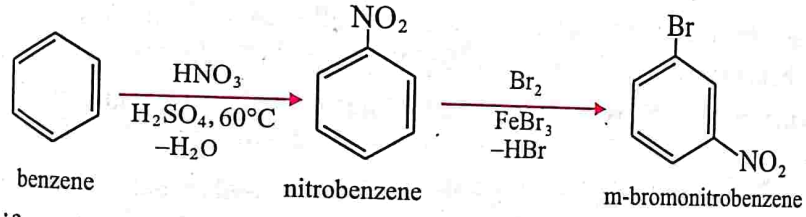
16.8.5.2.8 Making Polysubstituted Benzenes

Polysubstituted benzenes are the derivatives of benzene in which two or more hydrogen atoms have been substituted by other atoms or group of atoms. We have to keep in mind the activating and directing effect of first substituents on the ring while planning the synthesis of a polysubstituted benzene derivative.

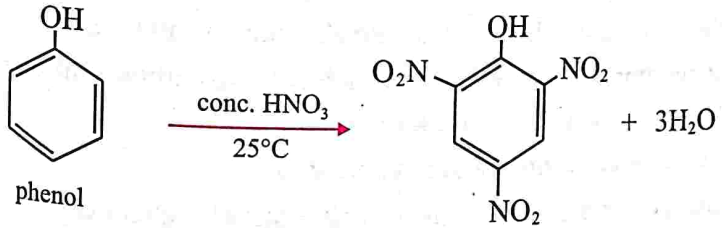
For example, the synthesis of bromonitrobenzene from benzene require the introduction of $-NO_2$ and –Br groups in two consecutive electrophilic substitution reactions i.e. nitration and bromination. Either of the two substituents can be introduced into the benzene ring first and then the other. If benzene is first brominated and then nitrated, we will get mainly a mixture of *o*- and *p*-bromonitrobenzene because bromo group is *ortho/para* orienting.



However, if we want to prepare *m*-bromonitrobenzene, we shall carry out the nitration first and then bromination, because the nitro group is *meta* orienting.



Similarly, if we plan to synthesize nitro derivatives of phenol, we must do it by nitration of phenol. Nitration of phenol can be carried out by using dilute or concentrated nitric acid. Nitration with dilute nitric acid gives mainly *ortho* and *para* mono-nitrophenols **(Section 16.8.5.2.7)**, but if we are using concentrated nitric acid, reaction cannot be stopped at mono-nitration stage and we get 2,4,6-trinitrophenol.



Society, Technology And Science

We use many hydrocarbons in our daily life. Natural gas which is a mixture of gaseous hydrocarbons used as fuel for domestic purposes and also for vehicles. Propane and butane are gases at room temperature and pressure, but they are easily liquefied at room temperature under moderate pressure and sold under the name of liquefied petroleum gas (LPG). Propane and butane have largely replaced by chlorofluorocarbons (Freons) as propellants in aerosol cans due to negative impact of CFC's on ozone layer. Butane is also used in cigarette lighter and portable stoves. Acetylene and Propyne are used as fuel for welding torches. Gasoline, diesel and kerosene oil that we use in our daily life are also mixtures of various hydrocarbons. Alkanes with more than 16 carbon atoms are most often used as lubricating. Paraffin wax is also used in a variety of industries. In solid form, hydrocarbons take the form of asphalt used in road constructions. Polymeric hydrocarbons like polyethylene, is used for making various things. e.g garbage containers, plastic bottles, packaging material, toys and bulletproof vests.

Key Points

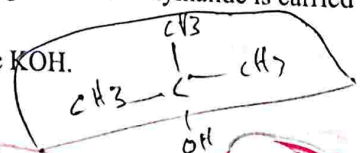
- Aliphatic hydrocarbons include the alkanes, alkenes and alkynes, which may be open chain (acyclic) or closed chain (cyclic).
- Aromatic hydrocarbons include benzene and those compounds which resemble benzene.
- Alkanes are open chain saturated hydrocarbons, which can be represented by general formula C_nH_{2n+2}.
- The general formula of cycloalkanes is C_nH_{2n}.
- Homolysis is the chemical bond cleavage generating two free radicals.
- Heterolysis is chemical bond cleavage generating cation and anion.
- Electrophile is a reagent which can accept electron pair in a reaction.
- Nucleophile is a reagent which can donate electron pair in a reaction.
- Alkenes are unsaturated hydrocarbons which contain carbon–carbon double bond. They can be represented by general formula C_nH_{2n}.
- Alkenes undergo electrophilic addition reactions.
- Polymerization is the process by which small molecules chemically join together to form large molecules.

- In conjugated alkenes carbon atoms are linked alternatively by single and double bonds.
- Compounds having the same molecular formula but different structures are known as 'isomers' and this phenomenon is called "Isomerism".
- Tautomerism is a special type of functional group isomerism, in which isomers are in dynamic equilibrium with each other.
- Stereoisomerism is caused by different arrangements of atoms or groups in space.
- A carbon atom which is bonded to four different atoms/groups is called chiral carbon.
- Alkynes contain carbon-corbon triple bond. They can be represented by general formula C_nH_{2n-2}.
- Benzene is aromatic hydrocarbon. Its molecular formula is C_6H_6.
- The representation of a real structure as a weighted average of two or more contributing structures is called resonance.
- The contributing structures are called canonical forms and real structure is called resonance hybrid.
- Electrophilic aromatic substitution reactions are those in which hydrogen of benzene is replaced by an electrophile.
- Carbocation contains a positive charge on carbon atom.
- The substituents which direct the second substituent to *ortho* and *para* position simultaneously are called *ortho/para* directing.
- The substituents which direct the second incoming substituent to *meta* position are called *meta*-directing.

Exercise

Q I. Choose the correct one from the given options.

1. The number of possible isomers for an alkane having the molecular formula C_5H_{12} is
   a. 2 b. 3 c. 4 d. 5
2. 2,2,3,3-terabromobutane when heated with zinc dust, yields
   a. but–1–yne b. but–2–yne
   c. isobutylene d. pent–1–yne
3. But–2–yne can be converted into *cis*–but–2–ene by using
   a. H_2/Ni b. Lindlar's catalyst
   c. Na/liq. NH_3 d. Zn/HCl
4. When excess of HCl is added to acetylene, the product is
   a. vinyl chloride. b. ethyl chloride.
   c. 1,2-dichloroethane. d. 1,1–dichloroethane.
5. The homolytic fission of C-H bond in an alkane results in
   a. carbanion. b. carbocation.
   c. alkyl free radical. d. all of these.
6. The groups that deactivate benzene ring and is *o/p*-directing
   a. $-NH_2$ b. $-OH$ c. $-OCH_3$ d. $-Cl$
7. Alkene that can be expected to exhibit geometrical isomerism
   a. but–1–ene b. 2–methylbut–2–ene
   c. 2–methylpropene d. none of these
8. How many isomers are possible for C_2H_6O?
   a. 2 b. 4 c. 8 d. 5
9. Addition of HBr to isobutylene mainly gives
   a. n–butyl bromide. b. isobutyl bromide.
   c. sec–butyl bromide. d. tert–butyl bromide.
10. An alkene upon ozonolysis yield a mixture of acetone and acetaldehyde. The alkene is
    a. isobutylene b. but–2–ene
    c. 2–methylbut–2–ene d. pent–2–ene
11. Dehydrohalogenation of alkylhalide is carried out in presence of
    a. Zn dust. b. conc. H_2SO_4.
    c. alcoholic KOH. d. aqueous KOH.



12. Which of the following molecules contain chiral center?
    a. *n*–butyl bromide b. isobutyl bromide
    c. sec–butyl bromide d. tert–butyl bromide
13. In the following reaction $C_6H_5CH_3 + Cl_2 \xrightarrow{\text{U.V. light}} C_6H_5CH_2Cl + HCl$, what type of reaction has taken?
    a. Electrophilic substitution b. Electrophilic addition
    c. Free radical substitution d. Free radical addition
14. A compound when treated with sodium amide yields a salt. The compound is
    a. C_2H_4 b. C_3H_4 c. C_6H_6 d. C_6H_{12}
15. Nitrobenzene reacts with chlorine in presence of $AlCl_3$. The major product obtained is
    a. o–chloronitrobenzene. b. m–chloronitrobenzene.
    c. p–chloronitrobenzene. d. no reaction occurs at all.

Q2. Write short answers of the following questions.

i. What is the difference between aliphatic and aromatic hydrocarbons?
ii. What is plane polarized mono chromatic light?
iii. How do you detect the unsaturation in alkenes?
iv. Why benzene is less reactive than ethene but more reactive than ethane?
v. Why halogens are deactivating groups although they are *ortho/para* directing?
vi. What is the basic difference between a chiral carbon and chirality?
vii. Why there are no geometrical isomers of but-1-ene?
viii. Why cyclopropane is more reactive than propane?
ix. How can you distinguish 1-alkyne from other non-terminal alkynes?
x. What is the main difference between tautomerism and resonance?

Q3. Write detail answers of the following questions.

1. (a) Describe the mechanism of chlorination of methane in detail.
   (b) Explain the structure and reactivity of cycloalkanes.
   (c) Write down the physical properties of alkanes and cycloalkane.
2. (a) What are hydrocarbons? Explain the different classes of hydrocarbons.
   (b) Give methods for preparation of ethene from;
   (i) ethyl alcohol (ii) ethyl bromide
   (c) Explain the relative stabilities of different alkenes.
3. (a) Describe any two methods for preparation of alkynes.
   (b) Discuss the acidity of terminal alkynes. How terminal alkynes can be distinguished from non-terminal alkynes.

(c) Starting from an alkene how would you prepare the following compounds?

(i) Vicinal dihalide (ii) Alcohol

(iii) Aldehydes and ketones (iv) Epoxide

4. (a) Describe the structure of benzene on the basis of MOT.

(b) Describe mechanism of electrophilic substitution reaction benzene.

(c) How would you prepare the following compounds from benzene?

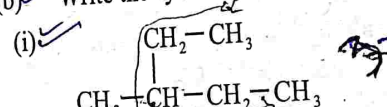
(i) Acetophenone (ii) Toluene

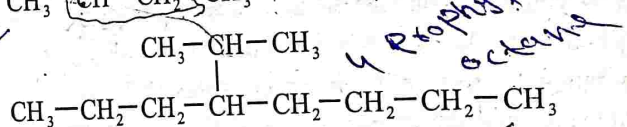
(iii) Nitrobenzene (iv) Benzenesulphonic acid

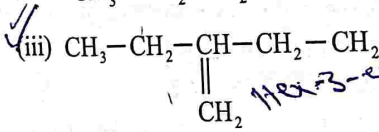
(v) Chlorobenzene (vi) Cyclohexane

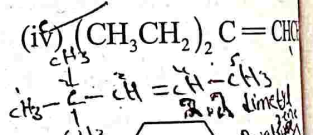
5. (a) Explain the directing and activitating effect in mono substituted benz derivatives.

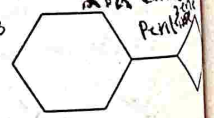
(b) Write the systematic names for the following organic compounds.

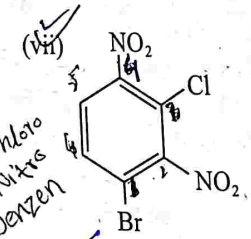
(i) 

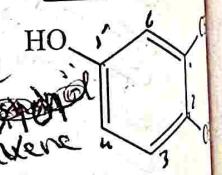
(ii) 

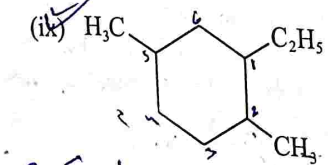
(iii) 

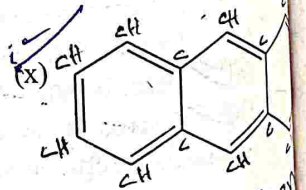
(iv) 

(v) $(CH_3)_3C-C\equiv C-CH(CH_3)CH_2CH_3$ (vi) 

(vii) 

(viii) 

(ix) 

(x) 

(a) Draw the structural formula of the following organic compounds.

i. 3–ethyl–4–methyloctane ii. 4–isopropyldecane

iii. *sec*-butylcycloheptane iv. 2,3–dimethyl–4–propylnonane

iv. 2,4,4–trimethylhex–2–ene v. cis–hex–3–ene

vi. phenanthrene viii. 1,2–dimethyl–4–propylbenzene

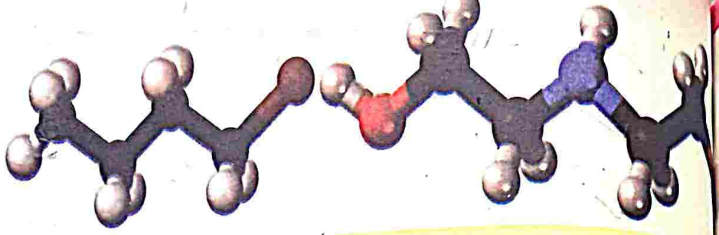
vii. hex-2-yne ix. cyclopropylbenzene

Project

Set up one small test tube in a test tube rack in the hood. Add 10 mg of a solid or 10 mL of a liquid organic compound containing carbon-carbon double bond. Add 1-3mL of distilled water (if compound is water soluble) or carbon tetrachloride (if compound is water insoluble), shake the mixtures for 2 minutes. Add bromine water reagent (5mL of bromine dissolved in 100 mL of water) for water soluble compound, or bromine in CCl_4 (5mL of bromine dissolved in 100mL of CCl_4) for water insoluble compound, drop by drop. Do not add an excess of the bromine reagent. The bromine reagent is brown or yellow-brown in color. Observe the dissipation of the brownish color of bromine.

Unit

17

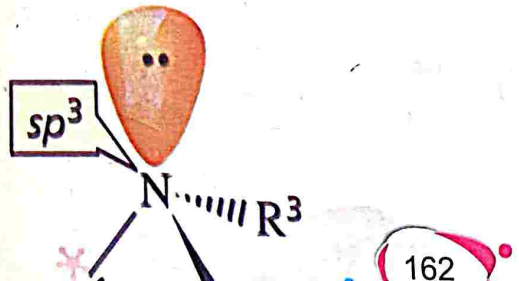


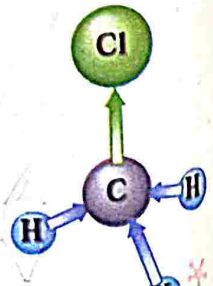
Alkyl Halides and Amines

Teaching	Assessment	Weightage %
11	1	8

After studying this unit, 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 radical halogenations of alkanes. (Applying)
- Describe the mechanism and types of nucleophilic substitution reactions. (Understanding)
- Describe the mechanism and types of elimination reactions. (Understanding)
- Describe the preparation and reactivity of Grignard's reagent. (Applying)
- Discuss chemistry of Grignard's reagents by the addition of aldehydes, ketones, esters carbon dioxide. (Understanding)
- Discuss nomenclature, structure and basicity of amines. (Applying).
- Describe the preparation of amines by alkylation of ammonia with RX and reductio nitriles, nitro and amide functional groups. (Applying).
- Discuss the reactivity of amines. (Applying)
- Describe the chemistry of amines by alkylation of amines with RX, reactions with aldeh ketones, preparation of amides and diazonium salts. (Applying).
- Describe isomerism of alkyl halides and amines. (Understanding)





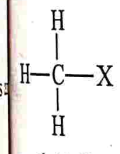
Introduction

17.1 Alkyl Halides

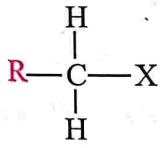
Halogen derivatives of alkanes are called haloalkanes. Haloalkanes are formed by replacing one or more hydrogen atoms from alkanes by halogens. They are also called organohalogen compounds. Haloalkanes may be monohaloalkanes, dihaloalkanes, trihaloalkanes etc., depending upon the number of halogen atoms present in the molecule.

Monohaloalkanes are usually called alkyl halides. The functional group of alkyl halides is halogen. They are represented by R–X, where R- is an alkyl group represented by C_nH_{2n+1} and –X is halogen which is the functional group. The general formula of alkyl halides is $C_nH_{2n+1}X$, where n represents the number of carbon atoms.

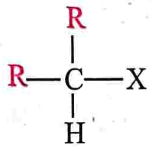
Alkyl halides are classified according to the nature of the carbon atom bonded to the halogen. If the halogen-bearing carbon is bonded to one carbon atom, it is primary (1°) and the alkyl halide is a primary alkyl halide. If two carbon atoms are bonded to the halogen-bearing carbon, it is secondary (2°) and the compound is a secondary alkyl halide. A tertiary alkyl halide (3°) has three other carbon atoms bonded to the halogen–bearing carbon atom. If the halogen-bearing carbon atom is a methyl group (bonded to no other carbon atoms), the compound is a methyl halide.



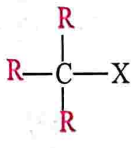
methyl halide



primary (1°) alkyl halide



secondary (2°) alkyl halide



tertiary (3°) alkyl halide

17.1.1 Nomenclature

There are two ways of naming alkyl halides. The common (trivial) system and systematic (IUPAC) nomenclature.

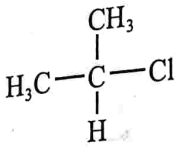
(a) Common system

Common or "trivial" names are constructed by naming the alkyl group followed by the term halide. This is the origin of the term alkyl halide. Common names are useful only for simple alkyl halides, such as the following:

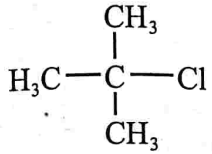
CH_3-Cl methyl chloride

CH_3-CH_2-Cl ethyl chloride

$CH_3-CH_2-CH_2-Cl$ n-propyl chloride



isopropyl chloride



tert-butyl chloride

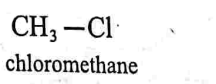
The two alkyl halides, n-propyl chloride and isopropyl chloride, given above example of position isomers.

(b) IUPAC System

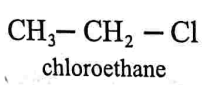
The systematic (IUPAC) nomenclature treats an alkyl halide as an alkane with a hal substituent: Fluorine is fluoro–, chlorine is chloro–, bromine is bromo–, and iodine iodo–. The result is a systematic haloalkane name. The following steps should followed for naming alkyl halides.

1. Select the longest continuous chain of carbon atoms, containing the halogen ato
2. Number the chain from the end closer to halogen atom. If both alkyl and halog are present in a molecule then number the chain from the end closer to alkyl gro or halogen atom.
3. Indicate the position of halogen and alkyl group by suitable locants.
4. Prefix di, tri, tetra etc. is used to indicate the number of halogen atoms.
5. If two different halogen atoms are present in a molecule at same position from two ends, the one to be assigned the lower locant is that one cited first alphabetical order. When an alkyl and halogen occupy equivalent positions, ag number the chain from the end to give lowest number to one that comes first alphabetical order.

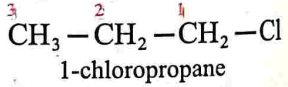
Examples



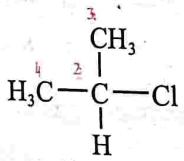
chloromethane



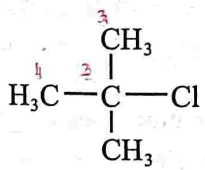
chloroethane



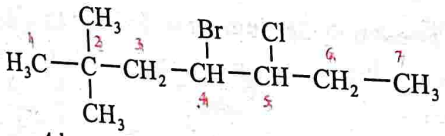
1-chloropropane



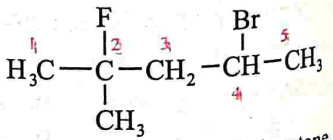
2-chloropropane



2-chloro-2-methylpropane



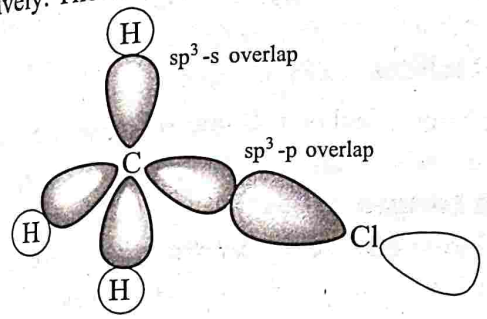
4-bromo-5-chloro-2,2-dimethylheptane



4-bromo-2-fluoro-2-methylpentane

17.1.2 Structure of Alkyl Halides

To understand the structure of alkyl halides, let us consider methyl chloride as an example. In this molecule the carbon atom is sp^3-hybridized and all the bonds of carbon are *sigma*. During the process of bond formation, one sp^3–hybrid orbital of carbon atom overlaps with the half-filled *p* orbital of chlorine atom and form carbon-chlorine *sigma* bond, while the remaining three sp^3-hybrid orbitals overlap with 1s orbitals of three hydrogen atoms and form three carbon-hydrogen sigma bonds **(Figure 17.1)**. The bond lengths of carbon-chlorine and carbon-hydrogen bonds are 178 pm and 108 pm respectively. The H–C–H and H–C–Cl bond angles are approximately equal to 109.5°.



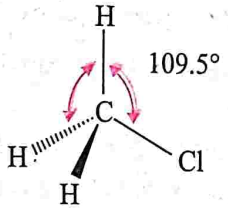


Figure 17.1 Orbital hybridization model of bonding in methyl chloride

17.1.3 Physical Properties

- Lower alkyl halides such as methyl fluoride, methyl chloride, methyl bromide, ethyl fluoride, ethyl chloride and propyl fluorides are gases at room temperature. Mostly higher n-alkyl halides up to C_{16} are liquids and above are solids.
- They have higher boiling points than the corresponding alkanes. For a given alkyl group the boiling points of alkyl halides increase with increasing size of the halogen atom, while for a given halogen atom the boiling points of alkyl halides increase with the increasing size of the alkyl group. For isomeric alkyl halides, the compound with the more highly branched alkyl group normally has the lowest boiling point.
- They are usually insoluble in water due to their inability to form hydrogen bonding with water. They are soluble in organic solvents.
- Alkyl chlorides and alkyl fluorides are lighter than water while alkyl iodides and alkyl bromides are denser than water. A mixture of an alkyl halide and water separates into two layers. When the alkyl halide is a fluoride or chloride, it is the upper layer and water is the lower. The situation is reversed when the alkyl halide is a bromide or an iodide.

Table 7.1 Boiling Points of Alkyl Halides

Name	Boiling Point (°C)			
	$X = F$	$X = Cl$	$X = Br$	$X = I$
methyl halide	–78	–29	–4	42
ethyl halide	–38	13	38	72
n-propyl halide	–2	47	71	102
n-butyl halide	32	78	101	130
isopropyl halide	–9	34	59	89
isobutyl halide	25	69	91	120

17.1.4 Preparation of Alkyl Halides

Alkyl halides can be prepared by different methods. Some of these are given under.

17.1.4.1 Reaction of alcohols with halogen halides

Alcohols react with halogen acids to form alkyl halides by replacement of hydroxyl group with halogen atom.

$$\underset{\text{alcohol}}{R-OH} + \underset{\text{halogen acid}}{H-X} \longrightarrow \underset{\text{alkyl halide}}{R-X} + H_2O$$

Reactivity of halogen acid increases with acid strength. In case of hydrogen chloride, anhydrous zinc chloride is used as catalyst while treating alcohol to produce alkyl chlorides. Tertiary alcohols are more reactive while primary alcohols are least reactive.

$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} + H-Br \longrightarrow \underset{\text{ethyl bromide}}{CH_3-CH_2-Br} + H_2O$$

$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} + H-I \longrightarrow \underset{\text{ethyl iodide}}{CH_3-CH_2-1} + H_2O$$

$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} + H-Cl \xrightarrow{\text{anhydrous } ZnCl_2} \underset{\text{ethyl chloride}}{CH_3-CH_2-Cl} + H_2O$$

17.1.4.2 Reactions of Alcohols with other Halogenating Agents ($SOCl_2$)

Conversion of alcohol to alkyl halides with halogen acid, has some limitations. In some cases, a side product is also formed due to rearrangement of intermediate carbocation. Secondly, alkenes are also formed as side product due to possible dehydration of alcohols **(Section 16.5.5.1)**. The formation of these side products can be avoided by the use of phosphorus trihalides or thionyl chloride to replace hydroxyl group with halogens.

a. Reaction of alcohol with phosphorous trihalides

Alcohols when treated with phosphorous trihalides, yield corresponding alkyl halides.

$$\underset{\text{alcohol}}{3R-OH} + \underset{\text{phosphorous trihalides}}{PX_3} \longrightarrow \underset{\text{alkyl halide}}{3R-X} + H_3PO_3$$

$$\underset{\text{methyl alcohol}}{3CH_3-OH} + PCl_3 \longrightarrow \underset{\text{methyl chloride}}{3CH_3-Cl} + H_3PO_3$$

$$\underset{\text{ethyl alcohol}}{3CH_3-CH_2-OH} + PBr_3 \longrightarrow \underset{\text{ethyl bromide}}{3CH_3-CH_2-Br} + H_3PO_3$$

Phosphorous tribromide and phosphorous triiodide are produced in situ by the reaction of red phosphorous with bromine and iodine respectively.

Tidbit

In chemistry, *in situ* typically means "in the reaction mixture''. Some of the reactants are produced *in situ* or in the reaction mixture, because they may be unstable or toxic, if synthesized outside of the reaction mixture.

b. Reaction of alcohols with thionyl chloride

Alcohols react with thionyl chloride in the presence of pyridine to yield the corresponding alkyl chlorides. Pyridine being a base absorbs hydrogen chloride just after its production in the reaction mixture.

$$\underset{\text{alcohol}}{R-OH} + \underset{\text{thionyl chloride}}{SOCl_2} \xrightarrow{\text{pyridine}} \underset{\text{alkyl chloride}}{R-Cl} + SO_2 + HCl$$

$$\underset{\text{methyl alcohol}}{CH_3-OH} + SOCl_2 \xrightarrow{\text{pyridine}} \underset{\text{methyl chloride}}{CH_3-Cl} + SO_2 + HCl$$

$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} + SOCl_2 \xrightarrow{\text{pyridine}} \underset{\text{ethyl bromide}}{CH_3-CH_2-Cl} + SO_2 + HCl$$

17.1.4.3 Free-Radical Halogenations of Alkanes

Alkanes react with halogens in the presence of ultraviolet light or at high temperature, to yield alkyl halides. In this process one or more hydrogen atoms of alkanes are replaced by halogens giving a mixture of different haloalkanes **(Section 16.3.2)**. That is why it is not a good method for preparation of pure alkyl halides.

17.1.5 Reactivity of Alkyl halides

Alkyl halides are reactive due to the polar nature of carbon-halogen ($C^{+\delta} - X^{-\delta}$) bond. The polarity is due to higher electronegativity of halogen than carbon atom, and therefore α–carbon of alkyl halides is electrophilic in nature.

The halogen atom is a good leaving group and detaches from carbon atom, with its bonding electron pair to form a stable halide ion. When a nucleophile attacks on α–carbon and replaces the halide ion, the reaction is a **nucleophilic substitution**. When the halide ion leaves along with another atom (often H) from the adjacent carbon atom, it forms a new *pi* bond, the reaction is an **elimination**. In elimination reactions, a molecule of HX is lost from the alkyl halide to give an alkene. These elimination reactions are called dehydrohalogenation **(Section 16.5.5.2)**, because a hydrogen halide has been removed from the alkyl halide. Substitution and elimination reactions often compete with each other **(Section 17.1.8)**.

Tidbit

Besides alkyl halides, many other types of compounds undergo substitution and elimination reactions. Substitutions and eliminations are introduced in this unit using the alkyl halides as examples. In unit 18, we encounter substitutions and eliminations in alcohols.

The strength of carbon–halogen bond decreases down the group from fluorine to iodine. This can be explained on the basis of their bond energies that are given in the Table **17.1**. The table shows that iodo compounds are most reactive while fluoro compounds are least reactive. Therefore, the reactivity of alkyl halides increases from fluorine to iodine and the reactivity order is; R–I > R–Br > R–Cl > R–F.

Table 17.1 Bond Energies of Carbon-Halogen Bond

Bond	Bond Energy (kJ/mol)
C–F	467
C–Cl	346
C–Br	290
C–I	228

17.1.6 Nucleophilic Substitution (S_N) Reactions

17.1.6.1 General Introduction

Alkyl halides undergo nucleophilic substitution reactions in which a stronger nucleophile replaces the halide ion **(Section 16.1.5)**. A general example of such a reaction is given as;

$$\underset{\text{alkyl halide}}{R\text{–}X} + \underset{\text{nucleophile}}{\ddot{\overline{N}}u} \longrightarrow \underset{\text{product}}{R\text{—}Nu} + \overline{X}$$

Alkyl halides undergo nucleophilic substitution reactions by two different types of mechanisms i.e. unimolecular (S_N1) and bimolecular (S_N2) nucleophilic substitution.

17.1.6.2 Important Concepts

17.1.6.2.1 Substrate and Leaving Group

The molecule which undergoes nucleophilic substitution reaction is called substrate. The group or species which leaves the substrate or which is being replaced by the incoming nucleophile is called leaving group or nucleofuge. In the above reaction, alkyl halide is substrates and halogen (halide ion) is the leaving group.

$$\underset{\text{alkyl halide (substrate)}}{R\text{–}X} + \underset{\text{nucleophile}}{\ddot{\overline{N}}u} \longrightarrow \underset{\text{product}}{R\text{—}Nu} + \underset{\text{halide ion (nucleofuge)}}{\overline{X}}$$

17.1.6.2.2 Nucleophile and Base

Any species neutral or negatively charged with an unshared pair of electrons can act both as a base and a nucleophile. Nucleophile is a species which donates electron pair to an electrophilic center in a molecule and undergoes nucleophilic substitution or addition reactions. A nucleophile is generally represented by $\ddot{\overline{N}}u$. The strength of nucleophile is called nucleophilicity and is a measure of how fast a nucleophile displaces a leaving group from a suitable substrate.

But a base is a species which has affinity for proton, and donate electron pair to a proton in a reaction, and generally represented by $\ddot{\overline{B}}$. Base give elimination reaction in alkyl halides. The strength of base is called basicity and represented in terms of equilibrium constant for abstraction of a proton.

17.1.6.2.3 Carbocations and their Stability

A carbocation is an ion in which a carbon atom has a positive charge and three bonds. Carbocation is formed when an electrophile adds to carbon-carbon double bond or when halogen atom detaches from the carbon atom of an alkyl halide as halide ion. The positive carbon of alkyl carbocation is sp^2-hybridized and has trigonal planar structure, with empty unhybridized *p* orbital perpendicular to the plane, as shown in **(Figure 17.2)**.

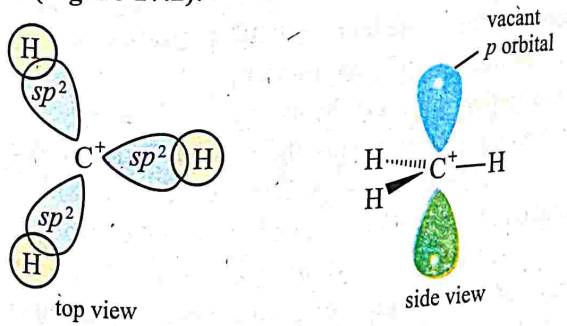


Figure 17.2 Trigonal planar structure of methyl cation.

Carbocations are classified as primary, secondary, or tertiary according to the number of carbons (alkyl groups) that are directly attached to the positively charged carbon. Primary alkyl halides produce primary carbocations while secondary and tertiary alkyl halides yield secondary and tertiary carbocations respectively.

Alkyl groups directly attached to the positively charged carbon stabilize a carbocation through its electron donating effect. Thus tertiary carbocations are more stable than secondary and secondary are more stable than primary ones. This stabilization comes from the stabilization of the positive charge of the carbocation by the electron donating alkyl groups directly attached. **(Figure 17.3)**

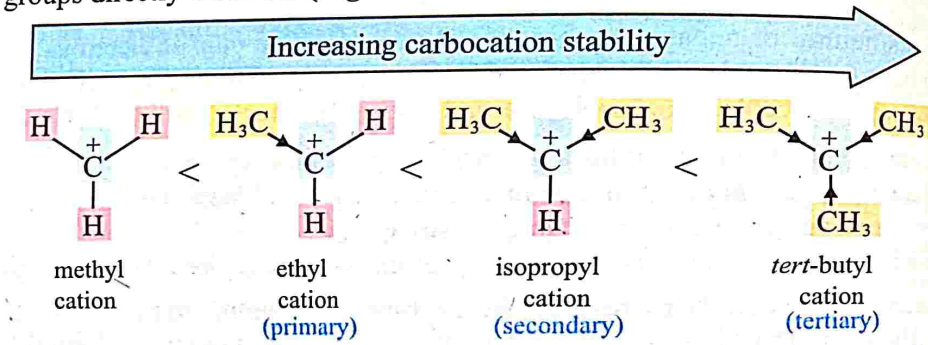
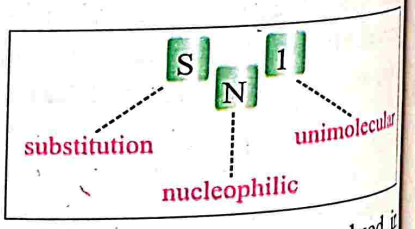


Figure 17.3 Realtive stability order of different types of carbocations.

Mechanisms of Nucleophilic Substitution reactions

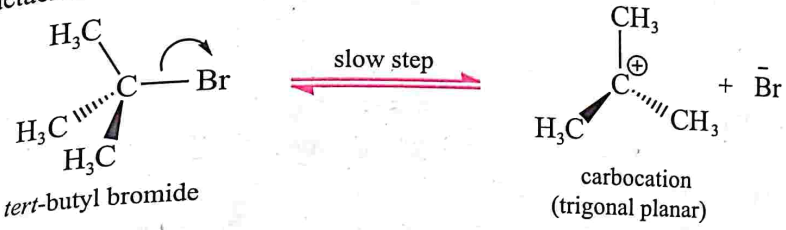
Alkyl halides can undergo nucleophilic substitution by two different types of mechanisms. The type of mechanism depends upon the nature of alkyl halides.

17.1.6.3 S_N1 Mechanism

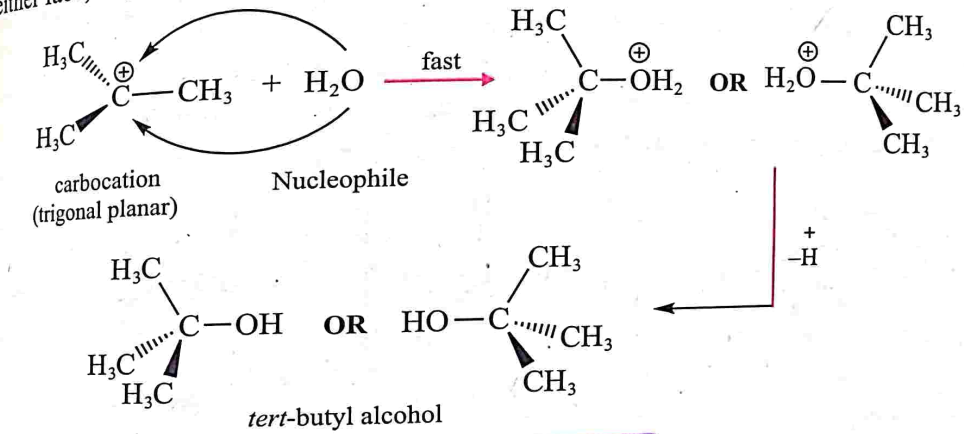


S_N1 stands for Substitution, Nucleophilic, unimolecular. It is a two-step mechanism. First step is slow (rate determining or rate limiting step) and involves the formation of intermediate carbocation by dissociation of alkyl halide or substrate. The term unimolecular means there is only one molecule involved in transition state of the *rate*-determing step. The second step is fast and involves the attack of nucleophile on planar carbocation and formation of product. S_N1 mechanism is generally followed by tertiary alkyl halides. As it involves the formation of carbocation, it is favored by highly ionizing polar solvents (having O–H, N–H bond). For example the hydrolysis of *tert*-butyl bromide follow S_N1 mechanism as shown below

Step–1: The substrate undergoes ionization and yield a carbocation. The bromine atom completely detaches from the substrate as bromide ion.



Step–2: In second step, the entering nucleophile attacks the planar carb either face, to produce the end product.



The kinetic studies have shown that reactions proceeding through S_N1 mechanism follow the first order kinetics. The rate of reaction depends only upon the concentration of substrate. The rate equation for above reaction is;

Tidbit

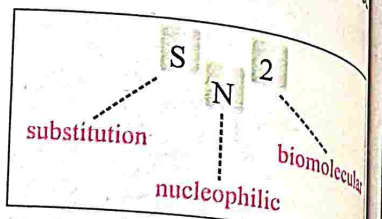
Two transition states are formed in S_N1 mechanism. One in first step during formation of intermediate, the other in second step during formation of product from intermediate.

$$\text{rate} = k\,[(CH_3)_3CBr]$$

The intermediate carbocation is planar, the nucleophile attack from either side. If a nucleophile attacks the carbocation from the side of the leaving group, the product molecule shows retention of configuration. Attack from the side opposite to leaving group, gives a product molecule showing inversion of configuration. If the reactant is chiral, mixture of two *enantiomers* **(Section 16.6.5)** are produced, called racemic mixture and this process is called racemization. Racemization is simply a combination of retention and inversion. However in S_N1, the product is rarely completely racemic

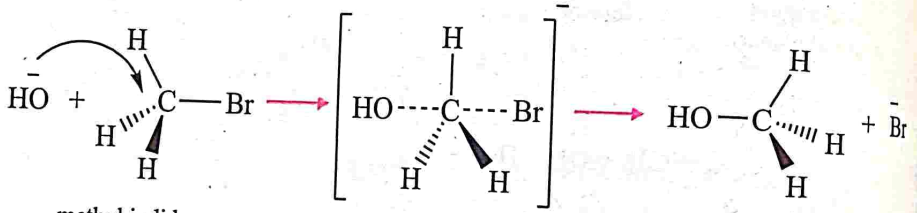
and there is often more inversion than retention of configuration. This is also called partial racemization.

17.1.6.4 S_N2 Mechanism



The abbreviation **S_N2** stands for **S**ubstitution, **N**ucleophilic, bimolecular. It is a single step concerted mechanism, with bonds breaking and forming at the same time. The entering nucleophile attacks the electrophilic carbon atom of the substrate before the leaving group departs. The middle structure is a transition state, rather than an intermediate. The term bimolecular means that the transition state of the rate-limiting step (the only step in this reaction) involves the collision of two molecules (or ions).

This mechanism is generally followed by primary alkyl halides and methyl halides. For example, the reaction of hydroxide ion with methyl bromide to form methyl alcohol follow S_N2 mechanism, shown below.



methyl iodide — transition state — methyl alcohol

It is clear from the above one-step mechanism, that entering nucleophile can attack only from the back side because the front side is blocked by the halogen atom. In the transition state, carbon–bromine bond begins to break as the carbon–oxygen bond begins to form. In other words, the extent of bond formation on one side is equal to the extent of bond breaking on the other side.

This one-step mechanism is supported by kinetic information. The rate is found to double when the concentration of either reactant (nucleophile and substrate) is to be doubled. The reaction is, therefore, first order in each of the reactants and second order overall. The rate equation has the following form:

$$\text{rate} = k\,[CH_3Br][^-OH]$$

Back-side attack of nucleophile literally turns the tetrahedron of the carbon atom inside out. In the product, the nucleophile assumes a stereochemical position in space, opposite to the position of the leaving group originally occupied. This is called inversion of configuration at the carbon atom, shown in above reaction. S_N2 mechanism is generally favored by polar aprotic solvents.

The type of mechanism followed by the secondary alkyl halides is governed by the nature of the solvent. If polar protic solvent is present, they follow S_N1 mechanism, while in polar aprotic solvents, S_N2 mechanism is followed.

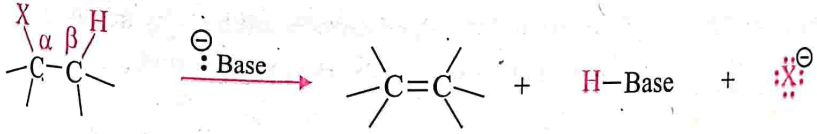
Table 17.2 Summary of Nucleophilic Substitution in Alkyl Halides

Factors and characteristics	S_N1	S_N2
Promoting factors		
Nucleophile	Weak Nucleophile	Strong Nucleophile
Substrate	3° > 2°	$CH_3X > 1° > 2°$
Solvent	Polar protic	Polar aprotic
Characteristics		
Kinetics	First Order	Second Order
Stereochemistry	Inversion and retention	Inversion

17.1.7 1,2-Elimination Reactions

17.1.7.1 Overview

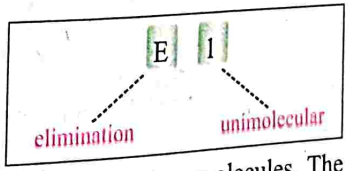
We have already discussed that alkyl halides undergo substitution as well as elimination reactions in **(Section 17.1.5)**. When treated with a strong base, an alkyl halide can undergo a type of elimination process, called 1,2-elimination, also known as β-elimination, in which a proton is removed from the β position, the halide is ejected as a leaving group from the α position and a double bond is formed between the α and β positions:



Alkene

Alkyl halides undergo elimination reactions by two different types of mechanisms.

17.1.7.2 E1 Mechanism

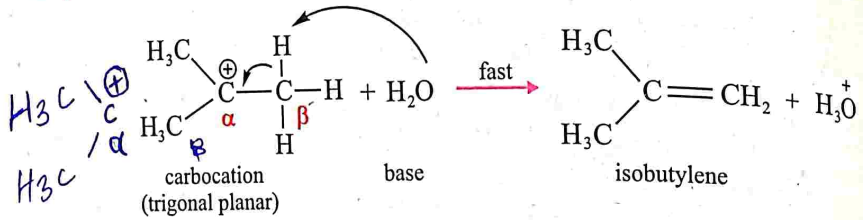


The abbreviation **E1** stands for **E**limination, unimolecular. The mechanism is called unimolecular because the rate-limiting transition state involves a single molecule rather than a collision between two molecules. The slow step of an E1 reaction is the same as in the S_N1 reaction: unimolecular ionization

to form a carbocation. In a fast second step, a base abstracts a proton from the carb atom adjacent to the positive carbon (β-carbon). These reactions are usually follow by *tertiary* alkyl halides, like S_N1 reactions. For example, reaction of *tert*-butyl bromi with water, upon β-elimination yield isobutylene.

Step–1: The first step is similar to S_N1 **(Section 17.1.6.3)**

Step–2: The base abstracts β-hydrogen of carbocation and yield isobutylene.

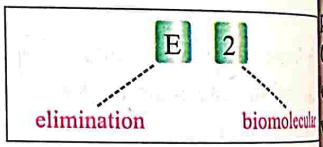


Because the rate-limiting step involves unimolecular ionization of the alkyl halide, t rate equation is first-order. The rate depends only on the concentration of the al halide and not on the concentration of the base.

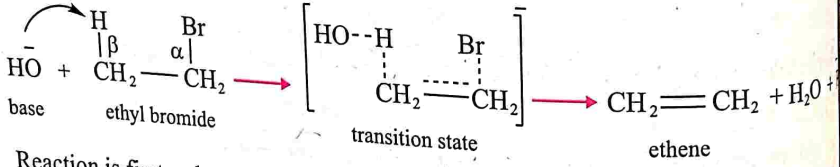
$$\text{rate} = k\,[\text{R–X}] \quad \text{or} \quad \text{rate} = k\,[(CH_3)_3C\text{–Br}]$$

17.1.7.3 E2 Mechanism

This is a bimolecular elimination process, with both the base and the alkyl halide participating in the transition state, so this mechanism is abbreviated **E2** for **E**limination, bimolecular. These are generally followed by primar alkyl halides. These reactions are completed in one step like S_N2 reactions.



For example, reaction of ethyl bromide with hydroxide ion to form ethene follow mechanism. The removal of proton from the **β**-carbon atom by hydroxide base and t removal of bromide ion from the **α**-carbon atom takes place simultaneously.



Reaction is first order with respect to each reactant, and second order overall.

$$\text{rate} = k\,[\text{substrate}]\,[\text{base}] \quad \text{or} \quad \text{rate} = k\,[CH_3CH_2Br][^-OH]$$

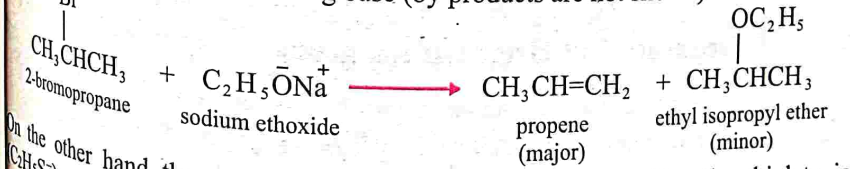
Table 17.3 Summary of Elimination Reactions in Alkyl Halides

Reaction	E1	E2
Promoting factors		
Base	Weak Base	Strong Base
Substrate	$3^\circ > 2^\circ$	$1^\circ > 2^\circ$
Solvent	Polar protic	Polar aprotic
Characteristics		
Kinetics	First Order	Second Order

17.1.8 Substitution versus Elimination

We have studied that an alkyl halide and a Lewis base can react together in either a substitution or an elimination reaction **(Section 17.1.5)**. Substitution and elimination reactions are very often in competition with each other. Two important factors i.e. nature of alkyl halide and nature of Lewis base, play a key role in deciding whether a principal reaction would be elimination or substitution. Crowding around the α–carbon in molecule of substrate generally favours elimination over substitution reaction. This is due to the greater steric hindrance when the nucleophile approaches towards α–carbon atom of the substrate. Thus, greater number of alkyl groups on the substrate favours elimination over substitution because these alkyl groups stabilize the alkene more than the substitution product.

As all the bases are also nucleophiles, the competition between substitution and elimination reactions is determined by the fact whether it is a better base or a better nucleophile. A stronger base will favour elimination while a stronger nucleophile will favour substitution in the same substrate. For example, 2–bromopropane on reaction with ethoxide ion ($C_2H_5O^-$) undergoes elimination and produces alkene as the major product because ethoxide is a strong base (by products are not shown).



On the other hand the same 2–bromopropane on reaction with ethanthiolate ion ($C_2H_5S^-$) undergoes substitution reaction because it is more nucleophilic and less basic than ethoxide ion.

$$\underset{\text{2-bromopropane}}{CH_3CH(Br)CH_3} + \underset{\text{sodium ethoxide}}{C_2H_5\bar{S}Na^+} \longrightarrow \underset{\text{propene (major)}}{CH_3CH=CH_2} + \underset{\text{ethyl isopropyl ether (minor)}}{CH_3CH(SC_2H_5)CH_3}$$

Other factors like temperature and nature of solvent, can also have some effect on the extent of elimination and substitution products.

17.2 Organometallic Compounds (Grignard Reagents)

All those organic compounds which contain at least one carbon–metal bond in their structures are known as organometallic compounds. You are already familiar with at least one organometallic compound, sodium acetylide ($Na^+C \equiv CH$), **(Section 16.7)** which has an ionic bond between carbon and sodium. Organometallic compounds are generally represented by the formula:

R–M or Ar–M

Where, M = Mg, Li, Hg, Cu, Pb, Zn etc. and R- and Ar- represent any alkyl or aryl groups respectively. They are named simply by adding the name of the metal to the organic group bonded directly to the metal. Examples;

CH_3-MgI (methylmagnesium iodide) $\quad (CH_3)_4Pb$ (tetramethyllead) $\quad CH_3-Zn-CH_3$ (dimethylzinc)

Alkyl or aryl magnesium halides (organomagnesium compounds) are commonly known as Grignard reagents. They were discovered, prepared and studied by Victor Grignard, therefore, they were named after him as Grignard reagents. They are highly reactive organic compounds, and are used in the synthesis of a large number of organic compounds. Due to this great achievement Grignard was awarded with Nobel Prize in 1912. The general formula of Grignard reagents is, R–MgX where R represent Alkyl group (can also be vinylic or aryl group) and X represent halogen atom.

Examples are;

$CH_3-Mg-Br$ (methylmagnesium bromide) $\quad CH_3-CH_2-Mg-Cl$ (ethylmagnesium chloride) $\quad C_6H_5-Mg-Br$ (phenylmagnesium bromide)

17.2.1 Preparation of Grignard Reagents

Grignard reagents are prepared in the laboratory by the action of alkyl or aryl halide on freshly prepared magnesium metal in anhydrous or dry ether i.e. diethyl ether or tetrahydrofuran.

$$\underset{\text{alkyl halide}}{R-X} + Mg \xrightarrow{\text{ether}} \underset{\text{Grignard reagent}}{R-MgX}$$

It is an example of heterogeneous reaction, in which solid magnesium react with alkyl halide in ether. Grignard reagent cannot be isolated, therefore, its ethereal solution is directly used in the synthetic reactions.

The ease of formation of Grignard reagent depends upon the nature of both alkyl and aryl group and the nature of halogen. Increasing size of the alkyl group makes the formation of Grignard reagent difficult. For the same alkyl group, the ease of formation increases down the group i.e. from fluorine to iodine. Alkyl magnesium fluorides and chloride are not obtained with good yield. Alkyl iodides are the most reactive but still bromides are used more commonly for preparation of Grignard reagent because bromides are less expensive and less toxic than iodides.

Diethyl ether used in the preparation of Grignard reagent plays two important roles. At one hand, it provides a medium for the reaction, at the other hand, it dissolves the Grignard reagent by the process of solvation. Crystalline Grignard reagent obtained by cooling ethereal solution of Grignard reagent, have been found to be dietherate in which magnesium has been coordinated with two molecules of ethers, in addition to having two covalent bonds. The four groups are arranged tetrahedrally around magnesium.

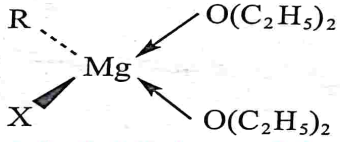


Figure 17.4 Tetrahedral dietherate of Grignard reagent.

17.2.2 Reactivity of Grignard Reagents

The carbon magnesium bond of Grignard reagent is polar in nature. This is due to higher electronegativity of carbon than magnesium. So the electronic density is lying close to carbon than magnesium. As a result of this electronegativity difference, the carbon atom has a partial negative while magnesium has a partial positive charge.

$$\overset{-\delta}{R}-\overset{+\delta}{Mg}X$$

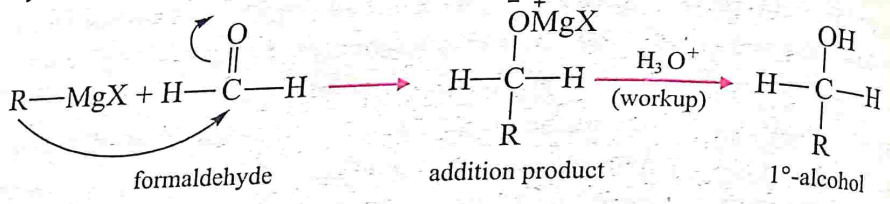
The alkyl group being an electron rich centre, acts as carbanion or nucleophile. It would attack polarized molecules at the point of low electronic density. Therefore, the characteristic reactions of Grignard reagents are nucleophilic substitution and nucleophilic addition reactions.

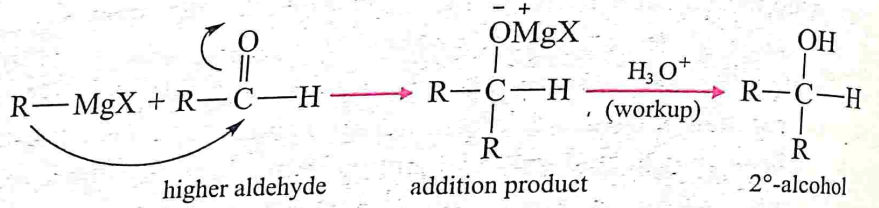
17.2.3 Reactions of Grignard Reagents

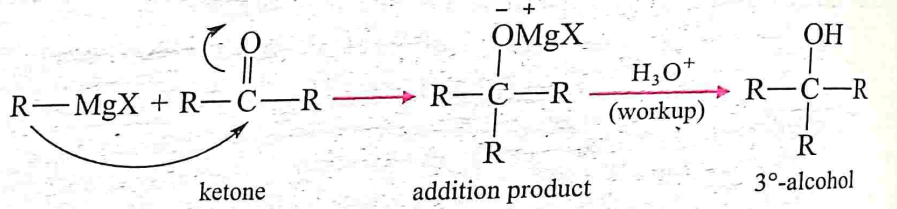
Grignard reagents are highly reactive compounds. Therefore, they react with many organic and inorganic compounds to produce a large number of valuable products. Some of these reactions are as follows.

17.2.3.1 Reactions with Aldehydes and Ketones

Grignard reagents react with aldehydes and ketones to yield addition products. Addition product upon workup with water or dilute acid solution yield alcohols. Formaldehyde produce primary alcohol, higher aldehydes produce secondary, while ketones produce tertiary alcohols on treatment with Grignard reagents.







Self-assessmnet

Write the reaction of methylmagnesium bromide with acetaldehyde and acetone, followed by acid workup. Also write the names of products.

17.2.3.2 Reactions with Esters

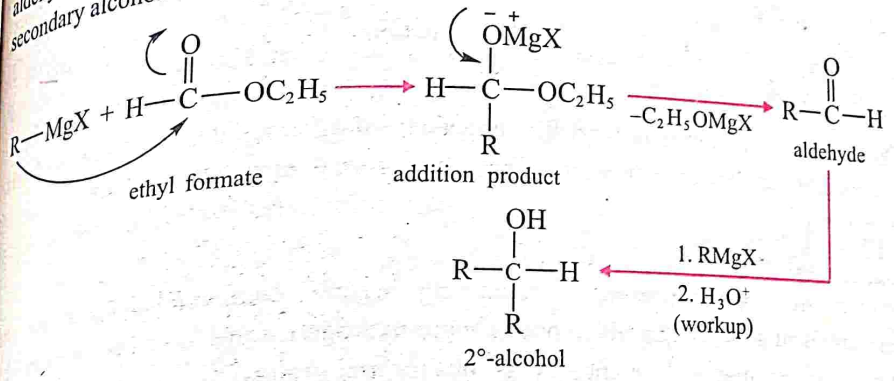
Grignard reagents react with esters to yield carbonyl compounds (aldehydes and ketones). These carbonyl compounds react with more of the Grignard reagent in the same reaction mixture and yield alcohols as the final products **(Section 17.2.3.1)**.

Tidbit

The second step, a "workup" with acid solution, occurs after our key Grignard reaction, and the remaining Grignard reagent is also destroyed by acid. Only water can also be used for workup.

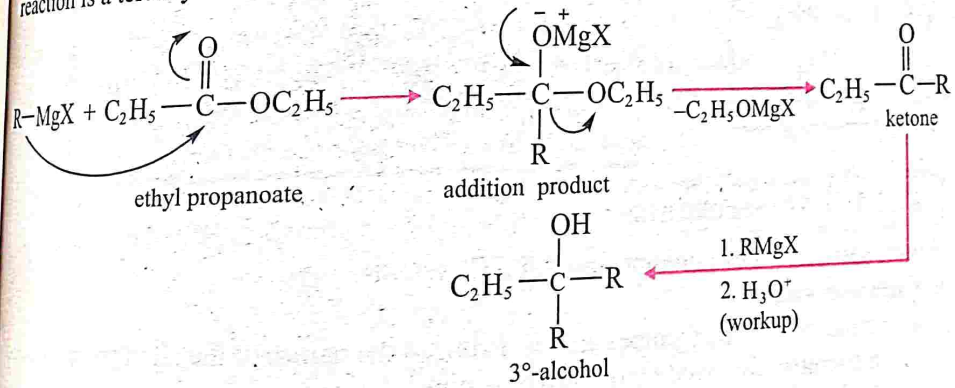
a. Reaction with esters of formic acid

Ester of formic acid is also called formate ester e.g. methyl formate, ethyl formate etc. Grignard reagent react with ethyl formate (or any other formate ester), yielding an addition product. Addition product undergoes elimination and forms an aldehyde. The aldehyde further reacts with another molecule of the Grignard reagent to yield a secondary alcohol as final product.



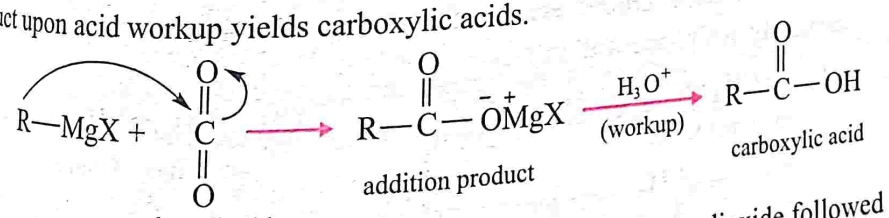
b. Reaction with esters of higher carboxylic acids

Ester of higher carboxylic acids yield tertiary alcohol as final product. For example, ethyl propanoate reacts in the same way as ethyl formate but the end product of this reaction is a tertiary alcohol, through intermediate ketone.

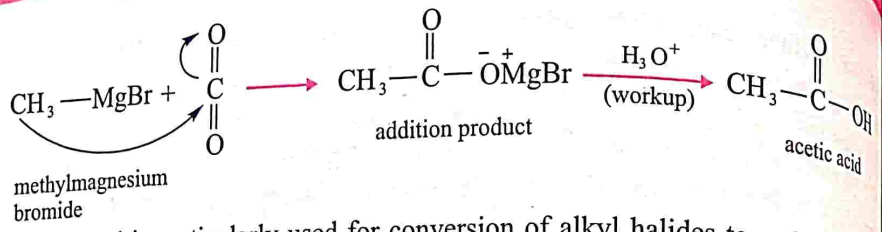


17.2.3.3 Reaction with carbon dioxide

Grignard reagents react with carbon dioxide forming an addition product. Addition product upon acid workup yields carboxylic acids.



For example methylmagnesium bromide upon addition to carbon dioxide followed by acid workup results acetic acid.

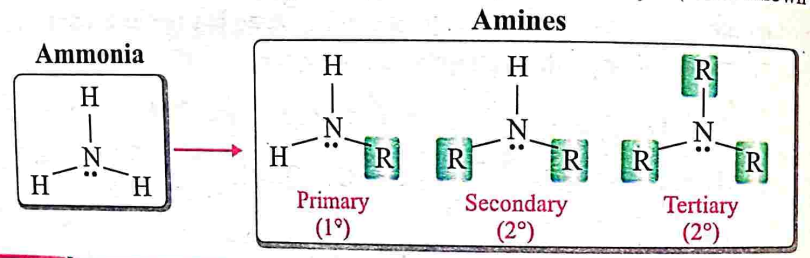


This method is particularly used for conversion of alkyl halides to carboxylic acids. The resulting carboxylic acids contain a carbon more than parent alkyl halide.

17.3 Amines

Amines are important nitrogen containing organic compounds. These are the derivatives of ammonia in which one or more hydrogen atoms have been replaced by one or more similar or different alkyl groups (or aryl groups).

On the basis of the number of alkyl or aryl groups directly bonded to nitrogen atom, amines have been classified into primary, secondary and tertiary amines shown below:



17.3.1 Nomenclature

Amines are named by common and IUPAC systems.

a. Common system

- Common names of amines are formed from the names of the alkyl groups bonded to nitrogen, followed by the suffix -amine.
- The prefixes di- and tri- are used to describe two and three identical substituents attached to nitrogen.
- If different alkyl groups are attached to the nitrogen, then they are named separately in alphabetical order.

$CH_3-CH_2-CH_2-NH_2$
n-propyl amine

$CH_3-CH_2-NH-CH_3$
ethyl methyl amine

$(CH_3)_3N$
trimethyl amine

$CH_3-N(CH_3)-C_2H_5$
ethyl dimethyl amine

b. IUPAC system

In IUPAC nomenclature of amines, the longest continuous chain of carbon atoms determines the root name. The *-e* ending in the alkane name is changed to suffix *-amine* and a number shows the position of the amino group along the chain. Other substituents on the carbon chain are given numbers, and the prefix *N-* is used for each substituent on nitrogen.

$CH_3-CH_2-CH_2-NH_2$
propan-1-amine

$CH_3-CH_2-NH-CH_3$
N-methylethanamine

$(CH_3)_2N-CH_2-CH_3$
N,*N*-dimethylethanamine

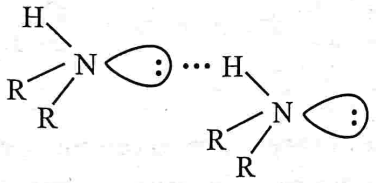
$CH_3-CH(NH_2)-CH(CH_3)-CH_3$
3-methylbutan-2-amine

Tidbit

Amines also possess metamerism. For example, ethyl methyl amine and trimethyl amine are metamers of each other.

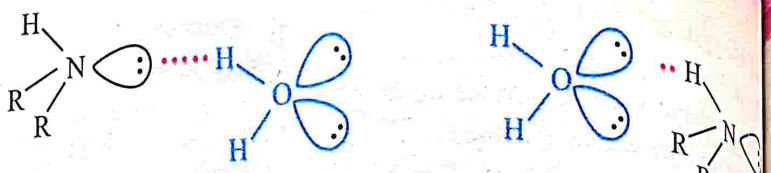
17.3.2 Physical Properties

- Low molecular weight amines are generally gases or low boiling liquids at room temperature. They possess a characteristic ammonia like smell.
- Amines have higher boiling points than alkanes of similar molecular weight due to the presence of intermolecular hydrogen bondings. The molecules of primary and secondary amines have high boiling points because they are able to form hydrogen bondings among their molecules.

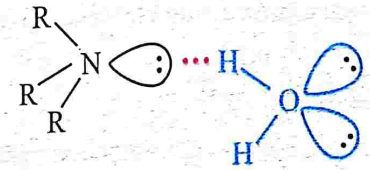


1° or 2° amine:
hydrogen bond donor and acceptor

- Molecules of tertiary amines cannot form hydrogen bonding among themselves, thus having lower boiling points than primary and secondary amines of the same molecular weight.
- However, all lower primary, secondary and tertiary amines can form hydrogen bonding with water and therefore lower amines are soluble in water.



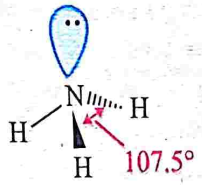
1° or 2° amine:
hydrogen bond donor and acceptor



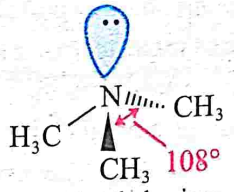
3° amine:
hydrogen bond acceptor only

17.3.3 Structure of Amines

Amines are derivatives of ammonia molecule where one or more hydrogen atoms have been replaced by alkyl or aryl groups. Since, ammonia molecule has trigonal pyramidal shape, the resulting amines also have the same geometry. Nitrogen atom in amines is sp^3-hybridized with a lone-pair in one of its sp^3–hybrid orbital. The bond angles in amines are close to 107.5°.



ammonia



trimethylamine

17.3.4 Basicity of Amines

Due to the presence of a lone pair of electrons on the nitrogen atoms, amines are capable of accepting a proton and are basic in nature. Amines react with acids to form ammonium salts.



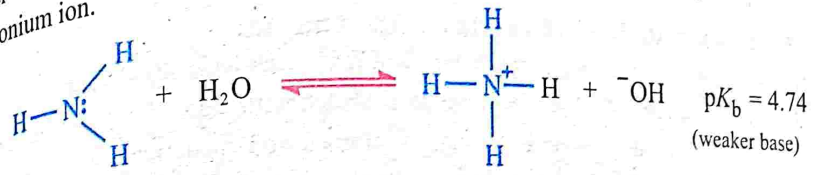
1°-amine → 1°-ammonium salt

Amines are weak bases and, therefore when dissolved in water, it abstracts a proton from water to form ammonium and hydroxide ion, and the following equilibrium is established.

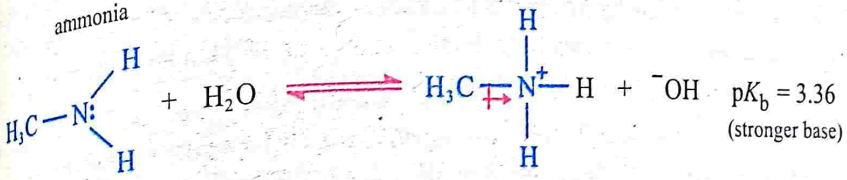


1°-amine → 1°-ammonium ion

Aliphatic amines are stronger bases than ammonia. This is due to the electron donating alkyl group which increases the electronic density of nitrogen, thereby increasing its power of accepting a proton from an acid, and also stabilizes the conjugate acid, ammonium ion.



ammonia — $pK_b = 4.74$ (weaker base)



methyl amine — $pK_b = 3.36$ (stronger base)

stabilized by the alkyl group

The greater the number of alkyl groups, the greater will be the electronic density on nitrogen and therefore, greater will be the power of nitrogen to accept proton. We might expect tertiary aliphatic amines would be the strongest and primary aliphatic amines would be weakest. However in aqueous solutions, secondary is more basic than primary and tertiary aliphatic amines. Because ammonium ions (conjugate acid) are charged, they are strongly solvated by water and the energy of solvation contributes to their stability. The additional alkyl groups around the ammonium ions of tertiary amines decrease the number of water molecules that can approach closely and solvate the ions. However, ammonium ions of primary and secondary amines are more stabilized by water through solvation. But the opposing trends of inductive stabilization and steric hindrance of solvation are balanced for secondary alkyl amines, which make them stronger bases than primary or tertiary alkyl amines in aqueous solutions. The pK_b values of some amines in water are given in **Table 17.4**.

Table 17.4 pK_b Values of some Amines in Water Solvent

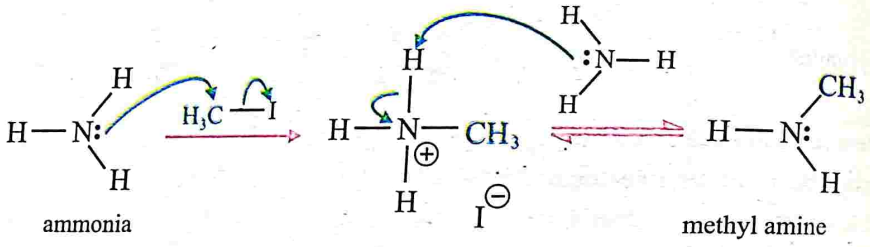
1°–amines	pK_b	2°–amines	pK_b	3°–amines	pK_b
methyl amine	3.36	dimethyl amine	3.28	trimethyl amine	4.25
ethyl amine	3.36	diethyl amine	3.01	triethyl amine	3.24
n-propyl amine	3.32	di-n-propyl amine	3.00	tri-n-propyl amine	3.35

17.3.5 Preparation of Amines

Amines can be prepared by a number of different methods. Some of these are given below.

17.3.5.1 Alkylation of Ammonia by Alkyl halides

Ammonia is a very good nucleophile and will readily undergo alkylation when treated with an alkyl halide. When an alkyl halide is heated with alcoholic ammonia, it yields a mixture of primary, secondary, tertiary amines and quaternary ammonium salt. During this reaction the hydrogen atoms of ammonia are replaced by alkyl groups of alkyl halide, therefore, this reaction is also known as alkylation of ammonia. The reaction of ammonia with methyl iodide is given below.



ammonia — methyl amine

$$CH_3-NH_2 + I-CH_3 \longrightarrow CH_3-NH-CH_3 + HI$$

methyl amine — dimethyl amine

$$CH_3-NH-CH_3 + I-CH_3 \longrightarrow CH_3-N(CH_3)-CH_3 + HI$$

dimethyl amine — trimethyl amine

$$CH_3-N(CH_3)-CH_3 + I-CH_3 \longrightarrow [CH_3-N^{+}(CH_3)_2-CH_3]\,I^-$$

trimethyl amine — quartenary methyl ammomium iodide

If the quaternary ammonium salt is the desired product, then an excess of the alkyl halide is used.

17.3.5.2 Reduction of Nitrogen Containing Functional Groups

17.3.5.2.1 Reduction of Nitriles

When nitriles are reduced they yield the corresponding primary amines. This reduction can be brought about by hydrogen in the presence of catalyst such as Ni, Pt or Pd (catalytic hydrogenation) or by lithium aluminum hydride in ether, followed by workup.

$$R-C\equiv N \xrightarrow[LiAlH_4\ /ether]{2H_2/Ni\ or} R-CH_2-NH_2$$

nitrile — 1°–amine

$$CH_3-C\equiv N \xrightarrow[2.\ H_2O]{1.\ LiAlH_4\ /ether} CH_3-CH_2-NH_2$$

ethanenitrile — ethanamine

$$CH_3-CH_2-C\equiv N + 2H_2 \xrightarrow{Ni} CH_3-CH_2-CH_2-NH_2$$

propanenitrile — propanamine

17.3.5.2.2 Reduction of Nitroalkanes

Primary amines are prepared by the reduction of nitroalkanes with hydrogen in the presence of Ni or Pt or Pd catalyst. They can also be reduced by Fe or Sn in hydrochloric acid.

$$CH_3-NO_2 + 3H_2 \xrightarrow{Ni} CH_3-NH_2 + 2H_2O$$

nitromethane — methanamine

$$CH_3-CH_2-NO_2 \xrightarrow{Fe/HCl} CH_3-CH_2-NH_2$$

nitroethane — ethanamine

17.3.5.2.3 Reduction of Amides

Amines are obtained when amides are reduced by lithium aluminum hydride in ether. Primary, secondary and tertiary amides yield corresponding primary, secondary and tertiary amines respectively.

$$R-C(=O)-NH_2 \xrightarrow[2.\ H_2O]{1.\ LiAlH_4\ /ether} R-CH_2-NH_2$$

primary amide — primary amine

$$R-C(=O)-NHR \xrightarrow[2.\ H_2O]{1.\ LiAlH_4\ /ether} R-CH_2-NHR$$

secondary amide — secondary amine

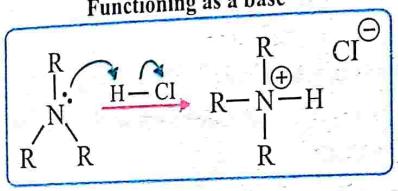
$$R-C(=O)-NR_2 \xrightarrow[2.\ H_2O]{1.\ LiAlH_4\ /ether} R-CH_2-NR_2$$

tertiary amide — tertiary amine

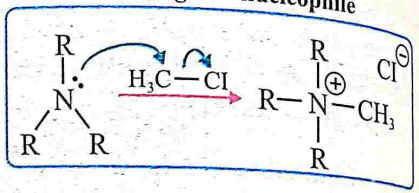
17.3.6 Reactivity of Amines

The chemistry of amines is mainly due to the lone pair of electron on nitrogen atom. This lone pair of electrons is available to the electron deficient reagents such as acids and electrophiles. Therefore, they can act as base or nucleophile in reactions. Therefore common chemical reactions are acid-base reactions, nucleophilic substitution and nucleophilic addition reactions.

Functioning as a base



Functioning as a nucleophile



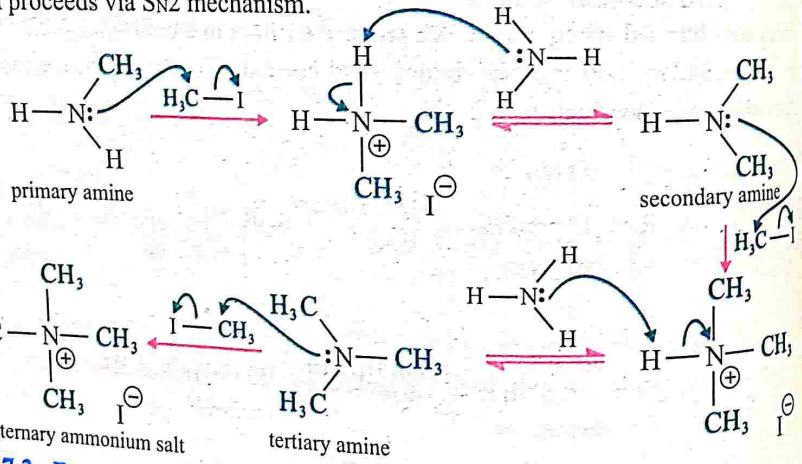
17.3.7 Reactions of Amines

17.3.7.1 Overview

Amines are important and reactive organic compounds. These react with a number of different substances to produce valuable organic compounds. Some of their reactions are

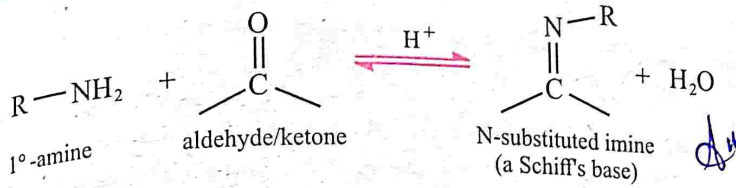
17.3.7.2 Alkylation of Amines by Alkyl Halides

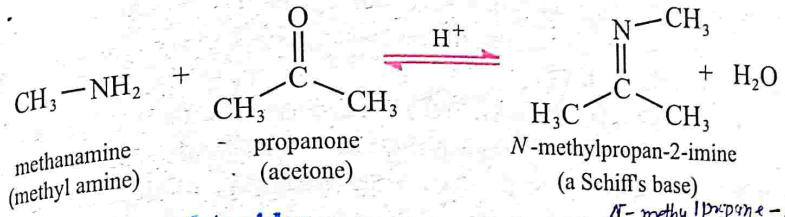
When a primary amine is treated with an alkyl halide, they produce a mixture of secondary, tertiary amines and quaternary ammonium salt. In this process the hydrogen atoms in the amine are successively replaced by the alkyl groups of alkyl halide. This reaction proceeds via S_N2 mechanism.



17.3.7.3 Reaction of Amines with Aldehydes and Ketones

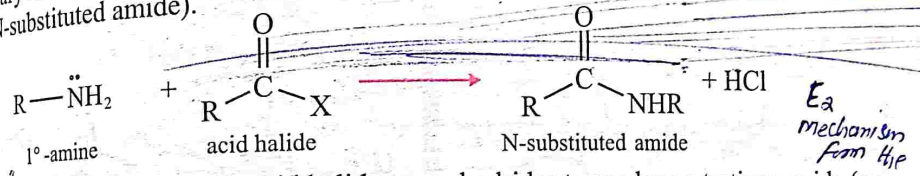
Primary amines react with aldehydes and ketones, in the presence of acid catalyst and yield condensation products called N-substituted imines or secondary imines. These imines are also known as Schiff's bases.



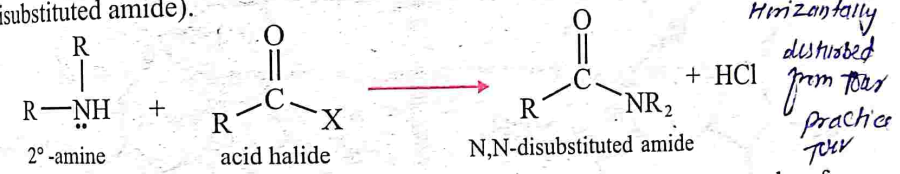


17.3.7.4 Preparation of Amides

Primary amine react with acid chloride or acid anhydride to produce a secondary amide (or N-substituted amide).



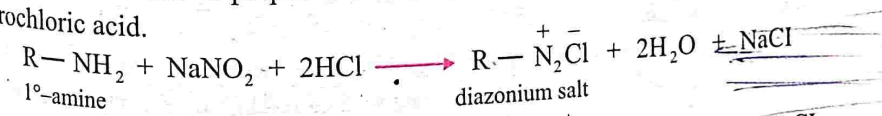
Secondary amines react with acid halides or anhydrides to produce a tertiary amide (or N,N-disubstituted amide).

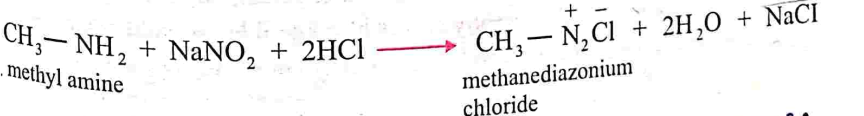


As tertiary amines have no hydrogen atom directly attached to the nitrogen, therefore, they donot react with acid chlorides or anhydrides to produce amides.

17.3.7.5 Preparation of Diazonium Salts

Diazonium salts are compounds that contain diazonium ion ($R/Ar–N_2^+$) as cation. When primary amines are treated with nitrous acid they yield highly unstable salts known as diazonium salts. This reaction is termed as diazotization reaction. Nitrous acid being an unstable acid is prepared *in situ* by the reaction of sodium nitrite and dilute hydrochloric acid.

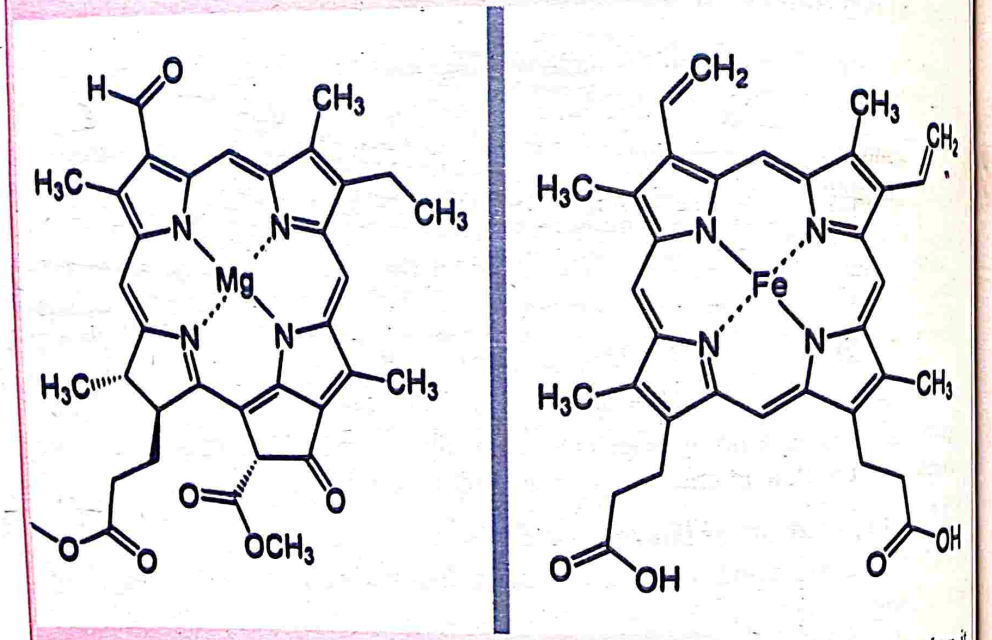




Chlorophyll is the substance which makes plants green. The chlorophyll molecule has the unique capacity to convert the energy of the sun into chemical energy (through photosynthesis), which the plant uses to make carbohydrates from carbon dioxide and water. Hemoglobin is the substance in human blood which carries oxygen from the lungs to the other tissues and cells of the body.

Hemoglobin and Chlorophyll have similar structures composed of four elements; carbon, hydrogen, oxygen and nitrogen. The main difference is that hemoglobin is built around iron (Fe), whereas chlorophyll is built around magnesium (Mg). The primary function for hemoglobin is to transport oxygen from the lungs to other parts of the body.

Chlorophyll | **Hemoglobin**



In sickle cell anemia, the abnormal hemoglobin (Hemoglobin-S) sticks together when it gives up its oxygen to the tissues. These clumps cause red blood cells to become stiff and shaped like a sickle.

Chlorophyll helps do the job of hemoglobin when ingested. Promote the health of circulation, cleanse the body, increase the number of red blood cells and therefore increase oxygen throughout the body, in other words, Chlorophyll helps build hemoglobin. This is exactly what our sickle cell babies and others need, to build hemoglobin.

Key Points

- General formula of alkyl halide is R–X.
- The molecule which undergoes substitution reaction is called 'substrate'.
- The group or species which leaves the substrate is called "leaving group".
- S_N1 mechanism is defined as that nucleophilic substitution reaction in which only one molecule is involved in rate determing or slow step.
- Those nucleophilic substitution reactions in which two species are involved in the rate determing or slow step are called S_N2 reactions.
- The primary alkyl halides undergo S_N2 mechanism while tertiary alkyl halides undergo S_N1 mechanism.
- In polar solvent secondary alkyl halides follow S_N1-mechanism while in non-polar solvents follow S_N2-mechanism.
- During elimination reaction two strong *sigma* bonds are broken and a new weaker *pi* bond is formed.
- E1 stands for unimolecular elimination while E2 stands for bimolecular elimination reaction.
- Those organic compounds which contain at least one carbon—metal bond in their structure are known as organometallic compounds.
- Amines are derivatives of NH_3 in which one or more hydrogen atom have been replaced by one or more similar or different alkyl group.
- Due to presence of lone pair of electrons on nitrogen atoms $(R-NH_2)$ amines are basic in nature.

Exercise

Q I. Choose the correct one from the given options.

1. The reaction of CH_3MgI with acetone followed by hydrolysis gives
   a. *tert*-butyl alcohol. b. *sec*-butyl alcohol.
   c. *n*-butyl alcohol. d. none of these.
2. Which one of the following halide is most reactive towards nucleophilic substitution reaction?
   a. C_2H_5Br b. C_2H_5I c. C_2H_5F d. C_2H_5Cl
3. An electron deficient specie is
   a. electrophile b. nucleophile c. Lewis base d. none
4. $R–CH_2–X$ is an example of
   a. primary alkyl halide. b. secondary alkyl halide.
   c. tertiary alkyl halide. d. both (a) and (b).
5. The carbon atom carrying positive charge and attached to three other atoms or groups is called
   a. Carbocation b. Carbanion
   c. Oxonium ion d. Carbene
6. Grignard reagent can be represented by general formula
   a. $R–Mg–NH_2$ b. R–Mg–OR
   c. R–Mg–OH d. R–Mg–X
7. The end product of reaction of a Grignard reagent with ethyl acetate is
   a. primary alcohol. b. secondary alcohol.
   c. tertiary alcohol. d. methyl alcohol.
8. An electron-pair donor is
   a. Lewis acid b. Electrophile
   b. Nucleophile d. Free radical
9. In secondary alkyl halides the carbon atom to which the halo group is attached is in turn bonded directly to
   a. one other carbon. b. two other carbons.
   c. three other carbons. d. four other carbons.
10. Characteristics of S_N1 reaction is
    a. 100% inversion b. 100% retention
    c. partial racemization d. none of these

11. Which of the following solvent is aprotic?
    a. Acetone b. Ethyl alcohol
    c. Water d. Formic acid
12. Which of the following will not affect the S_N1 mechanism?
    a. Nature of solvent. b. Carbocation stability.
    c. Nature of nucleophile. d. None of these.
13. Ethylmagnesium bromide on treatement with CO_2 and further hydrolysis gives
    a. acetic acid. b. propanoic acid.
    c. butanoic acid. d. benzoic acid.
14. Geometry of methyl chloride is
    a. trigonal planar. b. octahedral.
    c. square planar. d. tetrahedral.
15. The crowding around *alpha* carbon in alkyl halides favour
    a. elimination reaction. b. substitution reaction.
    c. addition reaction. d. all of these.

Q2. Write short answers of the following questions.

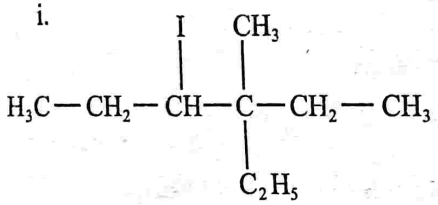
i. Compare nucleophilic substitution reaction and electrophilic substitution reaction.
ii. Why alkyl halides undergo nucleophilic substitution while benzene undergo electrophilic substitution reactions?
iii. Why tertiary carbocation is more stable?
iv. In a polar protic solvent, the S_N1 and E1 reaction for the same tertiary alkyl halide, have equal rates. Explain.
v. Fluoride ion is weak nucleophile in polar protic solvent and strong nucleophile in polar aprotic solvent. Explain.
vi. Why in S_N2 the nucleophile attack on opposite side of leaving group?
vii. Alkyl fluorides are least reactive while alkyl iodides are more reactive towards nucleophilic substitution. Why?
viii. Why secondary amines are more basic than tertiary in aqueous solution?
ix. The structure of methyl carbocation is trigonal planar but not pyramidal. Why?
x. Explain briefly the differernce between nuceophile and base.

Q3. Write detail answers of the following questions.

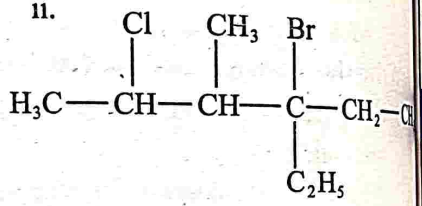
1. (a) Discuss various methods of preparation of alkyl halides.
   (b) Explain elimination reaction in alkyl halides.

2. (a) Discuss the mechanism of S_N1 and S_N2 reactions.
   (b) Define the following terms.
   (i) substrate (ii) leaving group (iii) carbocation
3. (a) How can you prepare Grignard reagent?
   (b) Discuss the reaction of Grignard reagent with.
   (i) aldehydes (ii) ketones (iii) esters
   (iv) carbon dioxide
4. (a) How amines are prepared? Discuss its structure and basicity.
   (b)Write down different reactions of amines.
5. (a) What are carbocations? Write any two methods for formation of carbocations?
   (b) Explain the stability order of different types of carbocations.
   (c) Write the systematic names for the following organic compounds;

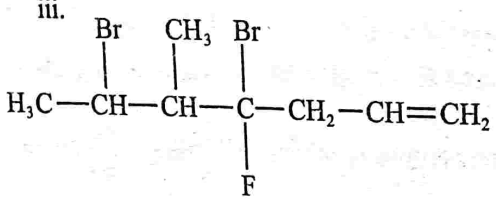
i.



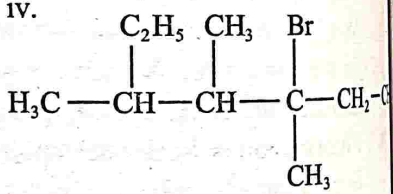
ii.



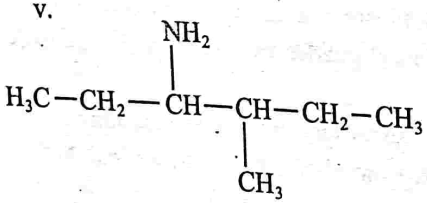
iii.



iv.



v.



(d) Draw the structural formula of the following organic compounds;

i. 3-methylpentane-2,3-diamine
ii. 2,3-dimethylhexane-2,3-diamine

iii. 2-bromo-3-fluoro-2,3-dimethylpentane
iv. 4-bromo-4-chloro-3-fluoro-2,3-dimethylhexane
v. 2-chloro-3,3-dimethylpentan-2-amine

Project

Hinsberg's test is used to distinguish primary, secondary and tertiary amines. The Hinsberg's reagent is a solution of aqueous sodium hydroxide and benzene sulfonyl chloride. In the Hinsberg's test, an amine is reacted with benzene sulfonyl chloride. If a product forms, the amine is either a primary or secondary amine because tertiary amines can not form sulfonamides. If the sulfonamide that forms dissolves in aqueous sodium hydroxide solution, it is a primary amine. If the sulfonamide is insoluble in aqueous sodium hydroxide, it is a secondary amine. The sulfonamide of a primary amine is soluble in an aqueous base because it still possesses an acidic hydrogen on the nitrogen, which can be lost to form a sodium salt.

Procedure

Add 4-5 mL of an amine to a large test tube. Add 5 mL of benzene sulfonyl chloride and 10 mL of 10% NaOH and shake vigorously to mix.

Check for the presence of a single layer (primary amine) or a double layer (secondary amine) in the solution.

If there is a double layer, draw off the lower aqueous layer with a separating funnel and check if the organic layer is soluble in 5% HCl. If yes, it is tertiary but if it is insoluble, then secondary amine is present.

Unit

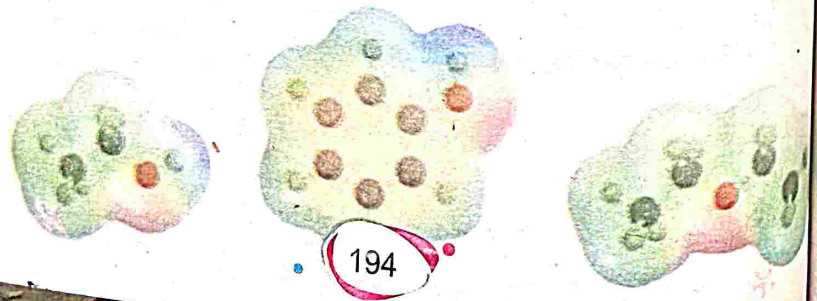
18

Alcohols, Phenols and Ethers

Teaching	Assessment	Weightage %
9	1	8

After studying this unit, 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, acid oxidation of cumene and hydrolysis of diazonium salts. (Applying)
- Discuss the reactivity of phenol and their chemistry by electrophilic aromatic substitution reaction with sodium metal and oxidation. (Applying)
- Differentiate between alcohol and phenol. (Understanding)
- Describe isomerism in alcohols and phenols. (Understanding)
- Identify ethers from their formula. (Understanding)



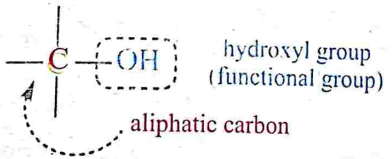
Introduction

Alcohols, phenols and ethers are derivatives of water. In alcohol and phenol one hydrogen of water has been replaced by an alkyl group and aryl group respectively. Whereas in ether both hydrogen atom have been replaced by two alkyl (or aryl) groups.

R – OH (Alcohols) Ar – OH (Phenols) Ar/R – $\ddot{O}$ – R/Ar (Ethers)

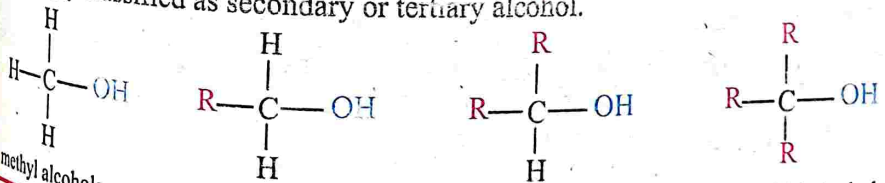
18.1 Alcohols

Alcohols are organic compounds, in which a hydroxyl group (–OH) is attached to an aliphatic carbon atom. Hydroxyl group is the functional group of alcohols. The general formula of alcohols (containing one –OH group) is R–OH or $C_nH_{2n+1}OH$ e.g. methyl alcohol (CH_3OH), ethyl alcohol (C_2H_5OH) etc.



Alcohols may be monohydric or polyhydric, depending upon the number of –OH groups in a molecule. Monohydric alcohol contain one –OH group, while polyhydric alcohols contain more than one –OH group. Polyhydric alcohols may further be classified into dihydric alcohols (or diols), trihydric alcohols (or triol), etc. containing two and three hydroxyl groups respectively. Dihydric alcohols (diols) are also called glycols because of their sweet taste. (Greek *glycys* means 'sweet') (Examples are given in nomenclature).

Monohydric alcohols may be primary, secondary or tertiary. When the hydroxyl group is attached to the primary carbon atom, it is classified as primary alcohol but when the hydroxyl group is attached to the secondary or tertiary carbon atom, the alcohol is accordingly classified as secondary or tertiary alcohol.



18.1.1 Nomenclature

Alcohols are named by common and IUPAC systems.

a. Common System

In this system, monohydric alcohols are named as "alkyl alcohols". That is alkyl group of the alcohol is named first, which is followed by the word alcohol. For example,

$CH_3 - OH$
methyl alcohol

$CH_3 - CH_2 - OH$
ethyl alcohol

$CH_3 - CH_2 - CH_2 - OH$
n–propyl alcohol

$CH_3-\underset{CH_3}{\underset{|}{CH}}-OH$
isopropyl alcohol

The *n*-propyl alcohol and isopropyl alcohol are isomers. The four isomeric butyl alcohols are names as follows.

$CH_3 - CH_2 - CH_2 - CH_2 - OH$
n–butyl alcohol

$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3$
sec–butyl alcohol

$CH_3-\underset{CH_3}{\underset{|}{CH}}-OH$
tert–butyl alcohol

$CH_3-CH-CH_2-OH$ (CH₃ branch)
isobutyl alcohol

Suffix glycols is used for dihydric alcohols (more commonly for vicinal diols).

$HO-CH_2-CH_2-OH$
ethylene glycol

$HO-CH_2-\underset{OH}{CH}-CH_3$
propylene glycol

$HO-CH_2-CH_2-CH_2-OH$
trimethylene glycol

The smallest trihydric alcohol is named as glycerol.

$HO-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-OH$
glycerol

b. IUPAC System

In this system alcohols are named as "alkanols". That is, the final '–e' of the corresponding alkane is replaced by suffix '–ol'.

The IUPAC rules are

1. Select the longest continuous carbon chain containing the –OH group(s).
2. The ending "–e" of the corresponding alkane is replaced by suffix "–ol".
3. Number the chain from one end or the other, so as to give lowest number to the carbon carrying the –OH group.
4. Mention the position of the hydroxyl group by putting its number before the suffix "–ol".
5. Indicate the position of the other substituents (if any) using the numbers of the carbon atoms, to which they are attached.
6. The substituents, along with their positions, are named in alphabetical order before the parent name.
7. If the number of carbon atoms carrying the hydroxyl group is the same from either side, then number the chain from the end which is heavily substituted.
8. In case of dihydric, trihydric and polyhydric alcohols, the prefix di, tri, tetra etc. is used before "–ol", along with the numbers of the carbon atoms to which these hydroxyl groups are attached.
9. If more than one hydroxyl groups are attached to the same carbon atom, the number of that carbon atom is repeated.

The following examples will illustrate the above rules.

$CH_3 - OH$
methanol

$CH_3 - CH_2 - OH$
ethanol

$^3CH_3-{}^2CH_2-{}^1CH_2-OH$
propan-1-ol

$^3CH_3-{}^2CH(OH)-{}^1CH_3$
propan-2-ol

$^1CH_3-{}^2CH(OH)-{}^3CH_2-{}^4CH_3$
butan-2-ol

$^1CH_3-{}^2C(CH_3)(CH_3)-{}^3CH(OH)-{}^4C(H)(CH_3)-{}^5CH_3$
2,2,4-trimethylpentan-3-ol

$^1CH_2(OH)-{}^2CH(OH)-{}^3CH_2(OH)$
propane-1,2,3-triol

$^1CH_2(OH)-{}^2CH_2(OH)$
ethane-1,2-diol

18.1.2 Physical Properties

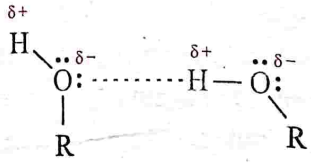
- Lower alcohols are colourless liquids while alcohols of high molecular mass are solids, at room temperature.
- They have characteristic sweet smell.
- The melting and boiling points are generally increase with the size of alkyl group, and also number of –OH groups

Tidbit

The -e ending of an alkane name is dropped before a suffix beginning with a vowel (-ol) and retained before one beginning with a consonant (-diol).

(Table 18.1). Among isomeric alcohols, the boiling points of straight ch alcohols are higher than that of branched.

- The boiling points of alcohols are much higher than those of correspondi alkanes and alkyl halides. The high boiling points of is due to hydrogen bondi among the alcohol molecules.



- Lower alcohols like methyl, ethyl and propyl alcohols are completely miscibl with water. However the solubility of higher alcohols in water falls rapidly, du to increase in size of non-polar hydrophobic alkyl group.

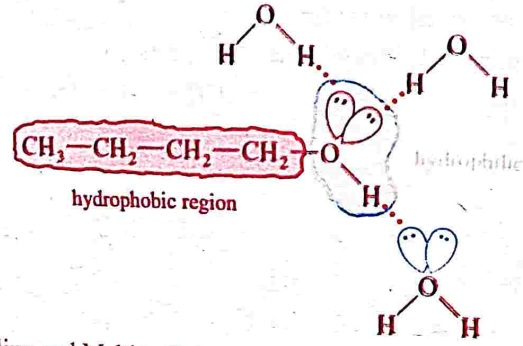


Table 18.1 Boiling and Melting Points of Some Alcohols

Name	Melting Point (°C)	Boiling Points (°C)
methanol	–97	64
ethanol	–115	78
n–propyl alcohol	–126	97
n-butyl alcohol	–90	118
isopropyl alcohol	–89	82
isobutyl alcohol	–108	108
sec-butyl alcohol	–114	99
tert-butyl alcohol	–25.5	82
ethylene glycol	–12	197
glycerol	18	290

18.1.3 Structure of Alcohols

Alcohols are alkyl derivatives of water molecules. Water molecule has an angular structure with H–O–H bond angle of 104.5°, which is slightly smaller than tetrahedral angle. Alcohol molecules have a similar geometry where C–O–H angle is higher than 104.5°, and the hybridization of oxygen is sp^3. For example the C–O–H bond angle in methyl alcohol is 108.9° **(Figure 18.1)**. The C–O and O–H bond lengths are 142 pm (1.42 Å) and 96 pm (0.96 Å) respectively.

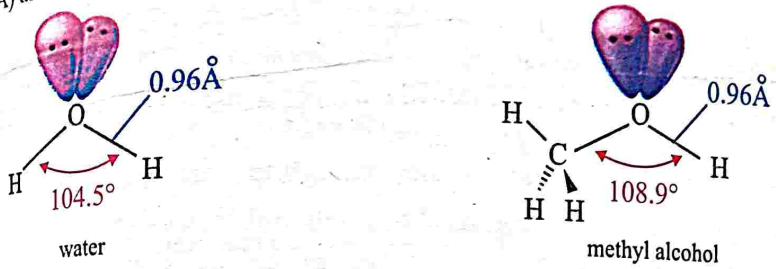


Figure 18.1 Structure of water and methyl alcohol.

18.1.4 Acidity of Alcohols

The acidic nature of alcohol is due to presence of polar oxygen-hydrogen (O–H) bond in alcohols.

$$R-\overset{\delta+}{O}-\overset{\delta-}{H}$$

This allows the release of hydrogen atom as proton. Due to this acidic behaviour, alcohols react with sodium or potassium to form alkoxide salt with the liberation of hydrogen gas.

$$\underset{\text{alcohol}}{2ROH} + 2Na \longrightarrow \underset{\text{sodium alkoxide}}{2R\overset{-}{O}\overset{+}{Na}} + H_2\uparrow$$

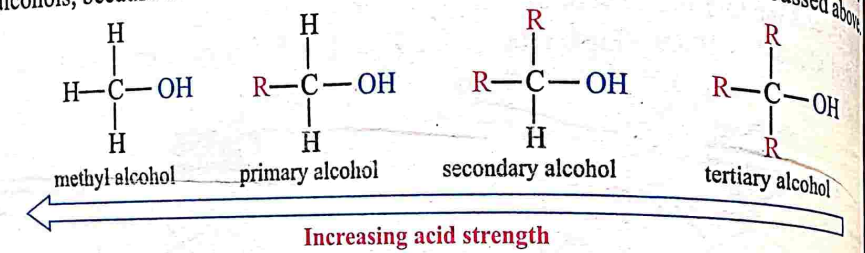
$$\underset{\text{ethyl alcohol}}{2CH_3CH_2OH} + 2Na \longrightarrow \underset{\text{sodium ethoxide}}{2CH_3CH_2\overset{-}{O}\overset{+}{Na}} + H_2\uparrow$$

However, alcohols are very weakly acidic, and even less acidic than water, as clear from pKa values.

$$\underset{\text{water}}{H_2O} + H_2O \rightleftharpoons \underset{\substack{\text{hydroxide ion}\\(\text{conjugate base})}}{H\overset{-}{O}} + H_3\overset{+}{O} \qquad pKa = 15.7$$

$$\underset{\text{alcohol}}{R-OH} + H_2O \rightleftharpoons \underset{\substack{\text{alkoxide ion}\\(\text{conjugate base})}}{R-\overset{-}{O}} + H_3\overset{+}{O} \qquad pKa = 16\text{-}18$$

The alkyl group in alcohols releases electrons (electron donating group) towards the oxygen atom and therefore decreases the stability of conjugate base of alcohol, alkoxide ion. That is why the alcohols are less acidic than water. Tertiary alcohols are less acidic than secondary alcohols and secondary alcohols are less acidic than primary alcohols, because of the same electron donating effect of alkyl groups discussed above.



It is to be noted that alcohols are not acidic enough to react with aqueous NaOH or KOH.

$$R{-}OH + NaOH \longrightarrow \text{no reaction}$$

18.1.5 Preparations of Alcohols

18.1.5.1 Hydration of Alkenes

Reaction of alkenes in the presence of sulphuric acid yield alcohol upon direct hydration **(Section 16.5.7.3).**

$$\underset{\text{ethene}}{H_2C{=}CH_2} + H_2O \xrightarrow[100°C]{H_2SO_4} \underset{\text{ethyl alcohol}}{CH_3{-}CH_2{-}OH}$$

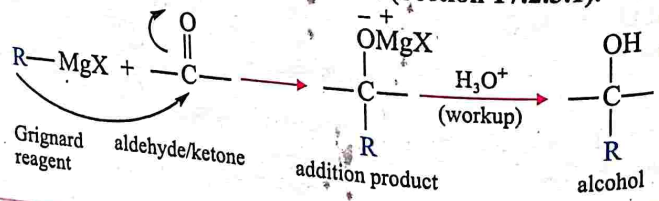
18.1.5.2 Hydrolysis of Alkyl halides

Alcohols can be prepared by the hydrolysis of alkyl halides by means of water or an aqueous alkali **(Sections 17.1.6.3 and 17.1.6.4).**

$$\underset{\text{methyl iodide}}{CH_3{-}I} + KOH \xrightarrow[H_2O]{\Delta} \underset{\text{methyl alcohol}}{CH_3{-}OH} + KI$$

18.1.5.3 Reaction of Grignard reagent with Aldehydes and Ketones

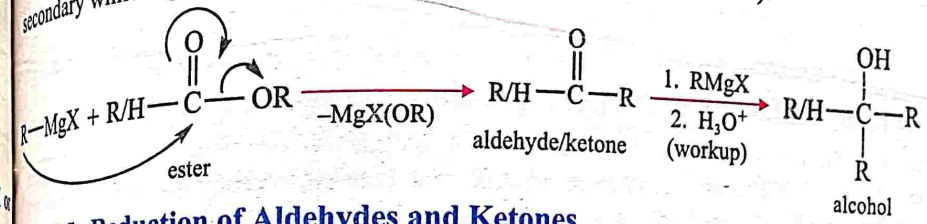
Grignard reagent adds to the carbonyl group of aldehyde and ketone to form an addition compound which on acid workup gives an alcohol **(Section 17.2.3.1).**



Formaldehyde reacts with Grignard reagents to produce primary alcohols. Other aldehydes give secondary alcohols. Ketones on reaction with Grignard reagent produce tertiary alcohols.

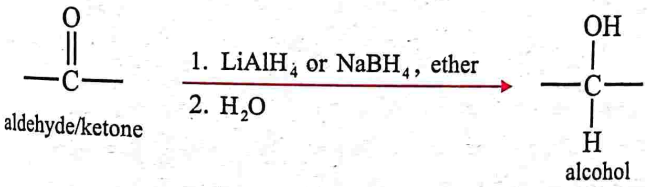
18.1.5.4 Reaction of Grignard reagent with Esters

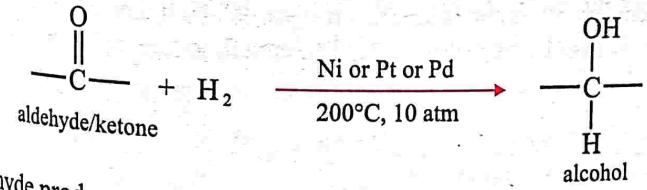
Grignard reagents react with esters to yield carbonyl compounds (aldehydes and ketones). These carbonyl compounds react with more of the Grignard reagent in the same reaction mixture and yield alcohols as the final products. Formate ester give secondary while higher esters yield tertiary alcohols **(Section 17.2.3.2).**



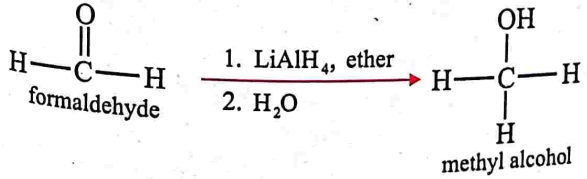
18.1.5.5 Reduction of Aldehydes and Ketones

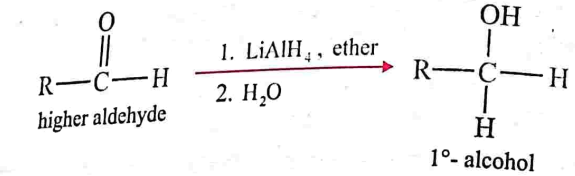
Carbonyl compounds (aldehydes and ketones) can easily be reduced to alcohols, either by hydrogenation in the presence of nickel, platinum or palladium catalysts at elevated temperature (200°C) and pressure (10 atmosphere); or by using reducing agents such as lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$) in ether. Following reduction with $LiAlH_4$ or $NaBH_4$, a separate workup step with acid or even with pure water is required to liberate the alcohol product.

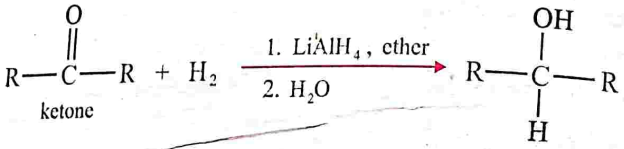




Formaldehyde produces methyl alcohol, higher aldehydes give primary alcohols while ketones yield secondary alcohols.

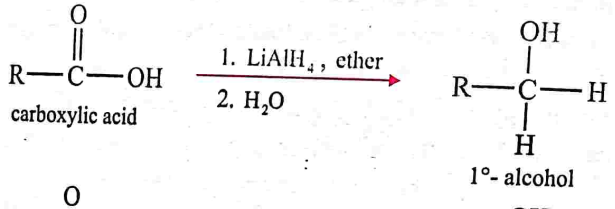


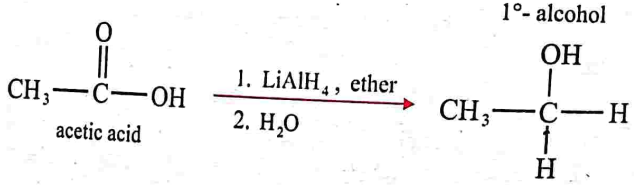




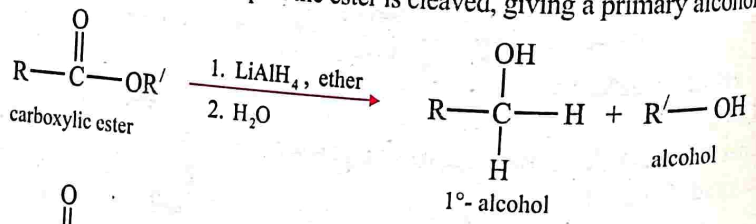
18.1.5.6 Reduction of Carboxylic Acids and Esters

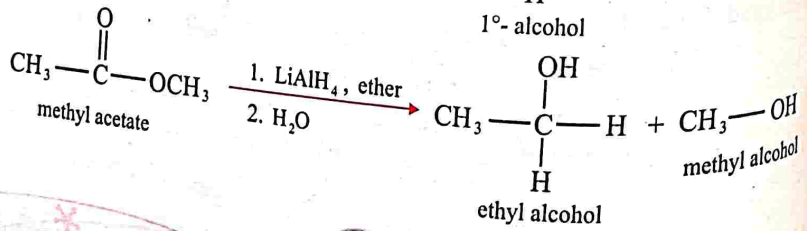
Carboxylic acids are exceedingly difficult to reduce. A very powerful reducing agent such as lithium aluminium hydride is required to convert a carboxylic acid to a primary alcohol. Sodium borohydride is not a potent hydride donor as lithium aluminium hydride and does not reduce carboxylic acids.





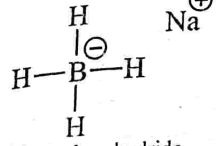
Esters can also be reduced by lithium aluminium hydride. Two alcohols are formed from each ester molecule. The acyl group of the ester is cleaved, giving a primary alcohol.

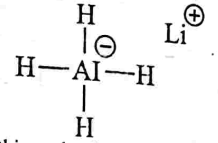




Tidbit

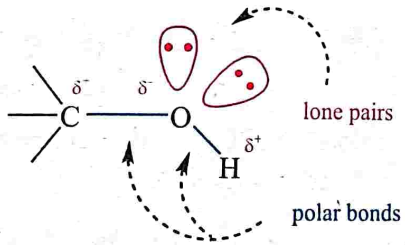
Lithium aluminium hydride and sodium borohydride are hydride ($\overline{H}$) donors. Lithium aluminium hydride is much stronger reducing agent than sodium borohydride.





18.1.6 Reactivity

The functional group of the alcohols is the hydroxyl group, which is the reactive site. This group has two reactive covalent bonds, the C–O bond and the O–H bond. The electronegativity of oxygen is substantially greater than that of carbon and hydrogen. Consequently, the covalent bonds of this functional group are polarized so that oxygen is electron rich and both carbon and hydrogen are electrophilic. The oxygen atom of alcohols has two unshared pairs of electrons and hence is an electron rich centre.

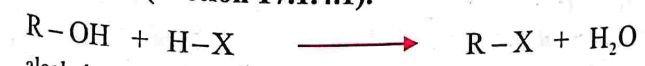


Alcohols are reactive compounds. They readily react with polar or ionic reagents. Generally, the reactions of alcohol involve the fission of either the O–H bond or the C-O bond. The common reactions of alcohols are substitution, elimination and oxidation reactions.

18.1.7 Reactions of Alcohols

18.1.7.1 Reaction with Halogen acids (HX) to give Alkyl halides

Alcohols react with halogen acids to form alkyl halides by replacement of hydroxyl group with halogen atom **(Section 17.1.4.1).**



Reactivity of halogen acid increases with acid strength. In case hydrogen chloride, anhydrous zinc chloride is used as catalyst while treating alcohol to produce alkyl

chlorides. HBr and HI require no catalyst. The mixture of concentrated hydrochloric acid and anhydrous zinc chloride (conc. HCl + $ZnCl_2$), is called Lucas Reagnt. Tertiary alcohols are more reactive while primary alcohols are least reactive.

Lucas Test: This test is used to distinguish between primary, secondary and tertiary alcohols. Alcohols react with Lucas reagent to form corresponding chlorides, which are insoluble and form cloudiness in the test tube.

$$\underset{\text{alcohol}}{R-OH} + HCl \xrightarrow{ZnCl_2} \underset{\text{alkyl chloride}}{R-Cl} + H_2O$$

The time taken, for cloudiness to appear corresponds to the reactivity of alcohol and therefore distinguishes primary, secondary and tertiary alcohols. Tertiary alcohol react with Lucas reagent immediately, a secondary alcohol react after some time, whereas primary and methyl alcohol do not react at room temperature.

18.1.7.2 Reaction with Phosphorous trihalides (PX_3) and Thionyl chloride ($SOCl_2$) to give alkyl halides

Alcohols when treated with phosphorous trihalides (PX_3), yield corresponding alkyl halides.

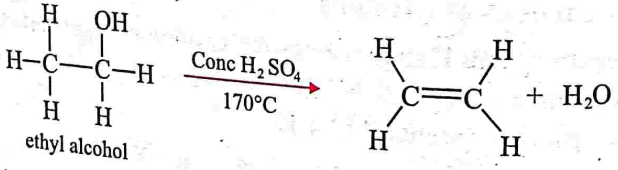
$$\underset{\text{alcohol}}{3R-OH} + PX_3 \longrightarrow \underset{\text{alkyl halide}}{3R-X} + H_3PO_3$$

Alcohols react with thionyl chloride ($SOCl_2$) in the presence of pyridine to yield the corresponding alkyl chlorides **(Section 17.1.4.2).**

$$\underset{\text{alcohol}}{R-OH} + \underset{\text{thionyl chloride}}{SOCl_2} \xrightarrow[-HCl]{\text{pyridine}} \underset{\text{alkyl halide}}{R-Cl} + SO_2$$

18.1.7.3 Acid catalysed Dehydration

Alcohols, when treated with concentrated sulphuric acid at 170°C, undergo dehydration to form alkenes **(Section 16.5.5.1).**

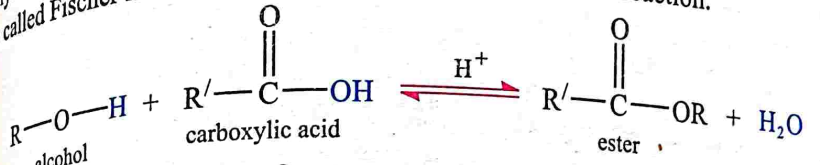


ethyl alcohol — ethene

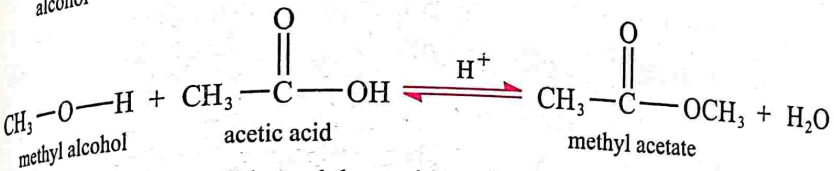
The order of rate of dehydration of different alcohols is;
tertiary alcohols > secondary alcohols > primary alcohols.

18.1.7.4 Preparation of Esters

Alcohols react with carboxylic acids in the presence of concentrated sulphuric acid catalyst to form esters. This method is commonly used for preparation of esters and also called Fischer Esterification. It is a type of condensation reaction.



alcohol — carboxylic acid — ester



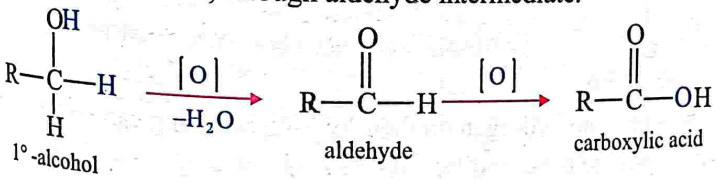
methyl alcohol — acetic acid — methyl acetate

Fischer esterification is reversible, and the position of equilibrium lies slightly to the side of products when the reactants are simple alcohols and carboxylic acids. When the Fischer esterification is used for preparative purposes, the position of equilibrium can be made more favorable by using either the alcohol or the carboxylic acid in excess, or removing water from the reaction mixture. For steric reasons, the order of alcohol reactivity in the Fischer esterification is; methyl alcohol > primary alcohol > secondary alcohol > tertiary alcohol.

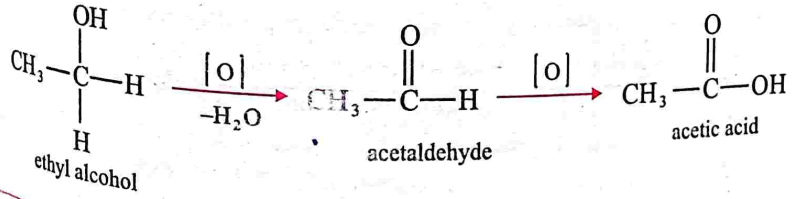
18.1.7.5 Oxidation

Oxidation of an alcohol yields a carbonyl compound. Whether the resulting carbonyl compound is an aldehyde, a ketone, or a carboxylic acid depends on the alcohol and on the oxidizing agent.

Primary alcohols may be oxidized either to an aldehyde or to a carboxylic acid. Vigorous oxidation with solutions of strong oxidizing agents like, acidified chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) or permanganate (MnO_4^-) solution leads to the formation of a carboxylic acid, through aldehyde intermediate.

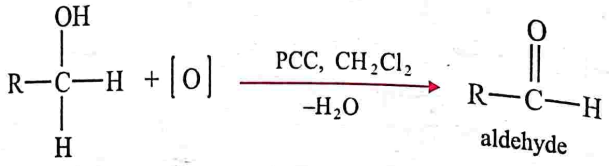


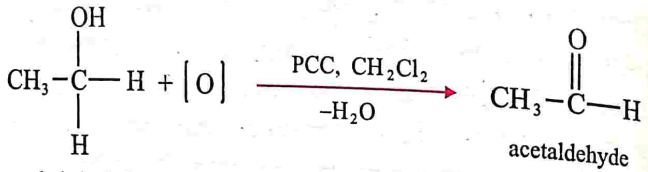
1°-alcohol — aldehyde — carboxylic acid



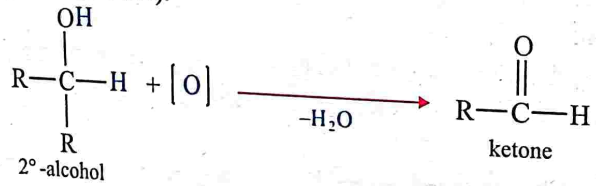
ethyl alcohol — acetaldehyde — acetic acid

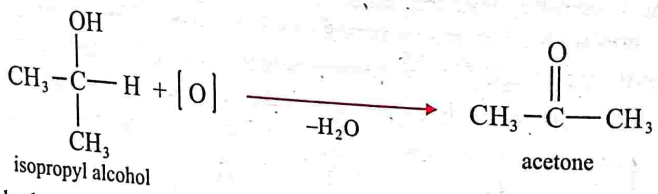
Assume that the oxygen shown in square brackets is delivered by any of the above oxidizing agents. Oxidation of primary alcohol to aldehydes requires special oxidizing agents such as Pyridinium Chlorochromate (PCC), $C_5H_5N^+HClCrO_3^-$. PCC is formed when chromic oxide is dissolved in HCl and then treated with pyridine in dichrolomethane solvent.



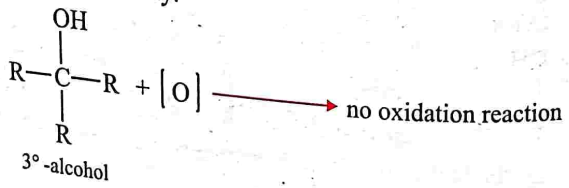


Secondary alcohols are oxidized to ketones by the same reagents that oxidize primary alcohols. The further oxidation of ketones to carboxylic acids needs even more drastic conditions **(Section 19.6.4).**





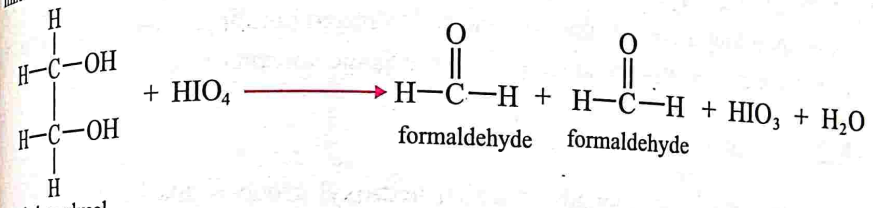
Tertiary alcohols have no hydrogen on their hydroxyl-bearing carbon (α-hydrogen) and do not undergo oxidation readily.

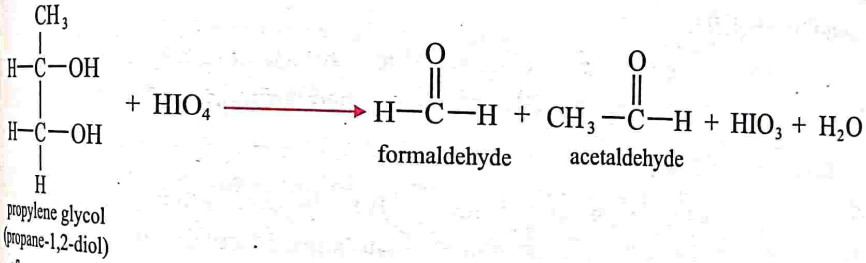


18.1.7.6 Cleavage of 1, 2 diols

1,2-diols or vicinal diols, are dihydric alcohols containing two hydroxyl groups on adjacent carbon atoms. They are also called glycols. For example, ethylene glycol, propylene glycol etc **(Section 18.1.1).**

A characteristic reaction of vicinal diols is their oxidative cleavage. The most common reagent used for oxidative cleavage of vicinal diol is periodic acid (HIO_4). The carbon–carbon bond of the vicinal diol unit is broken and two carbonyl groups result. Periodic acid is reduced to iodic acid (HIO_3). For example cleavage of ethylene glycol with periodic acid yields two molecules of formaldehydes, while propylene glycol yields mixture of formaldehyde and acetaldehyde.





Self-assessmnet

What are the oxidation states of the iodine in HIO_4 and HIO_3?

18.1.8 The Sulphur Analogues (Thiols, RSH)

Sulfur lies just below oxygen in the periodic table, and many oxygen-containing organic compounds have sulfur analogues. The sulfur analogues of alcohols (R–OH) are thiols (R–SH). The functional group –SH of thiol is also called *mercapto* group or *sulphydryl* group. Thiols are also called *mercaptans.*

Common names are formed like those of alcohols, using the name of the alkyl group with the word mercaptan. In IUPAC names, the suffix *-thiol* is added to the name of the corresponding alkane, and number the chain in the direction that gives the lower

locant to the carbon that bears the –SH group.

	CH_3-SH	CH_3-CH_2-SH	$CH_3-\underset{\displaystyle SH}{\underset{|}{CH}}-CH_3$
IUPAC System:	methanethiol	ethanethiol	propane-2-thiol
Common System:	methyl mercaptan	ethyl mercaptan	isopropyl mercaptan

Methanethiol is a gas, while higher members are colourless, volatile liquids at RTP. Lower members have strong repulsive odours. Ethanethiol is added to natural gas in minute amounts to make gas leakage detectable by smell. Thiols have lower boiling points than the corresponding alcohols, due to lack of hydrogen bonding. They are insoluble in water but soluble in ethanol, ether and other organic solvents.

Tidbit

Thiols have a marked tendency to bond to mercury and the word mercaptan comes from the Latin *mercurium captans*, which means "seizing mercury."

18.2 Phenols

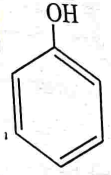
Phenols are organic compounds in which hydroxyl group is attached directly to an aromatic ring. The parent compound of this group is called phenol (C_6H_5OH).



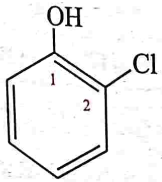
Just like alcohols, they may also be monohydric, dihydric or polyhydric, depending upon the number of –OH groups attached per molecule.

18.2.1 Nomenclature

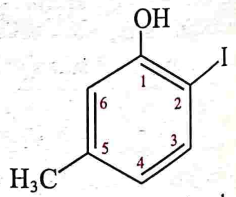
The systematic name for phenol is benzenol. But like other aromatic compounds, the common names of phenol and substituted phenols are acceptable IUPAC names. The substituted phenols are usually named as derivatives of the parent phenol.



phenol

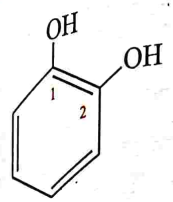


2-chlorophenol

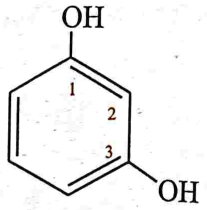


2-iodo-5-methylphenol

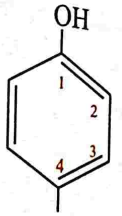
The three isomeric dihydroxy derivatives of benzene may be named as 1,2–, 1,3– and 1,4–benzenediol, respectively, but each one is more familiarly known by the common name indicated in parentheses below the structures shown here. These common names are permissible IUPAC names. Similar trihydroxy derivatives are named as benzenetriol and so on.



benzene-1,2-diol
(catechol)

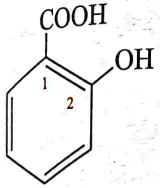


benzene-1,3-diol
(resorcinol)

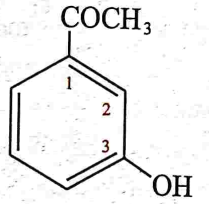


benzene-1,4-diol
(hydroquinone)

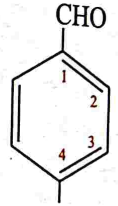
Carboxyl, acyl and other groups, that take precedence over the phenolic hydroxyl, should determine the base name. The hydroxyl is treated as a substituent in these cases.



2-hydroxybenzoic acid
(salicylic acid)



3-hydroxyacetophenone

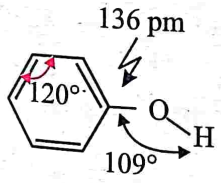


4-hydroxybenzaldehyde

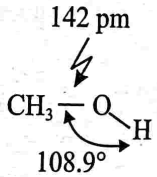
Some other examples of phenols are already discussed in **(Section 16.8.1)**.

18.2.2 Structure of Phenol

In phenol molecule, the hydroxyl group is attached to a benzene ring. The molecule is planar, with a C–O–H bond angle of 109°, almost the same as tetrahedral angle and not much different from the, C–O–H angle (108.9°) of methyl alcohol **(Section 18.1.3)**.



phenol

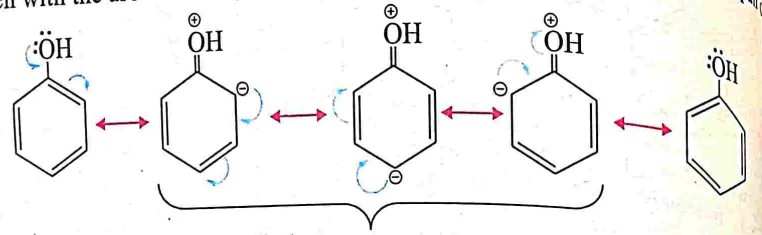


methyl alcohol

Figure 18.2 Comparison of structure of phenol and methyl alcohol

In phenol the six carbon atoms are sp^2–hybridized forming a hexagonal ring with internal angles of 120°. In the bonds C–O and O–H, bond lengths are 136 pm and 96 pm respectively. Since the bonds formed by sp^2–hybridized carbon, are shorter than those formed by sp^3-hybridized carbon, therefore the C–O bond length is slightly less than the C–O bond length in methanol (142 pm). In resonance terms, the shorter carbon–oxygen bond distance in phenol is attributed to the partial

double-bond character that results from conjugation of the unshared electron pair of oxygen with the aromatic ring.



dipolar resonance structures

18.2.3 Physical Properties

- Phenols are colourless liquids or low melting crystalline solids at room temperature and pressure.
- They have a characteristic odour.
- The boiling points of phenols are slightly higher than that of aliphatic alcohols of comparable molecular weights, due to the presence of stronger hydrogen bonding in phenols than in alcohols. The melting and boiling points of phenols is 41°C and 182°C respectively.
- Due to stronger hydrogen bonding, phenols are more soluble in water than alcohols of comparable molecular mass.

Tidbit

Phenol and its derivatives are used as disinfectant and germicide.

18.2.4 Acidity of Phenols

Phenols are much more acidic than alcohols and water but are less acidic than carboxylic acids. This is clear from the pKa values of these compounds, given in **Table 8.2.**

Table 18.2 Ka and pKa Values of some Compounds

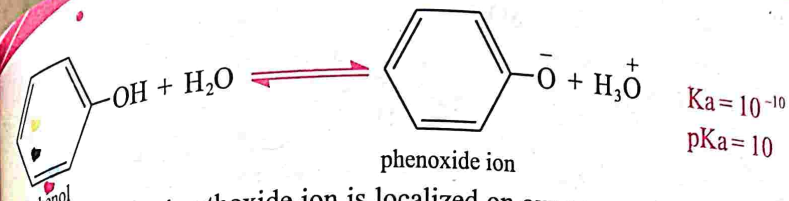
Compound	Formula	Ka (approx)	pKa
Phenol	Ph–OH	10^{-10}	10
Alcohols	R–OH	10^{-16}–10^{-18}	16 – 18
Carboxylic acids	R–COOH	$\approx 10^{-5}$	≈ 5
Water	H–OH	1.8×10^{-16}	15.7

To help us understand why phenols are more acidic than alcohols, let's compare the ionization equilibria for phenol and ethyl alcohol.

$CH_3-CH_2-OH + H_2O \rightleftharpoons CH_3-CH_2-\bar{O} + H_3\overset{+}{O}$

ethyl alcohol — ethoxide ion

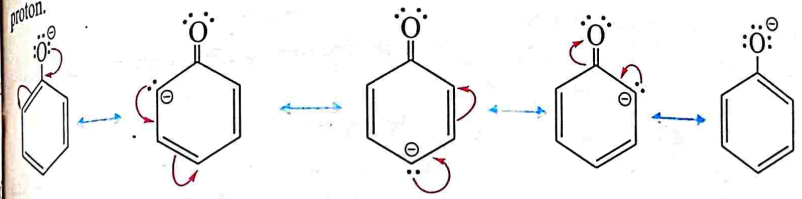
$Ka = 10^{-16}$, $pKa = 16$



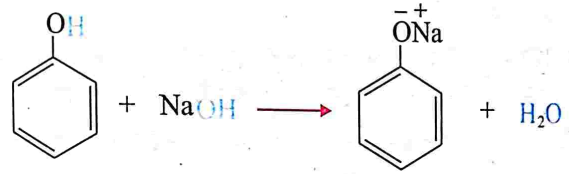
phenol — phenoxide ion

$Ka = 10^{-10}$, $pKa = 10$

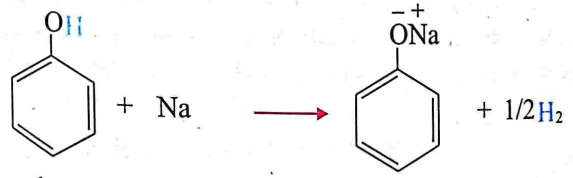
The negative charge in ethoxide ion is localized on oxygen and is stabilized only by solvation forces. While in phenoxide ion the negative charge spreads throughout the benzene ring and is thereby dispersed. This delocalization of the charge accounts for the stability of the phenoxide ion. The acidic nature of phenols, as compared to alcohols, can be attributed to the formation of stable phenoxide ions after loss of proton.



Being more acidic, phenol reacts with NaOH or KOH or sodium metal to form salt. Alcohols do not undergo reaction with NaOH and KOH but can react with sodium metal only.



phenol — sodium phenoxide



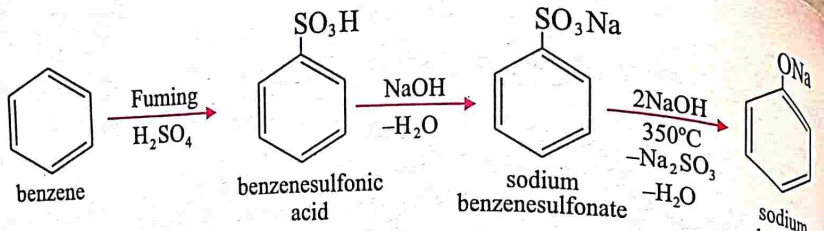
phenol — sodium phenoxide

18.2.5 Preparation of Phenols

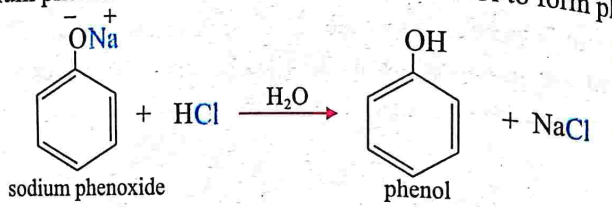
Phenols can be prepared by the following methods.

18.2.5.1 From Benzenesulphonic acid

This method involves the fusion of sodium benzenesulphonate with solid sodium hydroxide at 300–350°C. The benzenesulphonic acid is prepared by sulfonation of benzene with fuming sulphuric acid **(Section 16.8.5.2.3).**



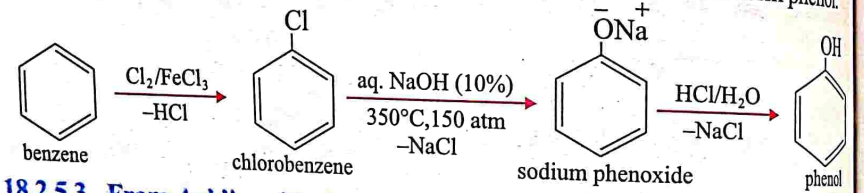
The resultant sodium phenoxide is then treated with dilute HCl to form phenol.



The process can also be used in laboratory, but due to vigorous conditions required for this process, limits its applications.

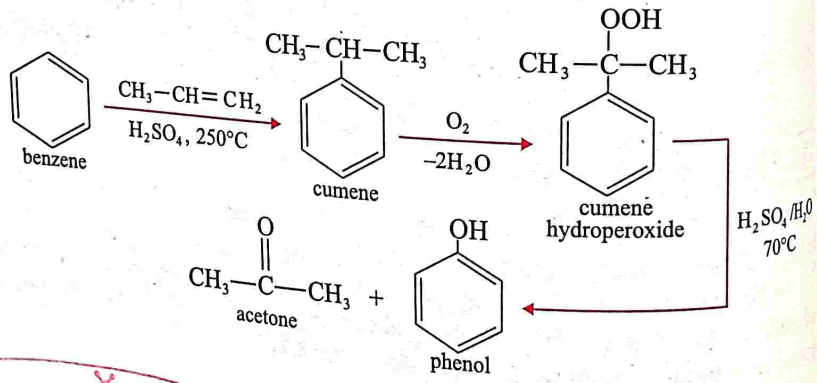
18.2.5.2 From Chlorobenzene (Dow Process)

In this method, chlorobenzene is hydrolysed with aqueous sodium hydroxide at high temperature and pressure. This process was developed by Dow Chemical Company of USA in 1928. The resultant sodium phenoxide is then treated with dilute HCl to form phenol.



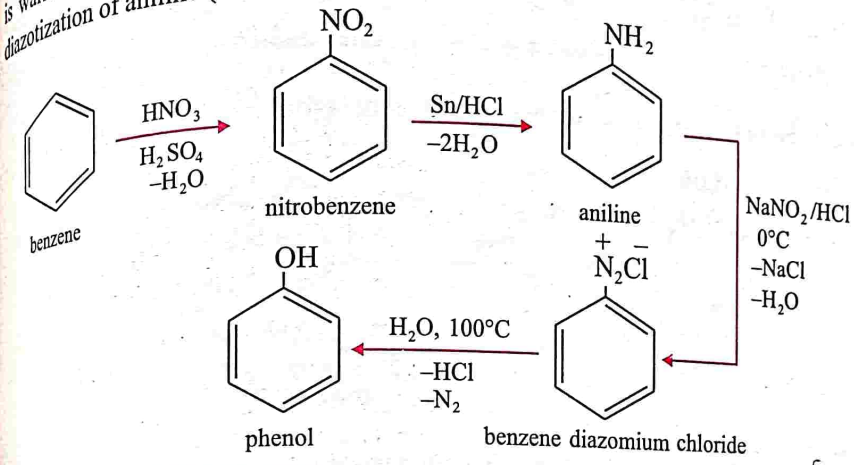
18.2.5.3 From Acidic oxidation of Cumene

This method involves air oxidation of cumene (isopropyl benzene) to cumene hydroperoxide, which on treatment with dilute hydrochloric acid forms phenol along with acetone. The cumene is prepared by alkylation of benzene **(Section 16.8.5.2.5).**



18.2.5.4 Hydrolysis of Diazonium Salts

This is a simple laboratory method in which a solution of benzenediazonium chloride is warmed on a water bath at 100°C. Benzenediazonium chloride is prepared by diazotization of aniline **(Section 17.6.7.5).**



18.2.6 Reactivity of Phenol

Generally phenols exhibit two types of reactions i.e. reactions of hydroxyl group and reactions of aromatic ring.

In the first type of reactions, usually involve the breaking of O–H bond in formation of salts, ethers, esters etc. In these reactions phenol somewhat resemble to alcohols. In the second type of reactions, the benzene ring of phenol undergoes electrophilic substitution reactions which are characteristic of most of the aromatic compounds e.g. nitration, sulphonation, halogenation, Friedel–Crafts alkylation and acylation etc.

The presence of hydroxyl group on the benzene ring in phenol increases electron density of the ring at *ortho* and *para* positions by giving its electron pair to the ring and hence increases the reactivity of the ring relative to benzene itself, for electrophillic substitution reactions **(Section 16.8.5.2.7).**

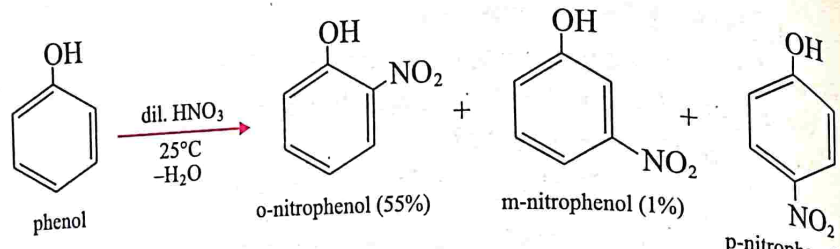
18.2.7 Reactions of Phenols

18.2.7.1 Electrophiilic Aromatic Substitutions

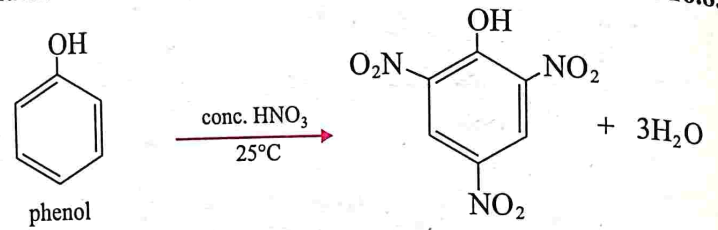
In these reactions an electrophile is introduced into the aromatic ring and the hydroxyl group remains intact. Some electrophilic substitution reactions are given below.

1. Nitration

Phenol reacts with dilute nitric acid to form, mainly *o*– and *p*–nitrophenol **(Section 16.8.5.2.7).**

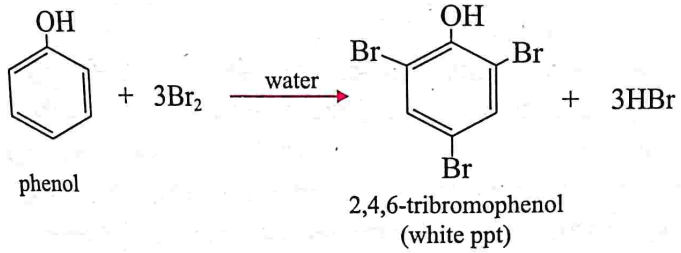


With concentrated nitric acid, 2,4,6–trinitrophenol is formed **(Section 16.8.5.2.8).**

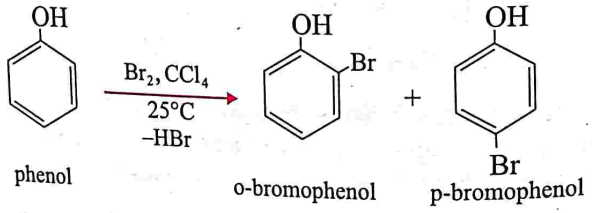


2. Halogenations

Phenol reacts with excess of halogen in aqueous solution to give 2,4,6–trihalophenol. For example, reaction of phenol with excess of bromine yield a white precipitate of 2,4,6–tribromophenol. The reaction is used for detection of phenol.

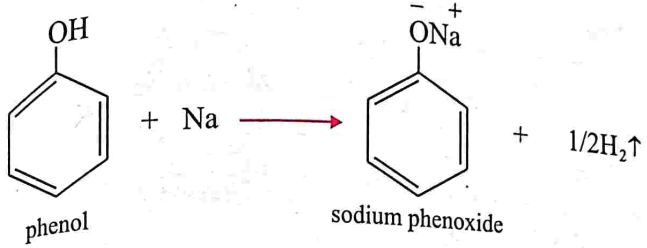


In the presence of a non–polar solvent like, carbon tetrachloride or carbon disulphide, at low temperature, phenol yields a mixture of *o*- and *p*-bromophenol. The two isomers differ in boiling point and can be separated by fractional distillation.



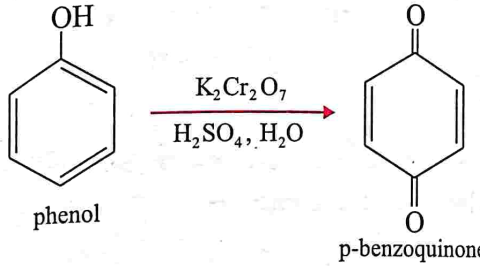
18.2.7.2 Reaction with Sodium Metal

Phenol, being acidic in nature, reacts with sodium metal to form salt, with the release of hydrogen gas **(Section 18.2.4).**



18.2.7.3 Oxidation

Phenol is observed to undergo oxidation even more readily than primary and secondary alcohols. The product is benzoquinone. Phenol can be oxidized into *p*-benzoquinone using dichromate or permanganate.



18.2.8 Difference between Alcohol and Phenol

In both alcohols and phenols hydroxyl group is the functional group. In phenols hydroxyl group is attached to an aromatic carbon e.g. phenol, cresols, catechol etc. While in alcohols the hydroxyl group is attached to an aliphatic carbon atom. Alcohols are further classified into aliphatic and aromatic. If an alcohol does not contain an aromatic ring, it is called aliphatic alcohol e.g. methyl alcohol, ethyl alcohol, cyclohexanol etc. But alcohols containing hydroxyl group in a side chain attached to an aromatic ring are called aromatic alcohols e.g. benzyl alcohol, 2-phenylethanol etc.

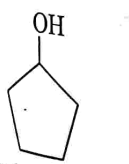
Some examples:

Aliphatic alcohols;

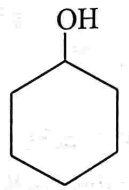
$CH_3 - OH$
methyl alcohol

$CH_3 - CH_2 - OH$
ethyl alcohol

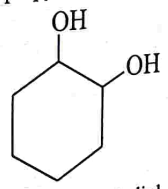
$CH_3 - CH_2 - CH_2 - OH$
n–propyl alcohol



cyclopentanol
(cyclopentyl alcohol)

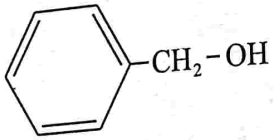


cyclohexanol
(cyclohexyl alcohol)

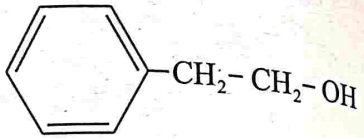


cyclohexane-1,2-diol

Aromatic alcohols;

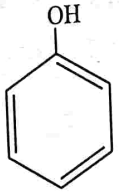


phenylmethanol
(benzyl alcohol)

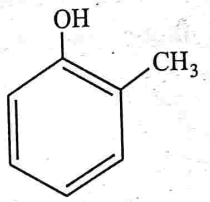


2-phenylethanol

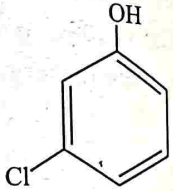
Phenols;



phenol



o-cresol



m-chlorophenol

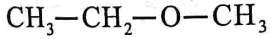
It should be noted that benzyl alcohol and cresols are also isomers. But benzyl alcoh is an aromatic alcohol, while cresols are phenols.

18.3 Ethers

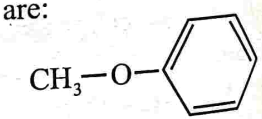
Ethers are a class of organic compounds in which the oxygen atom is linked to tw alkyl groups or two aryl groups or one alkyl and one aryl group. Thus the functiona group of ethers is C – O – C. They can be represented by the general formula R – O – Ethers are described as symmetrical or unsymmetrical depending on whether the tw groups bonded to oxygen are the same or different. Unsymmetrical ethers are als called mixed ethers. Diethyl ether is a symmetrical ether; ethyl methyl ether is a unsymmetrical ether (R – O – R′) . Examples of ethers are:



dimethyl ether
(R–O–R)



ethyl methyl ether
(R–O–R′)



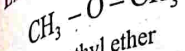
methyl phenyl ether

18.3.1 Nomenclature

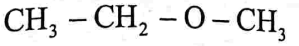
a. Common System

The two alkyl or aryl groups that are attached to the oxygen atom are named i alphabetical order and the word ether is added. When both alkyl groups are the same the prefix di- precedes the name of the alkyl group.

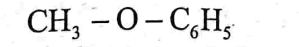
Examples



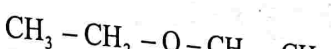
dimethyl ether



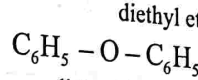
ethyl methyl ether



methyl phenyl ether
(anisole)



diethyl ether

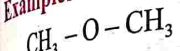


diphenyl ether

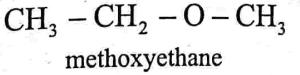
b. IUPAC System

Ethers are named in IUPAC nomenclature, as alkoxy derivatives of alkanes. The larger alkyl group is taken for parent name and the smaller alkyl group along with oxygen atom is named as *alkoxy* before the parent name.

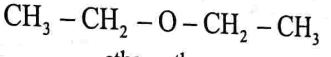
Examples



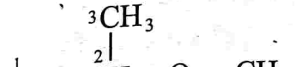
methoxymethane



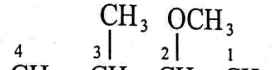
methoxyethane



ethoxyethane



2-methoxypropane



2-methoxy-3-methylbutane

18.3.2 Physical Properties

- Dimethyl ether and ethyl methyl ether are gases at RTP, while others are colourless volatile liquids with pleasant odours.
- Ethers are highly inflammable.
- They have much lower boiling points than those of alcohols of comparable molecular weights due to absence of hydrogen bonding **(Figure 18.3).**
- Low molecular weight ethers show some solubility in water as they can form hydrogen bonding with water **(Figure 18.3).** Ethers are readily soluble in organic solvents.
- Ethers are generally less dense than water.
- They are readily soluble in organic solvents.

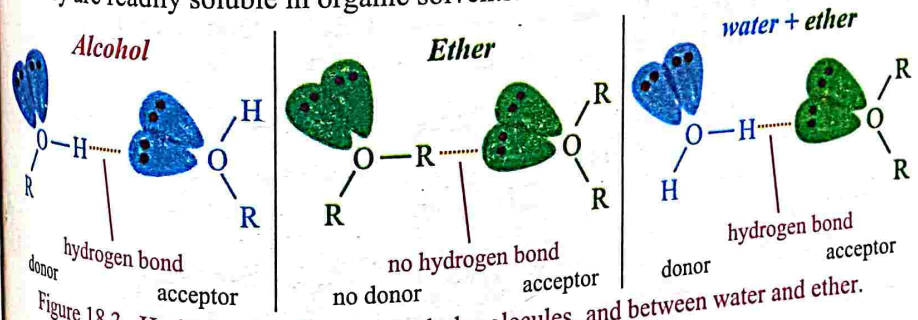


Figure 18.3 Hydrogen bonding in alcohol molecules, and between water and ether.

18.3.3 Preparation

Ethers can be prepared by the following methods.

1. Intermolecular dehydration of alcohols

Alcohols on intramolecular dehydration with concentrated sulphuric acid, give alkenes **(Sections 16.5.4.1 and 18.1.7.3).** However, intermolecular dehydration of alcohol with concentrated sulphuric acid at 140°C, yields ethers.

$$\underset{\text{alcohol}}{R-OH} + \underset{\text{alcohol}}{HO-R} \xrightarrow[140°C]{H_2SO_4} \underset{\text{ether}}{R-O-R} + H_2O$$

$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} + \underset{\text{ethyl alcohol}}{HO-CH_2-CH_3} \xrightarrow[140°C]{H_2SO_4} \underset{\text{diethyl ether}}{CH_3-CH_2-O-CH_2-CH_3} + H_2O$$

The reaction conditions must be well controlled otherwise at temperature higher than 140°C; the formation of alkenes is favoured. This method is useful for preparation of symmetric ethers because in an attempt to prepare an unsymmetrical ether, by mixing different alcohols, we usually obtain a mixture of ethers, which is too difficult to be separated.

2. Williamson's Synthesis

In this method, an alkoxide is treated with an alkyl halide. The alkoxide is usually derived from alcohols.

$$\underset{\text{alcohol}}{R-OH} + Na \longrightarrow \underset{\text{sodium alkoxide}}{R-\bar{O}\overset{+}{N}a} + \frac{1}{2}H_2$$

$$\underset{\substack{\text{sodium}\\\text{alkoxide}}}{R-\bar{O}\overset{+}{N}a} + \underset{\text{alkyl halide}}{R-X} \longrightarrow \underset{\text{ether}}{R-O-R} + NaX$$

For example ethyl methyl ether can be prepared as follows.

$$\underset{\text{ethyl alcohol}}{C_2H_5-OH} + Na \longrightarrow \underset{\text{sodium ethoxide}}{C_2H_5-\bar{O}\overset{+}{N}a} + \frac{1}{2}H_2$$

$$\underset{\text{sodium ethoxide}}{C_2H_5-\bar{O}\overset{+}{N}a} + \underset{\text{methyl chloride}}{CH_3-Cl} \longrightarrow \underset{\text{ethyl methyl ether}}{C_2H_5-O-CH_3} + NaCl$$

18.3.4 Chemical Reactivity

Ethers are quite stable compounds. They do not react with bases, active metals, oxidising and reducing agents. They are also stable to weak and dilute acids. However,

they form oxonium salts with strong and concentrated acids. The oxonium salts are unstable and can easily be cleaved. Their resistance to most of the reagents form the basis of their use as solvent for many organic reactions. The most important reaction of ether is the formation of oxonium salt and cleavage of ether linkage.

1. Formation of Oxonium Salts

Ethers react with cold concentrated hydrochloric acid and sulphuric acid to form oxonium salts. Ethers donate a pair of electrons to hydrogen ion to form these salts.

$$\underset{\text{ether}}{R-O-R} + \text{conc. } H_2SO_4 \longrightarrow \left[R-\overset{+}{\underset{H}{O}}-R\right] HSO_4^-$$

dialkyloxonium hydrogensulphate

$$\underset{\text{ether}}{R-O-R} + \text{conc. HCl} \longrightarrow \left[R-\overset{+}{\underset{H}{O}}-R\right] Cl^-$$

dialkyloxonium chloride

2. Cleavage of ether linkage

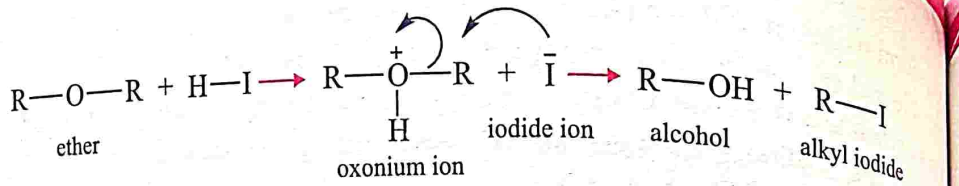
On prolong heating with dilute sulphuric acid, ethers undergo hydrolysis to original alcohols. The oxonium salt formed upon protonation, is further cleaved by attack of water nucleophile to form alcohols.

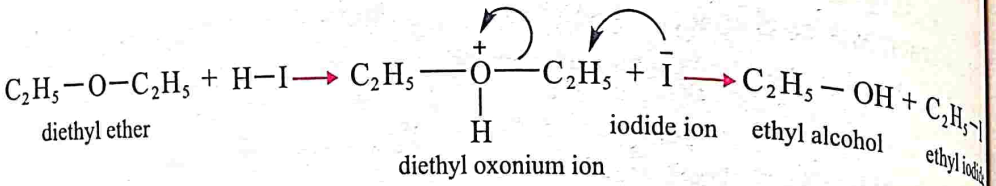
$$\underset{\text{ether}}{R-O-R'} \xrightarrow[-HSO_4^-]{H_2SO_4} \underset{\text{oxonium ion}}{R-\overset{+}{\underset{H}{O}}-R'} \xrightarrow{H_2O} \boxed{\underset{\text{alcohol}}{R-OH}} + R'-\overset{+}{O}H_2$$

$$R'-OH \xleftarrow{-H^+} R'-\overset{+}{O}H_2$$

$$\underset{\text{diethyl ether}}{C_2H_5-O-C_2H_5} \xrightarrow[-HSO_4^-]{H_2SO_4} \underset{\text{diethyloxonium ion}}{C_2H_5-\overset{+}{\underset{H}{O}}-C_2H_5} \xrightarrow[-H^+]{H_2O} \underset{\text{ethyl alcohol}}{2C_2H_5-OH}$$

Reaction of ethers with hot concentrated HI or HBr results in a mixture of alcohol and alkyl halide. The reaction involve the formation of oxonium ions, which is then cleaved by attack of iodide or bromide ion to form the corresponding alkyl halide and alcohol.





Society, Technology And Science

Antiseptics and disinfectants are very similar in that they are both used for killing microorganisms although they differ in structure and uses.

Antiseptics are used on living organisms, such as human skin, to kill any microorganisms living on the bodies' surface. Disinfectants are used on non-living things, such as countertops and handrails, to kill the microorganisms living on that inanimate surface.

Antiseptics are typically found to have a lower concentration of the particular biocide which is used in that product to clean the surface other than that of a disinfectant. Since the disinfectants are not meant for use on living tissues, but rather inanimate surfaces, they can use the higher concentration of biocide in the product since there is no skin or tissue to worry about irritation. Antiseptics require the lower concentration of biocide as too high concentrations of certain biocides could cause high amounts of skin irritation.

Some examples of antiseptics are mouthwash or hand sanitizer, both of which are safe to come in contact with your skin and also are able to be extremely effective at killing high amounts of microorganisms.

Phenols, bleach and formaldehyde are all examples of different types of disinfectants used to kill the microorganisms on the surface of any non-living objects.

It is essential for people to know the difference between antiseptics and disinfectants since they are both used for similar things but in different ways. Using a disinfectant as an antiseptic would likely irritate that tissue. Also, using an antiseptic as a disinfectant could result in a less sufficient job of cleaning that surface due to the lower concentration of biocide. Extreme caution must be taken to avoid contact with eyes and mucous membranes. The negative effect of disinfectant is that it is caustic to the skin, lungs and eyes.

Key Points

- Alcohols are compounds, in which a hydroxyl group (–OH) is attached to aliphatic carbon atom.
- Hydroxyl group is attached to aromatic carbon atoms in phenols.
- Lucas test is used to distinguish between primary, secondary and tertiary alcohols.
- The formation of ester from alcohol and carboxylic acid is called "esterification".
- Each carbon atom in phenol is sp^2-hybridized.
- Dow process is used for preparation of phenol from chlorobenzene and aqueous NaOH at high pressure and temperature.
- Ethers are a class of compounds in which, with oxygen atom two alkyl groups, two aryl groups or one alkyl and one aryl group are attached.
- General formula of ether is R–O–R.
- Ethers react with cold conc. HCl or H_2SO_4 to form oxonium salt.
- In Williamson synthesis method, sodium alkoxide is treated with an alkyl halide to produce ether.
- Hydrogen bonding in alcohols result in relatively high boiling points and good miscibility with water.

Exercise

Choose the correct one from the given options.

1. Isopropyl alcohol is a type of
   a. primary alcohol. b. secondary alcohol.
   c. tertiary alcohol. d. none of these.
2. Which of the following has the highest boiling point?
   a. Dimethyl ether b. Ethyl alcohol
   c. n–propyl alcohol d. Isopropyl alcohol
3. Trimethylene glycol is a
   a. vic–diol. b. gem–diol.
   c. triol. d. none of these.
4. The final product of oxidative cleavage of ethylene glycol with periodic acid is
   a. formaldehyde. b. acetaldehyde.
   c. formic acid. d. mixture of formaldehyde and acetaldehyde.
5. Oxygen carrying positive charge and bonded to three other atoms is called
   a. oxide ion. b. oxonium ion.
   c. carbocation. d. carbanion.
6. Which of the proper reagent used for oxidation of a primary alcohol to aldehyde?
   a. Acidified dichromate b. Acidified chromate
   c. Acidified permanganate d. PCC
7. Which one is an aromatic alcohol?
   a. methyl alcohol b. ethyl alcohol
   c. benzyl alcohol d. p–cresol
8. Compound which is added to natural gas to make gas leakage detectable?
   a. phenol b. ethanthiol
   c. methanol d. hydrogen sulphide
9. Which of the following is more reactive toward Lucas Reagent?
   a. methanol b. ethanol
   c. 2–methyl–2–propanol d. 2–butanol
10. Ethoxyethane when treated with conc. H_2SO_4 produces
    a. carbocation b. oxonium ion
    c. carbanion d. oxalate ion

11. Lucas Reagent is
    a. Zn–Hg/HCl b. $ZnCl_2 + HCl$
    c. $Zn + H_2O$ d. $Na + liq.NH_3$
12. The reaction of an alcohol with sodium produces
    a. ethane b. ethene
    c. alkoxide d. aldehyde
13. Benzene diazonium salt is a reactive salt and upon hydrolysis yields
    a. phenol. b. benzene.
    c. diazobenzene. d. benzoic acid.
14. Oxidation of secondary alcohol gives
    a. carboxylic acid b. ether
    c. aldehyde d. ketone
15. The appearance of cloudiness in the Lucas test for alcohol is due to formation of
    a. alkyl chloride. b. acid chlorides.
    c. aldehydes. d. ketones.

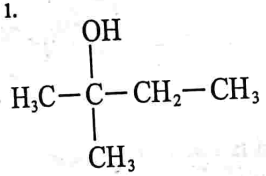
Q2. Write short answers of the following questions.

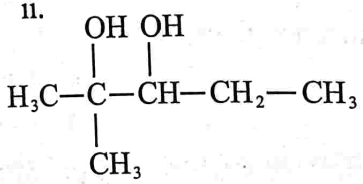
i. What is the basic difference between an alcohol and phenol, although both have same functional group?
ii. How many isomeric alcohols are possible for C_4H_9OH? Draw their structural formulae and write both common and IUPAC names.
iii. What is Lucas test? How Lucas test is used to distinguish alcohols?
iv. Why phenol is more acidic than alcohols?
v. What is meant by primary, secondary and tertiary alcohols?
vi. Why alcohol and ethers are easily protonated unlike phenol?
vii. Why intermolecular dehydration of alcohol is not a suitable method for synthesis of asymmetric ethers?
viii. How bromine water test in alkene differ from bromine water test for phenol?
ix. Why benzene diazonium salt is not much stable and hydrolyse to phenol easily?
x. Why tertiary alcohol can not be oxidized?

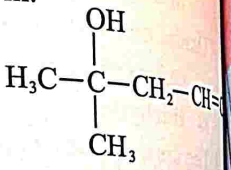
Q3. Write detail answers of the following questions.

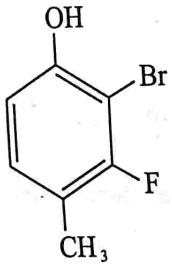
1. (a) Describe the reaction for preparation of diethyl ether, by dehydration of alcohol and Williamson's synthesis.
   (b) Write two chemical reactions of diethyl ether.
   (c) Enlist the physical properties of ether.
2. (a) What are phenols? Give method of preparation of phenol.
   (b) Discuss the acidic behaviour of phenol.

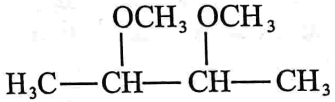
3. Give detail description of structure and chemical properties of phenols.
4. (a) Discuss the structure, synthesis and chemical reactions of alcohols.
   (b) How alcohols are slightly acidic?
5. (a) How alcohol can be prepared from Grignard reagents.
   (b) Mention the reaction for the formation of following compounds from alcohol.
   (i) ethene (ii) ethlyacetate (iii) acetone (iv) formaldehyde
   (c) Write the systematic names for the following organic compounds;

i. 

ii. 

iii. 

iv. 

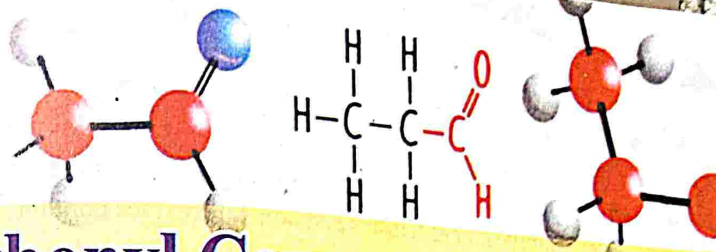
v. 

   (d) Draw the structural formula of the following organic compounds;
   i. pentan–2–ol
   ii. 3,4–dimethylhexan–2–ol
   iii. 4–methylpent–3–en–2–ol
   iv. 3,4–dimethyl–2–nitrophenol
   v. 2,3–dimethoxy–4–methylpentane

Project

Dissolve few drops or one small crystal of phenol in 10 mL of ethyl alcohol or methyl alcohol. Stir vigorously while adding bromine water, drop–wise. Rapid loss of reddish brown color of bromine water and formation of white precipitate of 2,4,6–tribromophenol suggests the presence of phenol **(Section 18.2.7.1).**

Unit 19

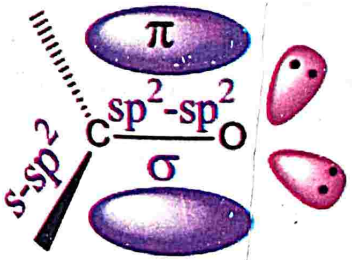


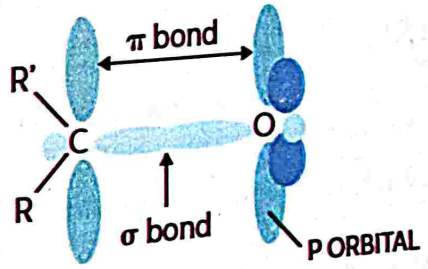
Carbonyl Compounds 1: Aldehydes and Ketones

Teaching	Assessment	Weightage %
14	1	4

After studying this unit, 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 alcohol and Friedel Craft's acylation of aromatics. (Applying)
- Describe the reactivity of aldehydes and ketones and their comparison. (Analyzing)
- Describe acid and base catalyzed nucleophillic 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

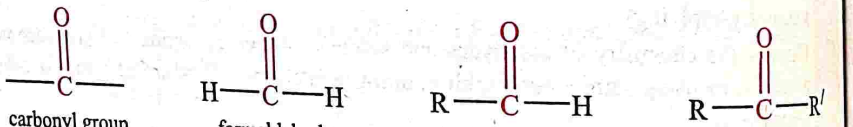
Some important classes of organic compounds like aldehydes, ketones, carboxylic acids, esters, amides, acid halides and acid anhydrides contain a group called carbonyl group (shown below), and are therefore called carbonyl compounds. Many of these compounds are important commercially and in biological processes. In addition to their uses as reagents and solvents, they are constituents of fabrics, flavorings, plastics, and drugs. Naturally occurring carbonyl compounds include proteins, carbohydrates and nucleic acids which constitute major portion of plants and animals body.

A carbonyl group is a functional group which is composed of a carbon atom doubly bonded to an oxygen atom.



carbonyl group

The simplest carbonyl compounds are ketones and aldehydes. A ketone has two alkyl (or aryl) groups bonded to the carbonyl carbon atom. An aldehyde has one alkyl (or aryl) group and one hydrogen atom bonded to the carbonyl carbon atom. The functional group of aldehyde, which is carbonyl group along with one hydrogen (–CHO), is also called formyl group. Formaldehyde is the simplest aldehyde, with two hydrogen atoms bonded to the carbonyl group.



carbonyl group | formaldehyde | higher aldehydes | ketones

If the two alkyl groups attached to carbonyl carbon are the same the ketone is called symmetrical and if different, it is called unsymmetrical ketone. Instead of alkyl, aryl group(s) can also be attached to carbonyl carbon, in aromatic aldehydes and ketones.

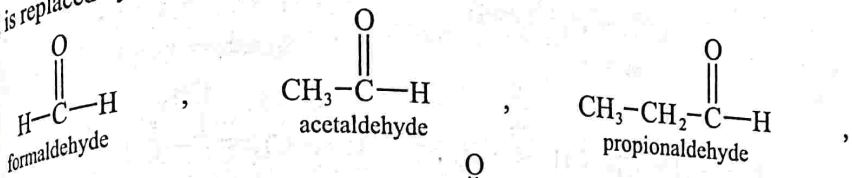
19.1 Nomenclature

Two types of naming systems are used for naming aldehydes and ketones. Common system and IUPAC system.

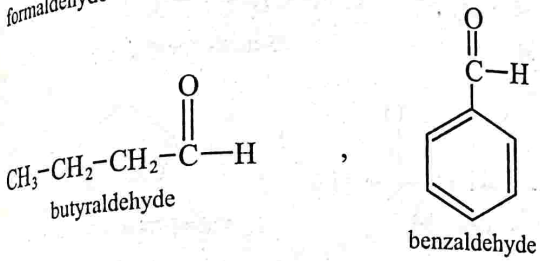
19.1.1 Nomenclature of Aldehydes

a. Common System

Common names of aldehydes are derived from the common names of carboxylic acids containing the same number of carbon atoms **(Section 20.1).** While naming aldehydes in this system, the ending "-ic acid" in the common name of corresponding carboxylic acid is replaced by the word "-aldehyde".

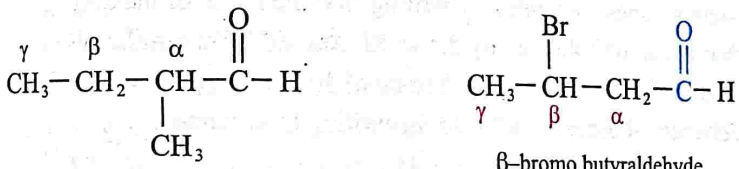


formaldehyde , acetaldehyde , propionaldehyde ,



butyraldehyde , benzaldehyde

The position of other groups on the chain are indicated by Greek letters, α, β, γ etc. Letter starts from the carbon atom adjacent to formyl group. The first letter, is given to the carbon atom next to the carbonyl group.



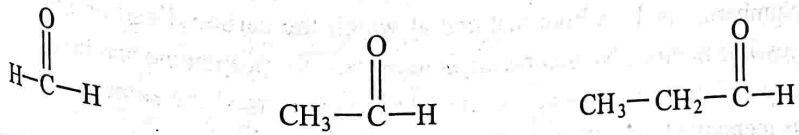
α–methyl butyraldehyde | β–bromo butyraldehyde

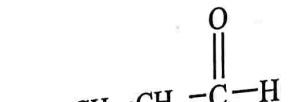
b. IUPAC System

In this system, following rules are used for naming aldehydes.

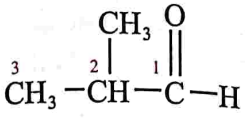
1. In IUPAC system, the ending "–e" of the corresponding alkane is replaced by "–al".
2. Prefixes di–, tri– etc. is added before suffix –al, when two or three carbonyl groups respectively, are present.
3. If the aldehyde group is attached to a ring, the suffix carbaldehyde is used.
4. Locate the longest chain of carbon atoms containing formyl group to get the stem name.
5. Carbon atoms of the selected chain are numbered from the carbon of formyl group (-CHO) because it is always at the terminal position. It is not necessary to mention the position of aldehydic carbonyl.
6. The rules for naming substituents are same as in case of alkanes.

Examples

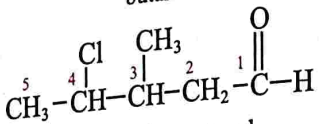




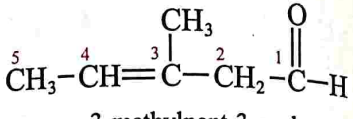
butanal



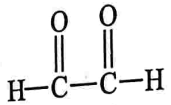
2-methylpropanal



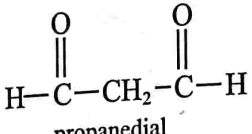
4-chloro-3-methylpentanal



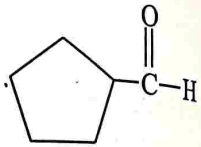
3-methylpent-3-enal



ethanedial



propanedial

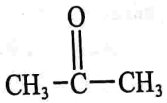


cyclopentanecarbaldehyde

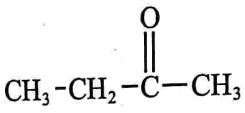
19.1.2 Nomenclature of Ketones

a. Common System

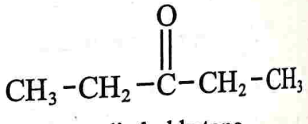
In this system ketones are named by writing first the name of the alkyl groups attached to the carbonyl carbon followed by the word "ketone". For similar alkyl or aryl groups prefix "di" is used before their name. In case of different groups attached to the carbonyl carbon, alphabetical order is followed for writing their names.



dimethyl ketone (acetone)



ethyl methyl ketone

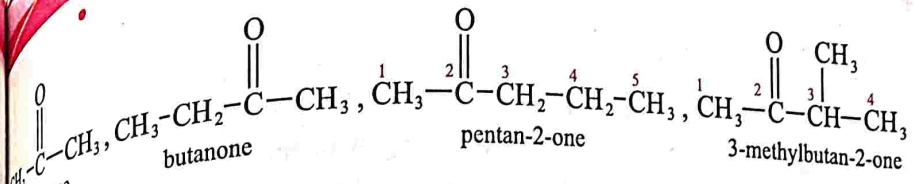


diethyl ketone

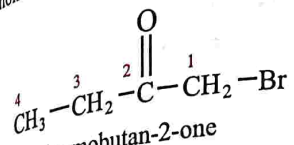
b. IUPAC System

While naming ketones in IUPAC system the following rules are followed;

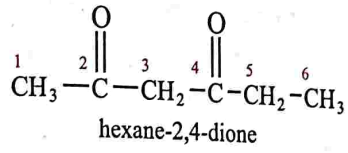
1. Select the longest chain for stem name of ketone, which is then named by replacing the ending "–e" of corresponding alkane by "–one".
2. Prefix di–, tri– etc. is added before suffix –one, if more than one carbonyl groups are present.
3. The carbons of the selected chain are numbered to mention the position of the carbonyl carbon before suffix –one because in ketones carbonyl group may occur at various positions on the carbon chain.
4. Numbering is done from that end at which the carbonyl carbon has the lowest possible number. No numbering is necessary for propanone and butanone.
5. If substituents are attached to the selected chain then the same rules are obeyed as mentioned for IUPAC names of alkanes.



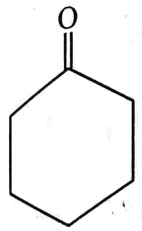
propanone, butanone, pentan-2-one, 3-methylbutan-2-one



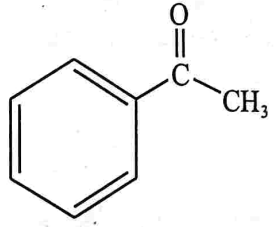
1-bromobutan-2-one



hexane-2,4-dione



cyclohexanone

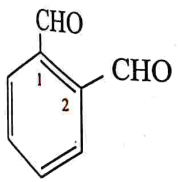


phenylethanone (acetophenone)

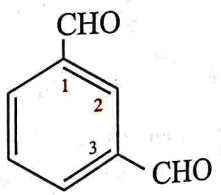
Isomerism in Aldehydes and Ketones

Aldehydes containing four or more carbon atoms and ketones containing five or more carbon atoms can exhibit chain isomerism. For example, butanal and 2-methylpropanal are chain isomers of aldehydes containing four carbon atoms, while pentan-2-one and 3-methylbutanone are chain isomers of ketone containing five carbon atoms.

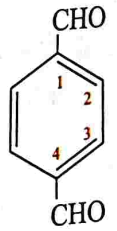
Ketones having five or more carbon atoms and aromatic aldehydes can exhibit position isomerism. For example, pentan-2-one and pentan-3-one are position isomers of ketone having five carbon atoms. Aromatic aldehydes can also show position isomerism e.g. benzene-1,2-dicarbaldehyde, benzene-1,3-dicarbaldehyde and benzene-1,4-dicarbaldehyde are position isomers.



benzene-1,2-dicarbaldehyde



benzene-1,3-dicarbaldehyde



benzene-1,4-dicarbaldehyde

Aldehydes and ketones have the same general formula, $C_nH_{2n}O$ and can exhibit functional group isomerism e.g. propanal and propanone are functional groups isomers. Aldehydes and ketones also show tautomerism **(Section 16.6.1)**.

19.2 Structure

Let us consider formaldehyde as an example to illustrate the structure of carbonyl group of aldehyde and ketone. The carbon and oxygen in the carbonyl group, present in aldehydes and ketones are linked by a *sigma* bond and a *pi* bond. Both carbon as well as oxygen of the carbonyl group are sp^2-hybridized. The carbon-oxygen sigma and pi bonds are formed by linear sp^2-sp^2 and sidewise overlap of *p* orbitals respectively. Two of the sp^2-hybrid orbitals of oxygen has two unshared electron pairs, while two of the sp^2-hybrid orbitals of carbon overlap with *s* orbitals of two hydrogen atoms to form carbon-hydrogen sigma bonds in formaldehyde **(Figure 19.1)**.

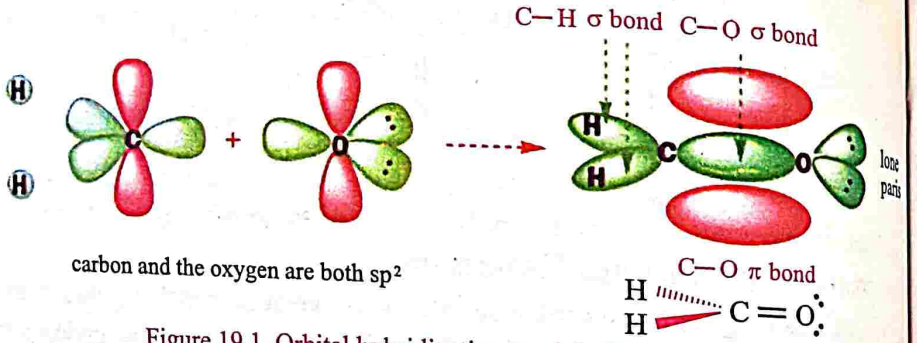


Figure 19.1 Orbital hybridization model of formaldehyde.

The three atoms attached to carbonyl carbon lie in a plane and are arranged in trigonal planar manner. The carbon-oxygen bond length is 120 pm, which is significantly shorter than carbon-oxygen bond length in alcohols and ether (142 pm). The bond angles around carbonyl carbon are approximately 120°. Slight deviation is observed depending upon nature of atoms or groups attached to carbon in various aldehydes and ketones. The bond angles in some of the known aldehydes and ketones are shown in **(Figure 19.2)**.

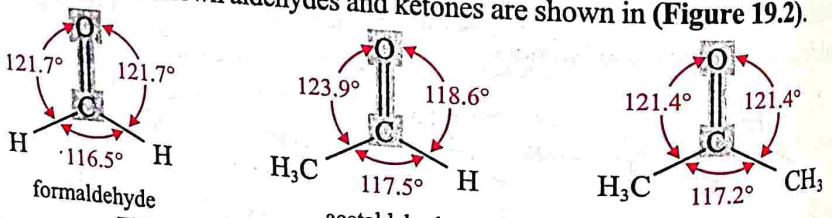
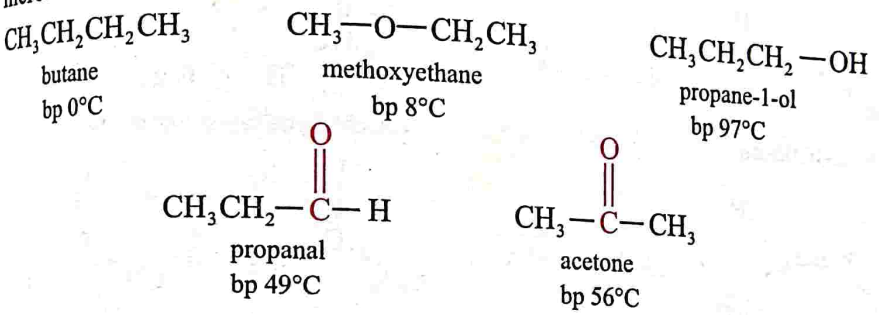


Figure 19.2 Bond angles in some aldehydes and ketones.

19.3 Physical Properties

- Lower aldehydes like formaldehyde and acetaldehyde have very sharp pungent odour whereas higher members of aldehydes as well as most of the ketones have pleasant odour.
- Formaldehyde is a gas at room temperature while other aldehydes are colourless volatile liquids. Formaldehyde is often stored and used as a 40% aqueous solution called formalin. Acetone and other members of ketone series are also colourless volatile liquids.
- Aldehydes and ketones are polar compounds due to high dipole moment of their C=O bond. As a result they have higher boiling points than the corresponding alkanes and non-polar compounds like ethers. But they cannot form hydrogen bonds with themselves, therefore they usually have lower boiling points than corresponding alcohols. Boiling point of aldehydes and ketones increase with the increase in the molecular mass.



- Lower aldehydes and ketones, upto four carbon atoms are water soluble. Water solubility decreases as the size of the non-polar alkyl group increases. Higher members of aldehydes and ketones are usually insoluble in water, while formaldehyde is highly soluble in water. Carbonyl compounds cannot form hydrogen bonds with themselves as there is no hydrogen on the carbonyl oxygen. However, their solubility in water is due to hydrogen bond formation of carbonyl oxygen with water molecules **(Figure 19.3)**

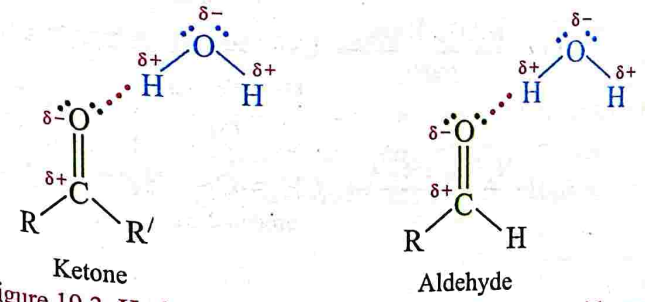


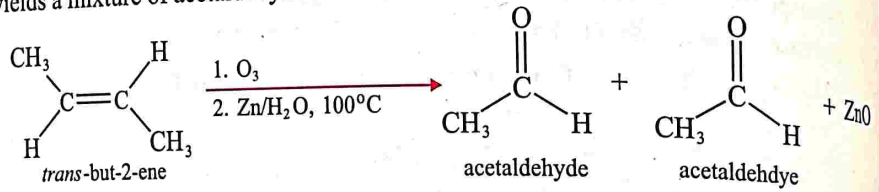
Figure 19.3 Hydrogen bond of aldehyde and ketone with water.

19.4 Preparation of aldehydes and Ketones

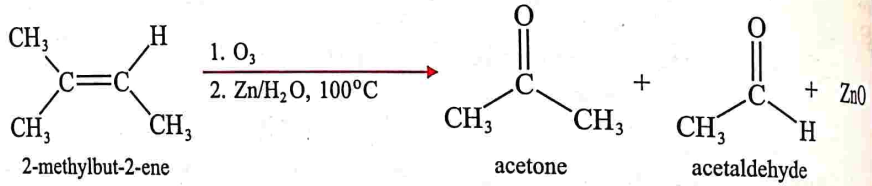
Aldehydes and ketones may be prepared by the following methods.

19.4.1 Ozonolysis of Alkenes

Ozone reacts vigorously with alkenes to form an unstable intermediate compound called ozonide. The ozonide is reduced directly to aldehydes and ketones by zinc and water, to produce aldehyde and/or ketones. The reaction is called ozonolysis. Symmetrical alkene produces single product while asymmetric alkene yield a mixture of aldehydes/ketones **(Section 16.5.7.7)**.For example, ozonolysis of symmetric but-2-ene (both *cis* and *trans*) gives only acetaldehyde, while asymmetric 2-methylbut-2-ene yields a mixture of acetaldehyde and acetone.



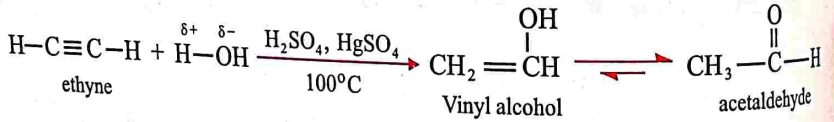
trans-but-2-ene — acetaldehyde + acetaldehdye



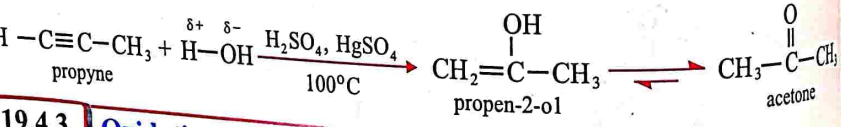
2-methylbut-2-ene — acetone + acetaldehyde

19.4.2 Hydration of Alkynes

Alkynes undergo acid-catalyzed addition of water across the triple bond in the presence of mercuric sulphate and sulfuric acid as a catalyst to produce carbonyl compounds. Acetaldehyde is produced in case of acetylene, while ketones are produced from higher alkynes **(Section 16.7.8.4)**.



ethyne → Vinyl alcohol ⇌ acetaldehyde

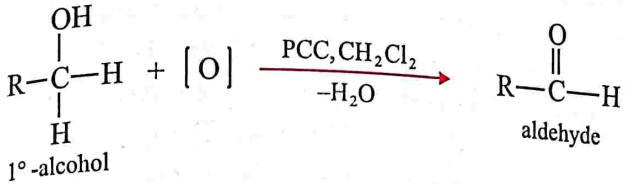


propyne → propen-2-ol ⇌ acetone

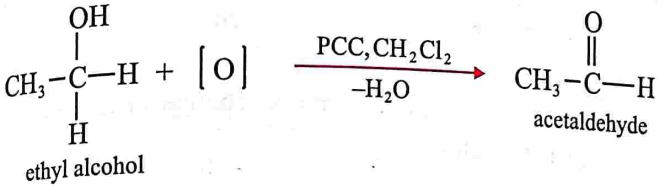
19.4.3 Oxidation of Alcohols

Oxidation of a primary alcohol with strong oxidizing agents like, acidified chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) or permanganate (MnO_4^-) solution leads to the formation of a carboxylic acid as final product, through aldehydes intermediate. However, good yield of aldehydes can be obtained using oxidizing agents such as

pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl, without over (excessive) oxidation **(Section 18.1.7.5)**.

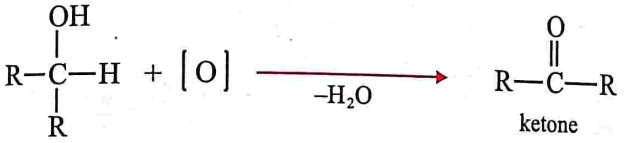


1° -alcohol → aldehyde

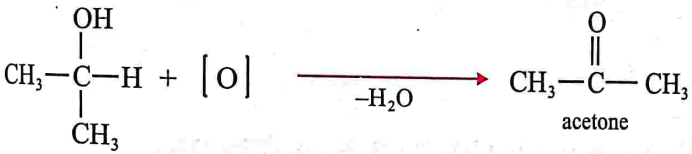


ethyl alcohol → acetaldehyde

Secondary alcohols are oxidized to ketones by the same reagents that oxidize primary alcohols.



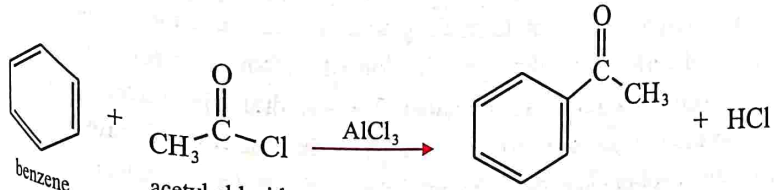
2° -alcohol → ketone



isopropyl alcohol → acetone

19.4.4 Friedel-Crafts Acylation of Aromatics

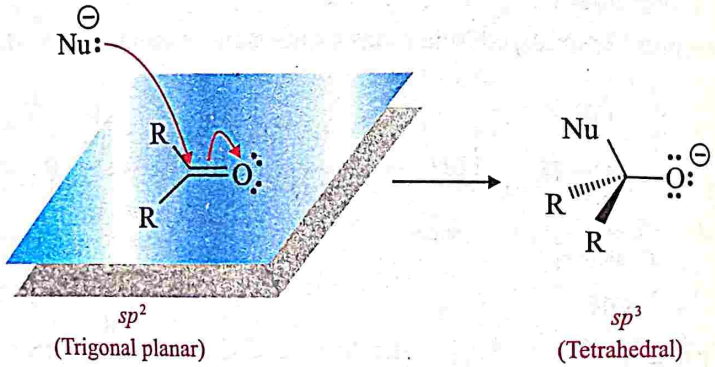
Benzene reacts with acid halides (or anhydrides) in the presence of a Lewis acid catalyst to give aromatic ketones. For example, benzene react with acetyl chloride in the presence of aluminum chloride catalyst to form acetophenone **(Section 16.8.5.2.6)**.



benzene + acetyl chloride → acetophenone

19.5 Reactivity of Carbonyl Group

Ketones and aldehydes undergo many reactions to give a wide variety of useful derivatives. Their most common reactions are nucleophilic addition; addition of a nucleophile and a proton across the C=O double bond. The reactivity of the carbonyl group arises from the high electronegativity of the oxygen atom and the resulting polarization of the carbon–oxygen double bond. The electrophilic carbonyl carbon atom is sp^2-hybridized and planar, and relatively unhindered (compare to tetrahedral carbon) and is more susceptible for attack by a nucleophile, from either side of the double bond. When a nucleophile attacks the carbonyl group, the carbon atom changes hybridization from sp^2 to sp^3, with corresponding change in geometry from trigonal planar to tetrahedral as shown below.

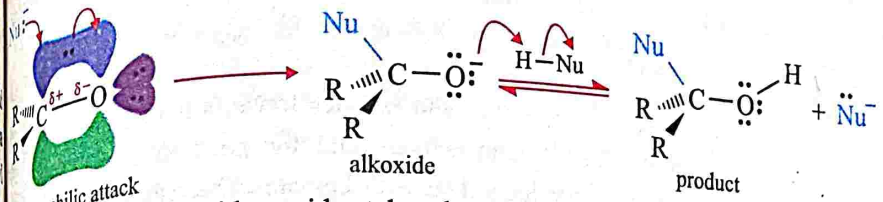


19.6 Reactions of Aldehydes and Ketones

Aldehydes and ketones are very reactive substances mostly undergoing nucleophilic addition reaction across C=O bond. These can also be oxidized as well as reduced. Some of their reactions are;

19.6.1 Nucleophilic Addition reactions: (Acid and Base catalyzed)

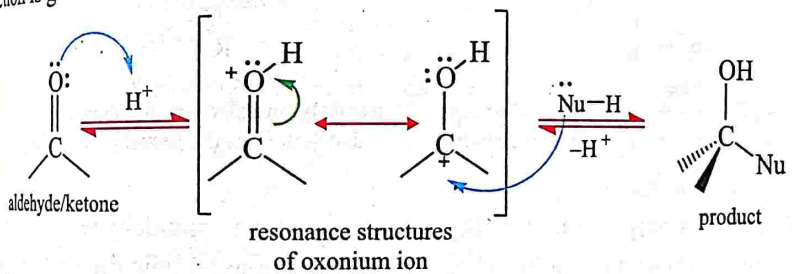
As already discussed in **Section 19.5**, that aldehydes and ketones mainly undergo nucleophilic additions reactions. In nucleophilic addition reaction, the nucleophile attacks on the carbonyl carbon, and the hybridization of carbon changes from sp^2 to sp^3. The geometry also changes from trigonal planar to tetrahedral. The electrons of the *pi* bond are forced out to the oxygen atom to form an alkoxide ion, which is protonated to give the product of nucleophilic addition. A generalized example of nucleophilic addition of a strong nucleophile ($\ddot{N}u^-$), followed by protonation of alkoxide ion is shown below.



These reactions may be either acid catalyzed or base catalyzed.

a. Acid-Catalyzed Addition Reactions

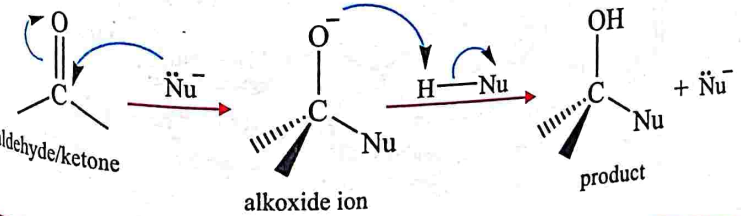
Because of the unshared electron pair on oxygen atom, carbonyl oxygen acts as Lewis base, and can be protonated. Acid can catalyze the addition of weak nucleophiles to carbonyl compounds by protonating the carbonyl oxygen atom, to form an oxonium ion. This increases the electrophilic nature of the carbonyl carbon by inducing more positive charge on it and thus enhances its ability to be attacked by weak nucleophiles. For example, the mechanism of acid-catalyzed nucleophilic addition of generalized reaction is given below.



Addition of water, alcohol, ammonia, amines etc. generally follow this mechanism. .

b. Base-Catalyzed Addition Reactions

A base-catalyzed nucleophilic addition will take place in the presence of a strong base, which is usually the conjugate base of a reagent used for nucleophilic addition. The base which is also a nucleophile, attacks at the carbon atom of the carbon–oxygen double bond, and pi electrons of C=O bond move to the oxygen atom, which can easily accommodate the negative charge, because of its high electronegativity. The reaction is completed by the abstraction of a proton, from the reagent by negative oxygen, to regenerate the base. Thus, base increases the nucleophilic character of the reagent to be added.



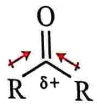
Addition of hydrogen cyanide in the presence of cyanide base to form cynohydrin follow this type of mechanism **(Section 19.6.3.3).**

19.6.2 Relative Reactivity

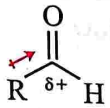
Generally aldehydes are more reactive than ketones towards nucleophilic addition. They usually react more quickly than ketones and the position of the equilibrium usually lies more toward the products than with ketones. The enhanced reactivity of aldehydes is due to an electronic effect and a steric effect.

(a) Electronic Effect

A ketone has two electron donating alkyl groups that can stabilize (neutralize) the partial positive on the carbon atom of the carbonyl group. In contrast, aldehydes have only one electron-donating group (formaldehyde has none); thus the partial positive charge of an aldehyde is less stabilized than a ketone. As a result, aldehydes are more electrophilic than ketones and therefore more reactive.



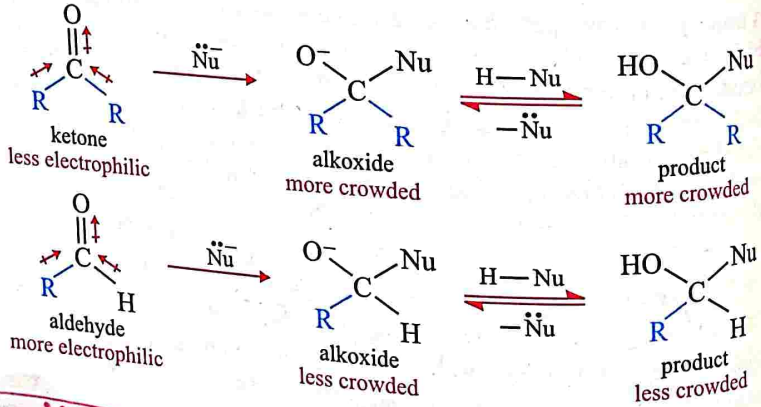
A ketone
has **two** electron-donating alkyl groups that stabilize the partial positive charge



An aldehyde
has **only one** electron-donating alkyl group that stabilizes the partial positive charge

(b) Steric Hindrance

An aldehyde has only one bulky alkyl group (except formaldehyde) while ketone has two alkyl groups with carbonyl carbon. Thus the aldehydic carbonyl carbon is more exposed toward nucleophilic attack, than ketones. Similarly the transition state of nucleophilic addition of aldehyde is less crowded and of lower energy than ketones.



19.6.3 Reduction of Aldehydes and Ketones

Addition of hydrogen to aldehydes and ketones is called reduction. Following are some important reactions of aldehydes and ketones that involve reduction.

Tidbit

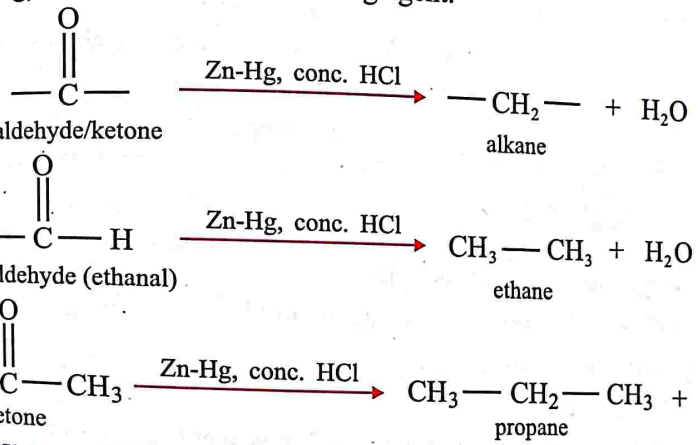
Formaldehyde is the most reactive than all other higher aldehydes and ketones. The high reactivity is attributed to the unavailability of electron donating bulky alkyl groups with carbonyl carbon of formaldehyde.

19.6.3.1 To Hydrocarbons

Aldehydes and ketones can be reduced to saturated hydrocarbons either by Clemmensen reduction or by Wolf-Kishner reduction.

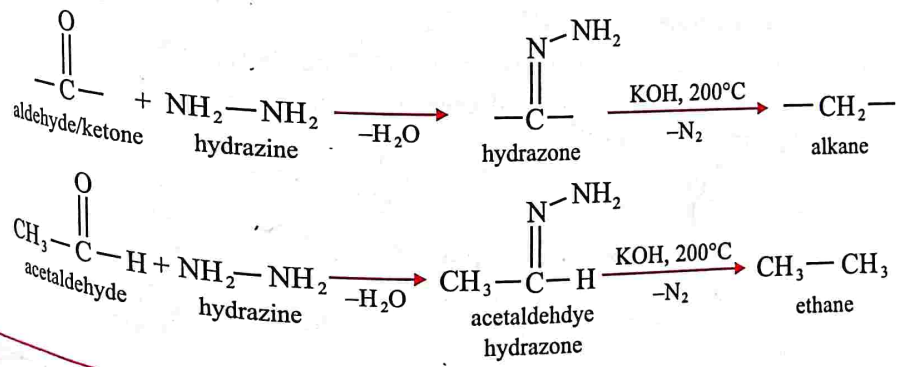
(a) Clemmenson Reduction

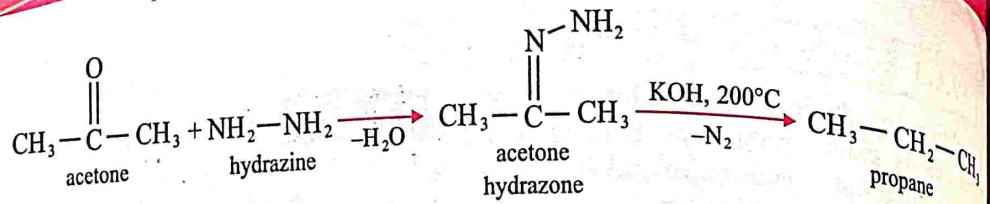
In this reaction aldehydes and ketones are reduced to alkanes in the presence of Zinc amalgam (Zn-Hg) and conc. HCl as reducing agent.



(b) Wolf-Kishner Reduction

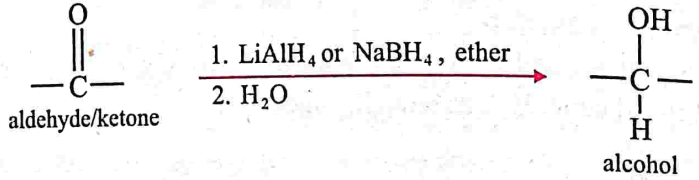
When an aldehyde or ketone is treated with hydrazine a corresponding hydrazone is obtained, which on heating with KOH in boiling ethylene glycol (200°C) gives corresponding alkanes.

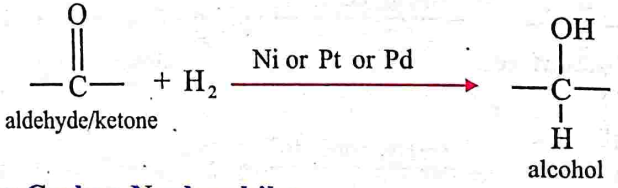




19.6.3.2 Using Hydrides to give Alcohols

Aldehydes and ketones are reduced to alcohols, by using catalytic method or metal hydrides **(Section 18.1.5.5)**. Formaldehyde produces methyl alcohol, higher aldehydes give primary alcohols while ketones yield secondary alcohols.





19.6.3.3 Using Carbon Nucleophiles

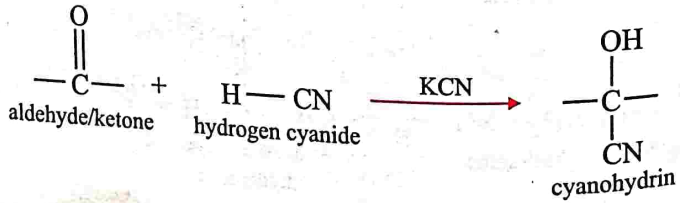
Carbon nucleophiles, such as Grignard reagent and hydrogen cyanide, can also convert the carbonyl group into hydroxyl group.

(a) Using Grignard Reagent

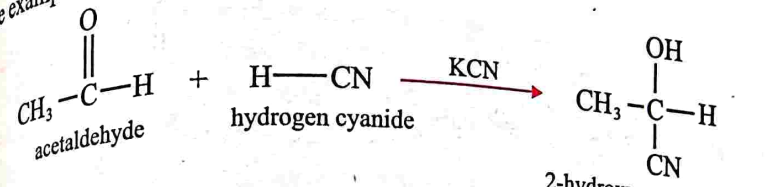
Grignard reagents act as carbon nucleophiles toward carbonyl compounds. The R- group of the Grignard reagent adds irreversibly to the carbonyl carbon, forming a new carbon-carbon bond in the intermediate alkoxide (addition product). The alkoxide upon acid workup gives alcohol **(Section 17.2.3.1)**.

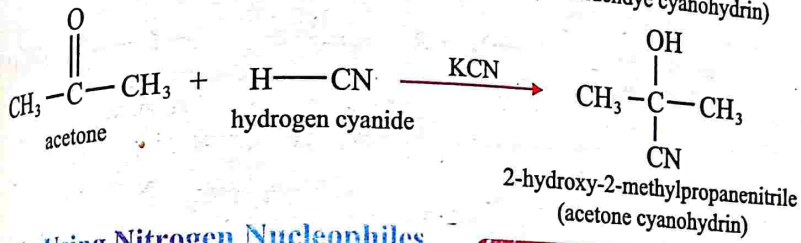
(b) Using Hydrogen Cyanide (HCN)

The carbon in hydrogen cyanide also acts as carbon nucleophile and undergoes nucleophillic addition to aldehydes and ketones in the presence of a cyanide base to yield cyanohydrins.



Some examples of cyanohydrins formation are given below.



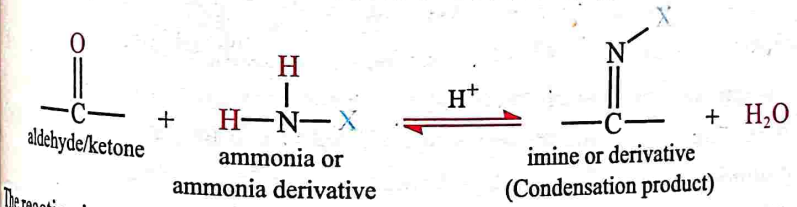


19.6.3.4 Using Nitrogen Nucleophiles

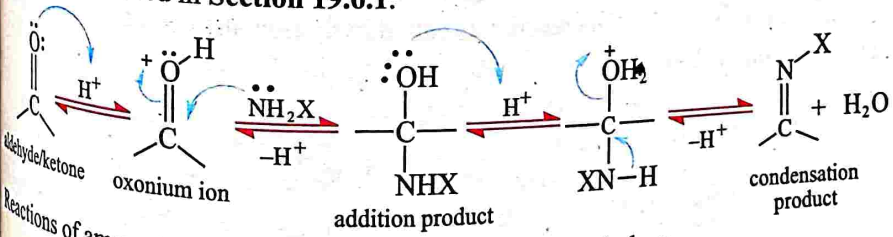
Ammonia and ammonia derivatives such as primary amines ($R–NH_2$), hydroxyl amine ($NH_2–OH$), hydrazine ($NH_2–NH_2$) and phenyl hydrazine ($NH_2–NH–C_6H_5$) add to carbonyl group of aldehyde and ketone in the presence of acid catalyst to form an unstable addition product. The stabilization of addition product is achieved by dehydration, to form a condensation product which are imine or imine derivatives.

Tidbit

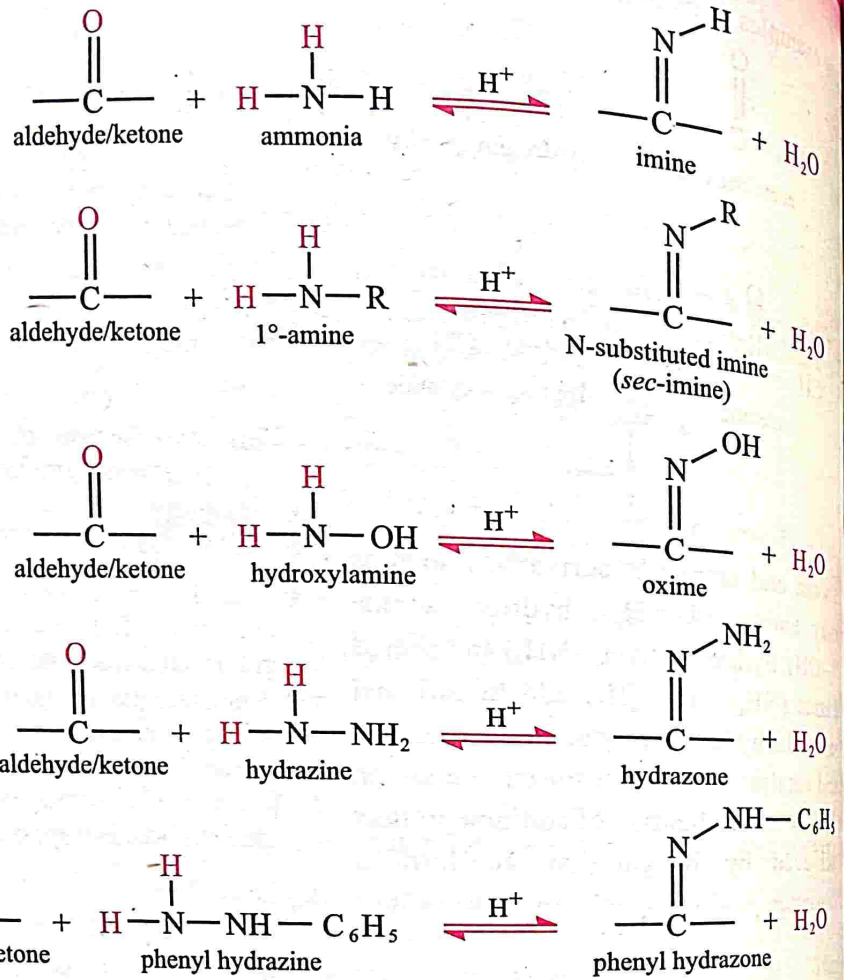
- Cyanohydrins are compounds with a hydroxyl (–OH) and cyano (–CN) groups attached to the same carbon.
- Ammonia and ammonia derivatives act as nucleophiles toward the carbonyl carbon atoms because of presence of unshared electron pair on nitrogen atom in these compounds.



The reaction is catalyzed by an acid. The mechanism is similar to general acid-catalysed mechanism discussed in **Section 19.6.1**.



Reactions of ammonia and ammonia derivatives are given below.

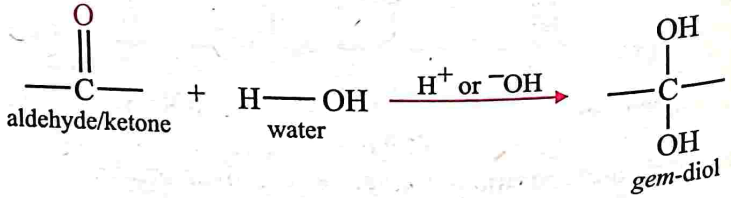


19.6.3.5 Using Oxygen Nucleophiles

Water and alcohols are oxygen nucleophiles. They can add to carbonyl group to form addition products.

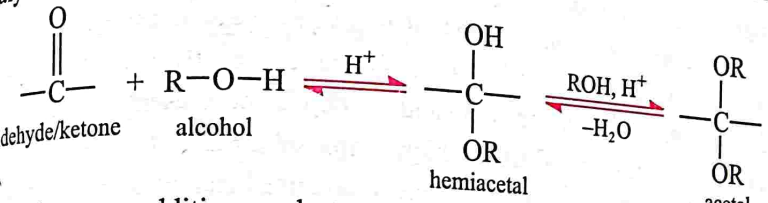
a. Using Water

When aldehydes or ketones react with water, they add a water molecule and form *geminal* diols (1,1-doils). The reaction is called hydration and can be catalyzed by acid or any hydroxide base.



b. Using Alcohol

Like water, alcohol also adds reversibly to carbonyl group, in the presence of acid catalyst and initially forms an addition product, generally called hemiacetal. Hemiacetal contains both hydroxyl and alkoxy groups bonded to same carbon. In the presence of excess of alcohol, hemiacetal reacts further to form acetal with removal of water. Acetal has two alkoxy group at the same carbon and are geminal diethers. Although hydration is catalyzed by either acid or base, acetal formation must be acid-catalyzed.



Aldehydes give more addition product at equilibrium than ketones.

19.6.4 Oxidation Reactions of Carbonyl Compounds

Both aldehydes and ketones undergo oxidation in the presence of oxidizing agents, however, aldehydes are more easily oxidized than ketones as the hydrogen atom attached to the carbonyl group in aldehydes is oxidized to -OH group.

Tidbit

Acetals formed from ketones are often called ketals, although this term has been dropped from the IUPAC nomenclature and the term acetal is now applied to the adducts of both aldehydes and ketones.

a. Oxidation of Aldehydes

Aldehydes are easily oxidized to carboxylic acids, in the presence of strong oxidizing agents like acidified permanganate or acidified dichromate, but also by mild oxidizing agents like Fehling's solution, Benedict's solution and Tollen's reagent. Oxidation with strong oxidizing agents is already discussed in **(Section 18.1.7.5)**. Oxidation with mild oxidizing agents such as Fehling's solution, Benedict's solution and Tollen's reagent are used to distinguish aldehydes from ketones, as ketones are not oxidized by these reagents.

i. Tollen's reagent test

Tollen's reagent is ammonical silver nitrate and prepared by adding dilute solution of ammonia to solution of silver nitrate until the initially formed precipitate of silver(I) oxide dissolves. Ammonia forms a complex of diamminesilver(I) hydroxide ($[Ag(NH_3)_2]OH$) which is water soluble. When aldehyde is heated with this Tollen's reagent, it oxidizes the aldehyde to corresponding carboxylate ion and the silver ion present in Tollen's reagent, is reduced to metallic silver which deposits on the walls of

test tube and forms a silver mirror. It is also called silver mirror test. Formation of silver mirror indicate the presence of aldehyde because ketone cannot be oxidized by Tollen's reagent.

$$RCHO + 2[Ag(NH_3)_2]OH \longrightarrow RCOO^-NH_4^+ + 3NH_3 + H_2O + 2Ag\downarrow$$

aldehyde — ammonium carboxylate — silver

ii. Fehling's solution test

Fehling's solution is alkaline solution of cupric ions complexed with tartarate ion. When Fehling solution is added to an aldehyde and gently heated, the aldehyde is oxidized to corresponding carboxylate and the cupric ion present in Fehling's solution is reduced to cuprous oxide (Cu_2O), which forms red precipitate. The formation of red precipitate indicates the presence of aldehyde because ketones do not give this test.

$$RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O\downarrow + 3H_2O$$

aldehyde — carboxylate ion — cuprous oxide (red ppt)

This test is widely used for the estimation of glucose in blood and urine.

iii. Benedict's solution test

Benedict's solution is an alkaline solution of cupric ions complexed with citrate ion. It react in the same way as Fehling's solution.

b. Oxidations of Ketones

In aldehydes, oxidation involve hydrogen that is attached to carbonyl carbon but in case of ketones no such hydrogen exists. Ketones having α-hydrogen can be oxidized by breaking of carbon-carbon *sigma* bond, using strong oxidizing agents like acidified dichromate or permanganate.

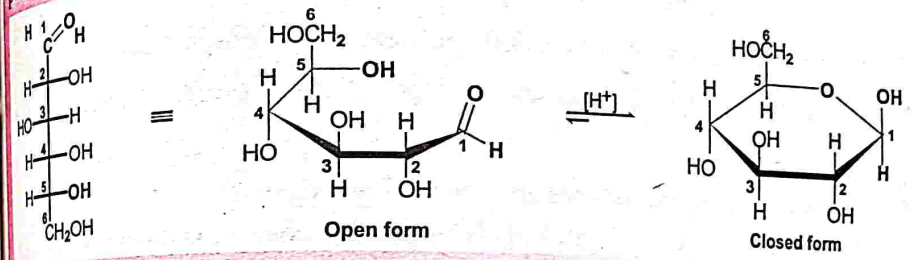
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 4[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-OH + CO_2 + H_2O$$

acetone — acetic acid

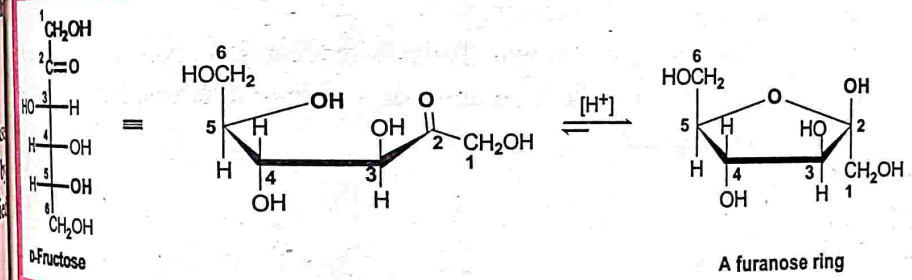
Society, Technology And Science

Carbohydrates are an important class of naturally occurring substances found in both plant and animal matter. Carbohydrates containing an aldehydic carbonyl are simply called as aldoses, while those containing ketonic carbonyl are known as ketoses. For example, glucose is a six-carbon aldehyde sugar, whereas fructose, the sugar that occurs widely in fruit, is a six-carbon ketone sugar.

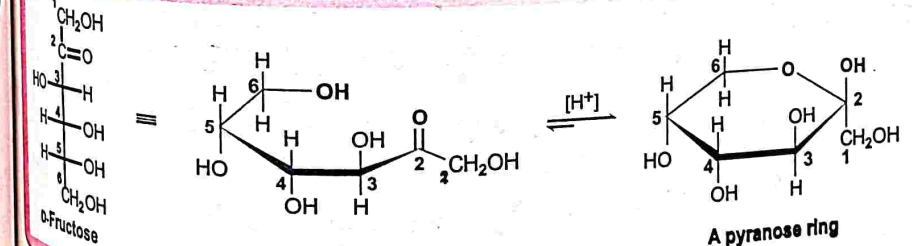
Glucose, having both alcohol and aldehyde functional groups and having a reasonably long and flexible backbone, and can react with itself to form a six-member ring structure, called pyranose ring, which is actually a hemiacetal as shown below. Indeed, only a small percentage of the glucose molecules are in the open-chain form in aqueous solution.



Fructose can also cyclize to form a five-member ring structure, called furanose ring, which is also a hemiacetal. The five-member rings formed when the -OH group on C-5 reacts with the carbonyl group on C-2.



D-Fructose can also cyclize to give pyranose forms that result from the reaction involving the hydroxyl group at C-6.



Key Points

- Aldehydes and ketones are two different classes of organic compounds containing carbonyl functional group.
- Oxidation of primary alcohols gives aldehydes and that of secondary alcohol gives ketones.
- The carbon-oxygen bond in aldehydes and ketones is highly polar and hence they are very reactive compounds.
- Both aldehydes and ketones undergo nucleophilic addition reactions.
- Generally, ketones are somewhat less reactive than aldehydes towards nucleophiles.
- Lower aldehydes and ketones are water soluble.
- Aldehydes are oxidized to alcohols in the presence of oxidizing agents like acidified dichromate and permanganate, as well a mild oxidising agent.
- Ketones are quit resistant to oxidation and can only be oxidised by strong oxidizing agents in drastic conditions.
- Aldehydes form silver mirror with Tollen's reagent and gives red precipitates with Fehling's and Benedict's solution on heating. Whereas, ketones do not undergo these reactions.

Exercise

Q1. Choose the correct one from the given options.

1. The carbon of the carbonyl group is
   a. sp^3–hybridized. b. sp^2–hybridized.
   c. sp–hybridized. d. dsp^2–hybridized.
2. The reduction of carbonyl to methylene is carried out with
   a. catalytic reduction b. Metal hydride
   c. Clemmensen method d. Lindlar's catalyst
3. Formaldehyde gives an addition product with methyl magnesium iodide which on hydrolysis gives
   a. n–propyl alcohol. b. isopropyl alcohol.
   c. methyl alcohol. d. ethyl alcohol.
4. Which of the following compounds can react with ammoniacal silver nitrate solution to form silver mirror?
   a. Acetone b. Ethanol c. Dimethyl ether d. Ethanal
5. Which of the following compounds will form a precipitate of cupric oxide from Fehling's reagent but does not react with sodium metal?
   a. C_2H_5OH b. C_2H_5CHO
   c. $CH_3CH(OH)CH_3$ d. CH_3COCH_3
6. IUPAC name of acetone is
   a. ethanone. b. propanone.
   c. ethanal. d. ethanoic acid.
7. Formalin is
   a. 10% aq. solution of formaldehyde.
   b. 20% aq. solution of formaldehyde.
   c. 40% aq. solution of formaldehyde.
   d. 5% aq. solution of formaldehyde.
8. An alkene upon ozonolysis gives only one type of aldehyde in product. Identify that alkene.
   a. but–1–ene b. propene
   c. but–2–ene d. 2,3–dimethylbut–2–ene
9. Which of the following alkyne would not yield a ketone upon hydration?
   a. acetylene b. propyne
   c. but–1–yne d. but–2–yne

10. Geminal diol can be obtained by
a. hydration of alcohol. b. hydration of aldehyde.
c. hydrogenation of ketone. d. hydration of both aldehyde and ketone.

11. Schiff base can be obtained by reaction of _____ amine with ketone
a. primary b. secondary
c. tertiary d. quaternary

12. A hemiacetal contains both
a. alcohol and aldehyde functional groups.
b. alcohol and ether functional groups.
c. aldehyde and ether functional groups.
d. alcohol and carboxylic acid functional groups.

13. Which aldehyde is more reactive towards nucleophilic addition?
a. Formaldehyde b. Acetaldehyde
c. Butyraldehyde d. Propionaldehyde

14. Which type of reaction is involved in the formation of acetals from alcohols on treatment with aldehydes?
a. Nucleophilic substitution b. Electrophilic substitution
c. Oxidation d. Nucleophilic addition

15. Which of the following method does not give ketones?
a. Hydration of alkyne b. Oxidation of primary alcohol
c. Oxidation of secondary alcohols d. Friedel-Crafts acylation

Q2. Write short answers of the following questions.

i. Both aldehydes and ketones contain carbonyl group, then what is the basic difference between an aldehyde and a ketone?

ii. How acid catalyst increases the electrophilic character of carbonyl carbon?

iii. Addition reaction is the characteristic of a double bond. Aldehydes and ketones undergo nucleophilic addition to carbon-oxygen double bond, while alkenes undergo electrophilic addition to carbon-carbon double bond. Why?

iv. Aldehydes are oxidized easily than ketones. Why?

v. Hydration of aldehyde and ketone can be catalyzed by both acid and base, but addition of hydrogen cyanide can only be catalysed by base. Why?

vi. Why addition of Grignard reagent to a carbonyl generally do not require any catalyst?

vii. How ketones are somewhat less reactive than aldehydes towards nucleophile?

viii. Why lower aldehydes and ketones are highly soluble in water, although there is no acidic hydrogen available in these compounds?

ix. The carboxylic acid(s) formed upon oxidation of ketones, must have carbon atoms less than parent ketone. Why?

x. Briefly explain a test that can be used for detection of aldehydes from ketones in laboratory.

Q3. Write detail answers of the following questions.

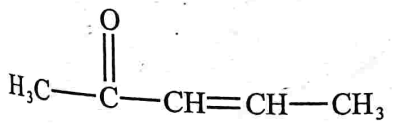
1. (a) Write the structural formulae and give IUPAC names for all possible aldehydes and ketones isomers of the molecular formula $C_5H_{10}O$.
(b) Explain the structure and reactivity of carbonyl compounds.

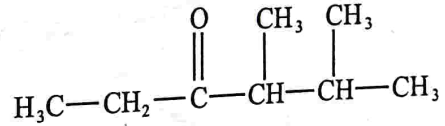
2. (a) Give a reaction for the formation of the following from aldehydes and ketones.
i. Cyanohydrin ii. Oxime iii. Imine
iv. Hydrazone v. Acetal
(b) Using appropriate Grignard reagent and aldehyde or ketone, how each of the following can be prepared?
i. butan-1-ol ii. ethyl alcohol iii. butan-2-ol
iv. 2-methylbutan-2-ol

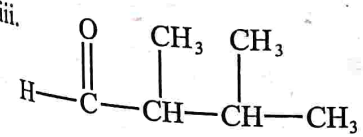
3. (a) Write any three methods for preparation of aldehydes.
(b) How does acetaldehyde react with the following reagents?
i. Ethyl magnesium iodide ii. Zinc-mercury amalgam in HCl
iii. Lithium aluminium hydride iv. Acidified dichromate

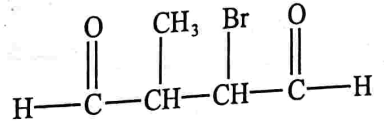
4. (a) How aromatic ketones are prepared by Friedel-Craft acylation?
(b) Starting from acetone, how will you prepare each of the following?
i. propane ii. propan-2-ol iii. acetone cyanohydrin
iv. acetone hydrazone v. acetic acid

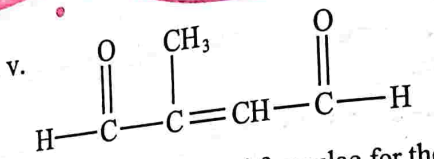
5. (a) Explain the acid and base-catalysed mechanism of nucleophilic addition to carbonyl group.
(b) Discuss the physical properties of aldehydes and ketones.
(c) Write the systematic names for the following organic compounds;

i. 

ii. 

iii. 

iv. 

v. 

(d) Draw the structural formulae for the following organic compounds;

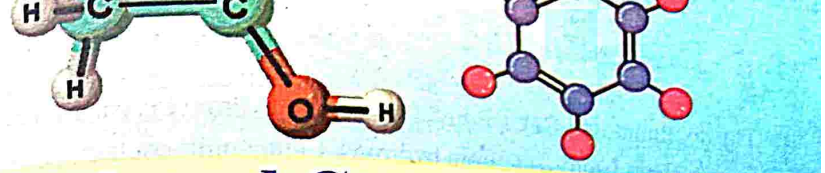
i. 2,4–dimethylpent–2–enal
ii. 2,2–dimethylbutanal
iii. 3,3–dimethylhex–4–en–2–one
iv. 4–methylhex–5–en–3–one
v. pent–4–yn–2–one

Project

Identify aldehydes and ketones in the laboratory tests.

Add 50 mL of 0.1 M $AgNO_3$ to the beaker and add NH_4OH to this. A brown precipitate will form. Continue adding NH_4OH until the solution becomes clear. To this, add 25 mL of 0.8 M KOH. Again, add NH_4OH until solution becomes clear.

To perform demonstration, add 5 mL of glucose solution to a flask (or test tube) and to this add 25 mL of Tollen's reagent. Stopper the flask and swirl the solution so that the whole of the inner surface of the flask is wetted. The solution will turn yellow and brown then become cloudy and dark before silver begins to form on the inside of the flask. This should take a couple of minutes. When a satisfactory mirror has formed, rinse the flask and analyse the silver mirror.



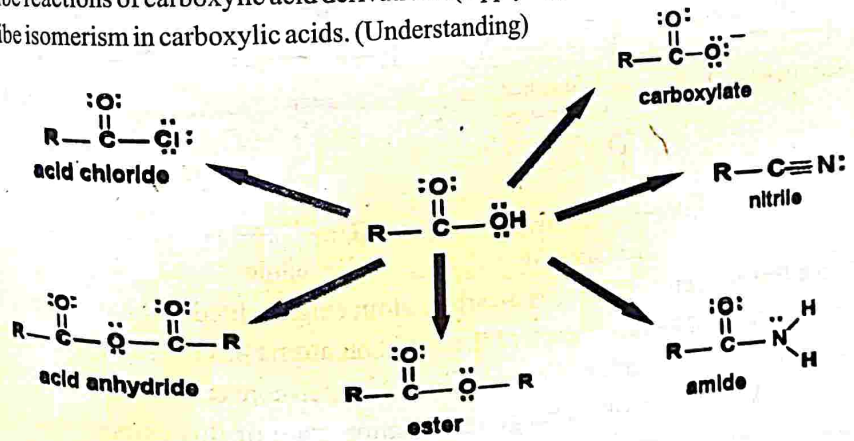
Unit 20

Carbonyl Compounds 2: Carboxylic Acids and Functional Derivatives

Teaching	Assessment	Weightage %
7	1	6

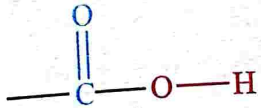
After studying this unit, students will be able to:

- 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 benzene. (Applying)
- Discuss reactivity of carboxylic acids. (Applying)
- Describe the chemistry of carboxylic acids by conversion to carboxylic acid derivatives i.e. 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)



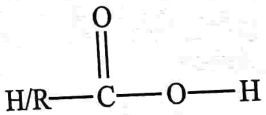
Introduction

The combination of a **carbonyl** group and a hydr**oxyl** is called a carboxyl group; carb- from carbonyl and –oxyl from hydroxyl. Compounds containing the carboxyl group are distinctly acidic and are called carboxylic acids.

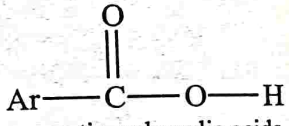


carboxyl group

Carboxylic acids may be aliphatic or aromatic depending upon whether carboxyl group is attached to an alkyl group or an aryl group. The simplest acid is formic acid (HCOOH), with a hydrogen atom bonded to the carboxyl group, and also an aliphatic acid. Fatty acids are long-chain aliphatic carboxylic acids derived from the hydrolysis of fats and oils. Acids containing one such functional group are known as mono carboxylic acids, while those containing two carboxyl groups are called dicarboxylic acids.

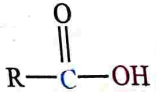


aliphatic carboxylic acids

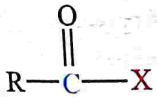


aromatic carboxylic acids

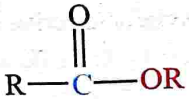
Carboxylic acids have many derivatives in which the –OH of an acid is replaced by other functional groups. Carboxylic acid derivatives are compounds with functional groups that can be converted to carboxylic acids by a simple acidic or basic hydrolysis. The most important acid derivatives are acid halides, esters, anhydrides, amides and nitriles.



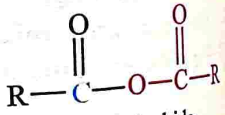
carboxylic acid



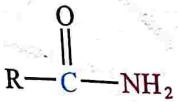
acid halide (acyl halide)



ester



acid anhydride



acid amide



nitrile

Notice that in each case there is a carbon atom (highlighted in blue) with three bonds to heteroatoms. As a result, each of these carbon atoms has the same oxidation state as the carbon atom of a carboxylic acid. Thus, the inter-conversion of carboxylic acid and derivatives, do not involve change in oxidation state of this carbon. Although all of these derivatives (except nitrile) exhibit a carbonyl group, the presence of a carbonyl

group is not a necessary requirement to qualify as a carboxylic acid derivative. Any compound with a carbon atom that has three bonds to heteroatoms that can be converted to carboxylic acids by a simple acidic or basic hydrolysis will be classified as a carboxylic acid derivative.

20.1 Nomenclature

Nomenclature of carboxylic acid

Following two types of naming is employed for naming of carboxylic acids.

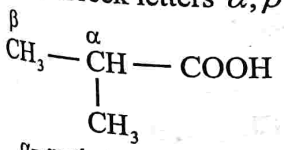
(a) Common or Trivial Names

Many of the acids have common names. These names usually come from some Latin or Greek words that indicates the original source of the acid. Following table 20.1 lists some common aliphatic carboxylic acids, with their common names.

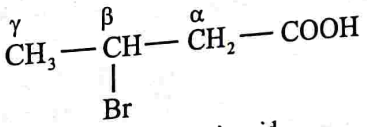
Table 20.1 Common Names of few Organic Acids

Carbon atoms	Formula (common name)	Sources
1	HCOOH formic acid	From Latin word *formica* means 'ant'
2	CH_3COOH acetic acid	From Latin word *acetum* means 'vinegar'
3	CH_3CH_2COOH propionic acid	From Greek word *protos* means 'first' and *pion* means 'fat'
4	$CH_3CH_2CH_2COOH$ butyric acid	From Latin word *butyrum* means 'butter'
5	$CH_3CH_2CH_2CH_2COOH$ valeric acid	Isolated from roots of valerian plant

In case of branched acids, the common name of the acid is also used. Substituents are located with Greek letters $\alpha, \beta, \gamma, \delta$ etc. as given below.



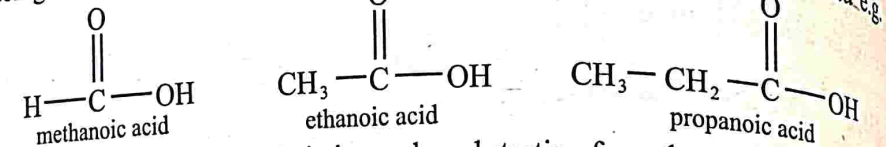
α– methylpropionic acid (isobutyric acid)



β– bromobutyric acid

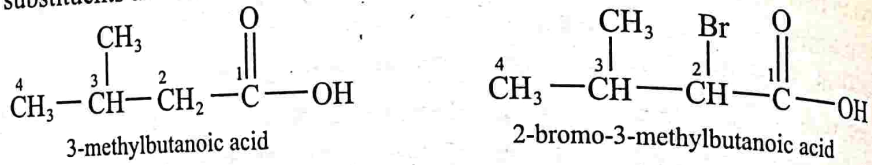
(b) IUPAC Nomenclature

Aliphatic monocarboxylic acids are named as alkanoic acids. These are obtained by replacing the ending *'-e'* of the corresponding alkane with the suffix *'–oic acid'* e.g.



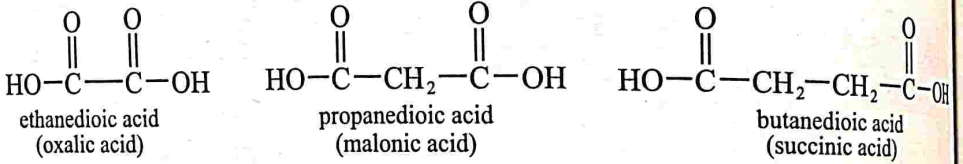
methanoic acid — ethanoic acid — propanoic acid

In case of branched acids, the chain is numbered starting from the carboxyl carbon atom and substituents are located in the usual way e.g.



3-methylbutanoic acid — 2-bromo-3-methylbutanoic acid

Carboxylic acids containing two carboxyl groups are named as alkanedioic acid. Their trivial names are also given in parenthesis.



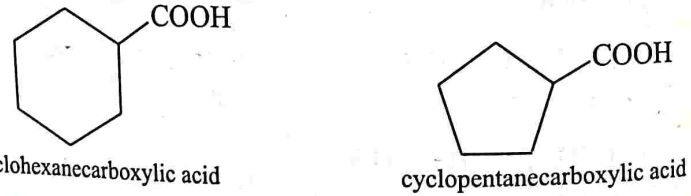
ethanedioic acid (oxalic acid) — propanedioic acid (malonic acid) — butanedioic acid (succinic acid)

Similarly, the unsaturated carboxylic acids are named as alkenoic acid, alkynoic acid e.g.



propenoic acid — 2-butynoic acid (but-2-ynoic acid)

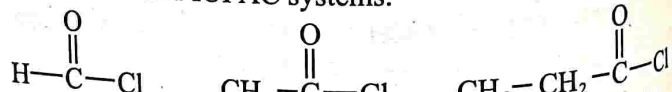
If carboxyl group is attached to a cyclic ring, it is named by adding suffix –carboxylic acid to name of cycloalkane.



cyclohexanecarboxylic acid — cyclopentanecarboxylic acid

Nomenclature of acid halides

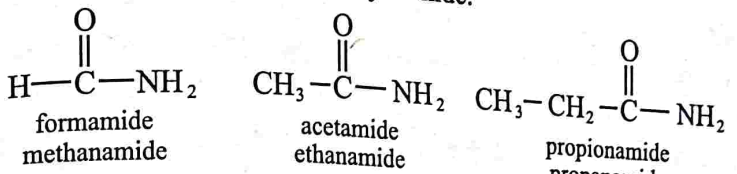
The names of acid halides are derived from the names of corresponding carboxylic acids. The ending *–ic* of the name of acid is replaced by *–yl*, and the word acid is replaced by halide, in both common and IUPAC systems.



Common name:	formyl chloride	acetyl chloride	propionyl chloride
IUPAC name:	methanoyl chloride	ethanoyl chloride	propanoyl chloride

Nomenclature of amides

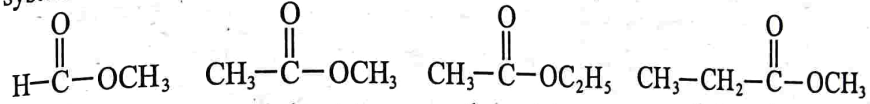
Names of amides are also derived from carboxylic acids. The ending –ic acid of common names and *–oic acid* from IUPAC name is replaced by –amide.



Common name:	formamide	acetamide	propionamide
IUPAC name:	methanamide	ethanamide	propanamide

Nomenclature of esters

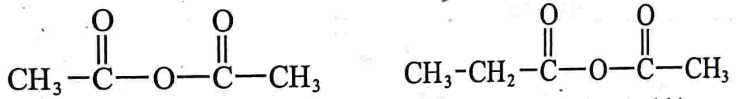
The names of esters consist of two words. The first word is derived from the alkyl group of the alcohol (alkyl group attached to oxygen), and the second word from the carboxylate group of the carboxylic acid, with the ending *–ic acid* is replaced by *–ate* in both common and IUPAC systems.



Common name:	methyl formate	methyl acetate	ethyl acetate	methyl propionate
IUPAC name:	methyl methanoate	methyl ethanoate	ethyl ethanoate	methyl propanoate

Nomenclature of acid anhydrides

Anhydrides are named by replacing the word 'acid' of the parent acid by anhydride. For mixed anhydrides, the parent name of each acid is written in alphabetic order, followed by word anhydride.

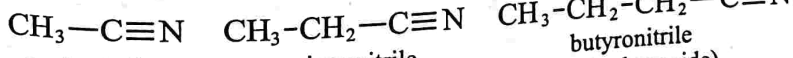


Common name:	acetic anhydride	acetic propionic anhydride
IUPAC name:	ethanoic anhydride	ethanoic propanoic anhydride

Nomenclature of nitriles

Nitriles contain the cyano (–C ≡ N) group. Although nitriles lack the carbonyl group of carboxylic acids, they are classified as acid derivatives because they hydrolyze to give carboxylic acids and can be synthesized by dehydration of amides.

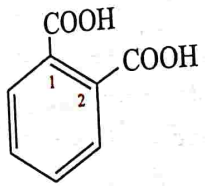
Common names of nitriles are derived from the corresponding carboxylic acids. Begin with the common name of the acid, and replace the suffix *-ic* acid with the suffix *-onitrile*. They can also be named as alkyl cyanides in common system, written in parenthesis. The IUPAC name is constructed from the alkane name, with the suffix *-nitrile* added.



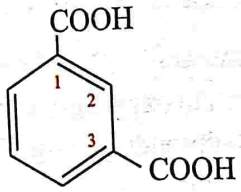
Common name:	acetonitrile (methyl cyanide)	propiononitrile (ethyl cyanide)	butyronitrile (n-propyl cyanide)
IUPAC name:	ethanenitrile	propanenitrile	butanenitrile

Isomerism in carboxylic acids

Chain isomerism is exhibited by carboxylic acids that contain four or more carbon atoms. For example butyric acid and isobutyric acid are chain isomers of each other. Aromatic carboxylic acids can also exhibit position isomerism. For example, benzene-1, 2-dicarboxylic acid, benzene-1, 3-dicarboxylic acid and benzene-1, 4-dicarboxylic acid are position isomers.



benzene-1,2-dicarboxylic acid



benzene-1,3-dicarboxylic acid

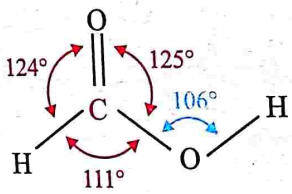


benzene-1,4-dicarboxylic acid

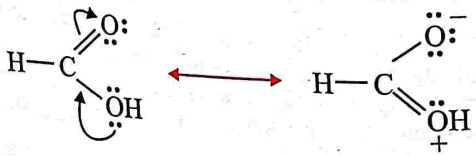
Carboxylic acids and esters having same molecular formula are functional groups isomers of each other. For example, acetic acid and methyl formate are functional group isomers.

20.2 Structure

The Structural features of the carboxyl group are most apparent in formic acid. It is planar, with one of its carbon–oxygen bonds shorter than the other and with bond angles at carbon close to 120°.



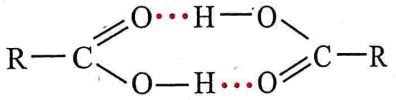
The C=O, C—O, H—C and O—H bond lengths are 122 pm, 134 pm, 108 pm and 96pm respectively. Similarly, the angles H–C=O, H–C–O and O–C=O are 124°, 111° and 125° respectively. This suggest sp^2-hybridization at carbon, and a carbon-oxygen double bond similar to that of aldehydes and ketones. Additionally, sp^2-hybridization of hydroxyl oxygen allows one of its unshared electron pair to be delocalized by orbital overlap with the *pi* system of the carbonyl carbon. In resonance terms, this electron delocalization is represented as:



Lone-pair donation from hydroxyl oxygen makes the carbonyl group less electrophilic than that of aldehyde and ketones, which will be discussed in **Section 20.6.**

20.3 Physical Properties

- The lower members of the aliphatic monocarboxylic acids upto nonanoic acids (C_9) are liquids with distinctive penetrating odours.
- Decanoic acid and higher members are solids, with little odour because of their low volatility.
- Anhydrous acetic acid freezes at 17°C, to form a solid which look like ice. It is, therefore, known as glacial acetic acid.
- Acetic acid constitutes about 4-5% of vinegar, has a characteristic smell which is recognizable in vinegar. Butyric acid is the substance that can be smelled in rancid butter.
- Carboxylic acids are more polar than alcohols. They form hydrogen bonds with themselves or with their own molecules. That is why they have high melting and boiling points, than corresponding alcohols. For example the boiling points of acetic acid and ethyl alcohol are 118°C and 78°C respectively.
- The hydrogen bonding in carboxylic acids is so pronounced that in solid and liquid state and even in non-polar solvents, they mostly exist in cyclic dimeric form.



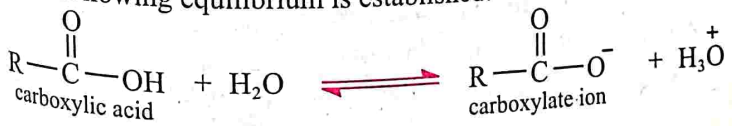
carboxylic acid dimer

- Hydrogen bonding also explains the water solubility of low molecular mass carboxylic acids which form hydrogen bond with water molecules. Solubility of these acids in water decreases as their relative molecular mass increases.

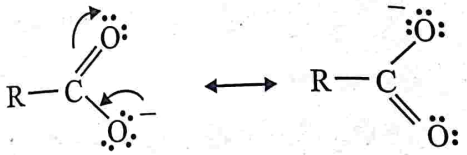
20.4 Acidity

Carboxylic acids are the most acidic class of organic compounds. They are much stronger acids than water, alcohols and phenols but weaker than mineral acids, with ionization constants *K*a of the order of 10^{-5} (p*K*a ≈ 5).

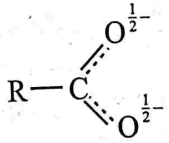
Carboxylic acids dissociate in water, yielding carboxylate anion and a hydronium ion. The withdrawal of electrons away from the carboxyl hydrogen atom weakens the oxygen-hydrogen bond. As a result the carboxyl group can lose a proton in aqueous medium and the following equilibrium is established.



The carboxylate ion exists as a resonance hybrid of two canonical forms.



The resonance hybrid can be represented as



To understand the greater acidity of carboxylic acids compared with alcohols, consid the ionization and Ka (and pKa) values of ethyl alcohol and acetic acid.

Ionization of ethyl alcohol:

$C_2H_5—OH + H_2O \rightleftharpoons C_2H_5—O^- + H_3O^+$

ethyl alcohol → ethoxide ion; hydronium ion

$Ka = 10^{-16}$, $pKa = 16$

Ionization of acetic acid:

$CH_3—C(=O)—OH + H_2O \rightleftharpoons CH_3—C(=O)—O^- + H_3O^+$

acetic acid → acetate ion; hydronium ion

$Ka = 1.8 \times 10^{-5}$, $pKa = 4.76$

The ionization of ethanol yields ethoxide ion, in which the negative charge is localiz on oxygen. However, the carboxylate ion is stabilized by the delocalization of negati charge on two oxygen atoms.

The acidities of the carboxylic acids vary considerably with the nature of the substituents present in the molecule. Any substituent that stabilizes the negatively charged carboxylate ion promotes dissociation and vice versa. Electron withdrawing substituents (e.g. –X, $–NO_2$ etc.) enhance the strength of an acid by withdrawing electron density from the carboxylate ion. This inductive effect can be quite large if one or more strongly electron–withdrawing groups are present on the carbon atom adjacent to carboxyl carbo

Tidbit

Electron-withdrawing groups enhance acidity because they help to stabilize the negative charge of the conjugate base (the carboxylate ion).

The amount of stabilization depends on: the number of electron-withdrawing groups, the strength of the electron-withdrawing groups and the position of the electron-withdrawing groups from the COOH group.

Whereas an electron donating substituent (e.g. alkyl groups) will tend to destabilize the carboxylate ion and thus decreases the acidity of the acid. **(Table 20.2)** lists values of pKa for some substituted carboxylic acids, showing how electron-withdrawing groups and electron-donating groups affect the strength of an acid.

Table 20.2 pKa Values of some Substituted Carboxylic Acids

Carboxylic acid	Formula	pKa
propionic acid	CH_3CH_2COOH	4.87
acetic acid	CH_3COOH	4.76
formic acid	$HCOOH$	3.68
bromoacetic acid	$BrCH_2COOH$	2.90
chloroacetic acid	$ClCH_2COOH$	2.86
fluoroacetic acid	FCH_2COOH	2.59
nitroacetic acid	O_2NCH_2COOH	1.68
dichloroacetic acid	$Cl_2CHCOOH$	1.29
trichloroacetic acid	Cl_3CCOOH	0.65

20.5 Preparations of carboxylic Acids

Following methods of preparation are used for carboxylic acids.

20.5.1 Carbonation of Grignard Reagent

Carboxylic acids can be prepared by the action of Grignard reagent with carbon dioxide. This reaction is known as carbonation or carboxylation of Grignard reagent. Grignard reagent reacts with carbon dioxide to give initially an addition product, which on acid workup finally yield a carboxylic acid **(Section 17.2.3.3)**.

$R—MgX + O=C=O \xrightarrow{\text{dry ether}} R—C(=O)—OMgX \xrightarrow[\text{(workup)}]{H_3O^+} R—C(=O)—OH$

carbon dioxide; addition product; carboxylic acid

The acid obtained by the carboxylation of Grignard reagent has one more carbon atom than alkyl or aryl halide from which Grignard reagent is prepared, so the reaction provides a way to extend the length of carbon chain.

20.5.2 Hydrolysis of Nitriles

Hydrolysis of nitriles with aqueous acid or base yields a carboxylic acid. In the presence of base catalyst, the final product is actually salt of carboxylic acid, which on acidic workup yields carboxylic acid.

Acid-catalyzed hydrolysis:

$$\underset{\text{nitrile}}{R-C\equiv N} + 2H_2O + HCl \longrightarrow \underset{\text{carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH} + NH_4Cl$$

Base-catalyzed hydrolysis:

$$\underset{\text{nitrile}}{R-C\equiv N} + H_2O + NaOH \longrightarrow \underset{\text{sodium carboxylate}}{R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}Na^{+}} + NH_3$$

The reaction proceeds through the formation of an amide intermediate which may be isolated if desired. Hydrolysis of methanenitrile yield acetic acid.

$$\underset{\text{methanenitrile}}{CH_3-C\equiv N} + 2H_2O \xrightarrow{H^+ \text{ or } {}^-OH} \underset{\text{acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + NH_3$$

20.5.3 Oxidation of Primary Alcohols

Primary alcohols can be oxidized to carboxylic acids by oxidizing agents like acidified permangnate or dichromate, through intermediate aldehyde. **(Section 18.1.7.5)**

$$\underset{\text{1° -alcohol}}{R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-H} \xrightarrow[-H_2O]{[O]} \underset{\text{aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{[O]} \underset{\text{carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH}$$

$$\underset{\text{ethyl alcohol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-H} \xrightarrow[-H_2O]{[O]} \underset{\text{acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{[O]} \underset{\text{acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH}$$

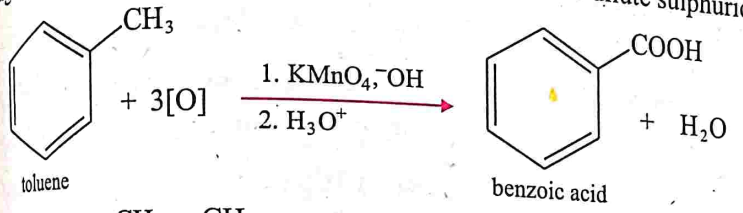
20.5.4 Oxidation of Aldehydes

Oxidation of an aldehyde in the presence of oxidizing agents like acidified permanganate dichromate or silver oxide gives a carboxylic acid with the same number of carbon atoms **(Sections 18.1.7.5 and 19.6.4).**

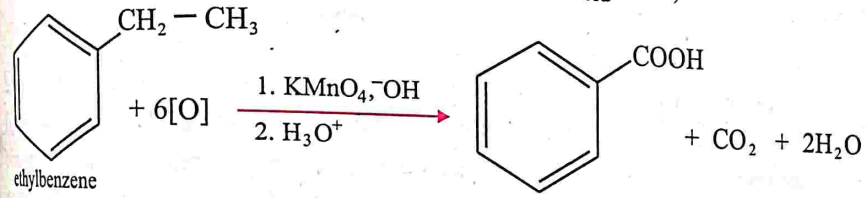
$$\underset{\text{aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{[O]} \underset{\text{carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH}$$

20.5.5 Oxidation of Alkyl Benzenes

Benzoic acid can be prepared by the oxidation of alkyl side chain present on the benzene ring, with oxidizing agent like alkaline permanganate. Any side chain is converted to carboxyl group, and benzoic acid is formed in product. The purple colour of the potassium permanganate is eventually replaced by a dark brown precipitate of manganese dioxide. The mixture is finally acidified with dilute sulphuric acid.



toluene — benzoic acid



ethylbenzene — benzoic acid

The reaction illustrates the striking stability of aromatic rings towards oxidizing agents.

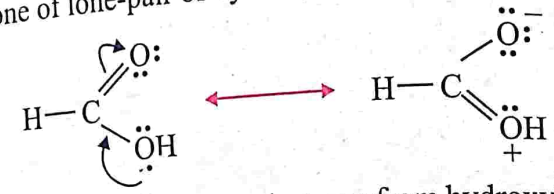
20.6 Reactivity

The carboxylic group is so named because it contains a carboxyl group and, a hydroxyl group. The two groups influence each other to such an extent that the reactivity of carboxylic acids shows little resemblance to those of carbonyl compounds (aldehydes and ketones) on one hand and alcohols on the other hand.

Although the carboxylic acid (and its derivatives) also contain a carbonyl group, but still they do not exhibit the characteristic reactions of aldehydes and ketones. For example, they do not undergo nucleophilic addition reactions and more commonly react by nucleophilic acyl substitution, where one nucleophile replaces another on the acyl (C=O) carbon atom, shown below.

$$\underset{\substack{\text{carboxylic acid}\\ \text{or derivative}}}{R-\overset{\overset{O}{\|}}{C}-Z} + \ddot{\overset{-}{N}}u \longrightarrow \underset{\text{substitution product}}{R-\overset{\overset{O}{\|}}{C}-Nu} + \ddot{\overset{-}{Z}}$$

The carboxyl group is also less susceptible to nucleophilic attack than aldehydes and ketones, because the carbon atom of the carboxyl group is less electrophilic, due to delocalization of one of lone-pair of hydroxyl group with carbonyl **(Section 20.2)**.



Similarly the carbonyl group withdraws electrons from hydroxyl, making the O–H bond more polar and it becomes easier for the hydrogen atom to ionize than O–H bond of alcohols. Hence, carboxylic acids are more acidic than alcohols.

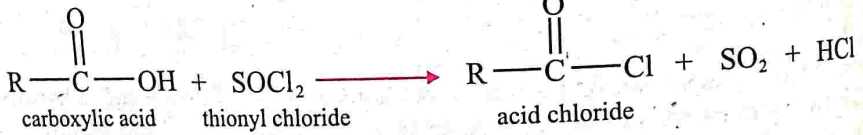
20.7 Reactions of Carboxylic Acids

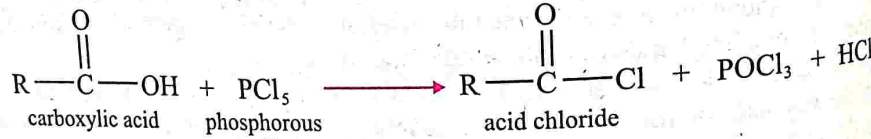
Following are some of the reactions of carboxylic acids that involve the conversion of the carboxylic acids to their derivatives as well as synthesis of some other compounds.

20.7.1 Conversion to Carboxylic Acid Derivatives

20.7.1.1 Conversion to Acyl Halides

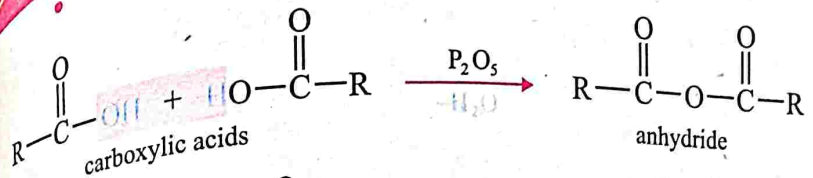
Acyl halides or acid halides are the most reactive of carboxylic acid derivatives and they can be used for preparation of other functional derivatives of carboxylic acid. Acyl chlorides are more common and less expensive than bromides and iodides. They are usually prepared by replacing the –OH of carboxyl with –Cl, using thionyl chloride or phosphorous pentachloride.

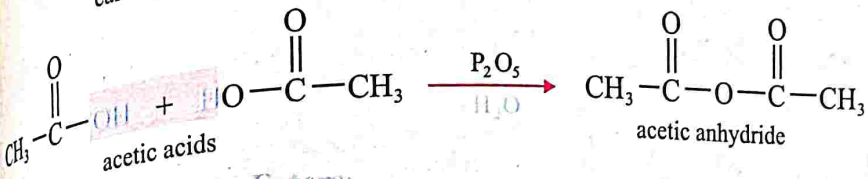




20.7.1.2 Conversion to Acid Anhydrides

Acid anhydrides are derived from acids by removing water from two carboxylic acid molecules. As the name indicates, these are anhydrous carboxylic acids. They are actually diacyl oxides. The dehydration of water from carboxylic acid to form anhydride, can be accomplished by using dehydration agents like phosphorous pentaoxide.

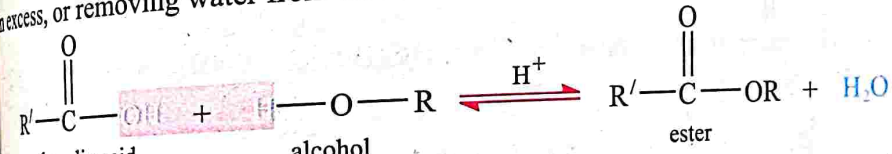




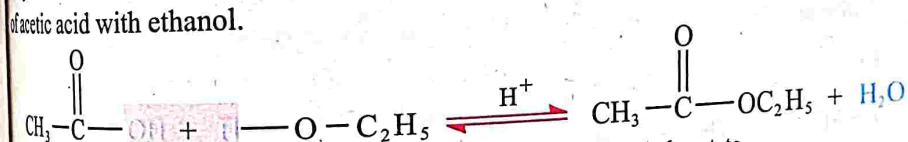
20.7.1.3 Conversion to Esters

Esters are a class of organic compounds that are derived from acids by replacing the hydroxyl group (–OH) by an alkoxy group (–OR). They are obtained by elimination of water molecule from an acid and an alcohol.

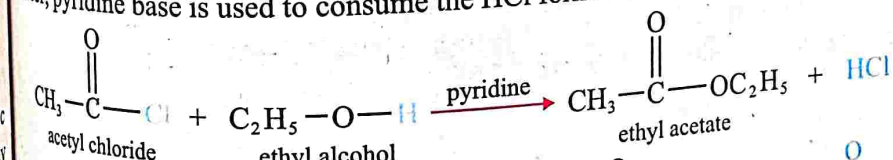
When a carboxylic acid and an alcohol are heated in the presence of an acid catalyst, an equilibrium is established with the formation of ester and water. This reaction is reversible and called esterification **(Section 18.1.7.4)**. The position of equilibrium can be made more favorable in the right, by using either the alcohol or the carboxylic acid in excess, or removing water from the reaction mixture.

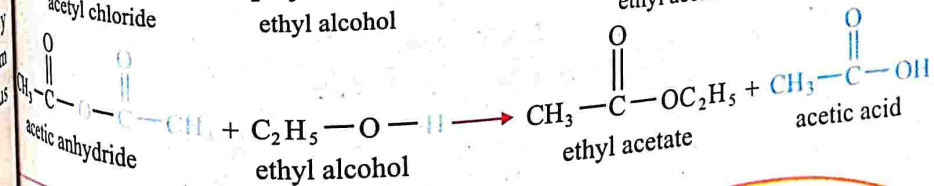


Ethyl acetate is an important ester which can be prepared by this method by the reaction of acetic acid with ethanol.



Esters can also be prepared by the reaction of an alcohol with acid halide or acid anhydride (alcoholysis of acid halide or anhydride). In case of conversion of acid halide to ester, pyridine base is used to consume the HCl formed in reaction.

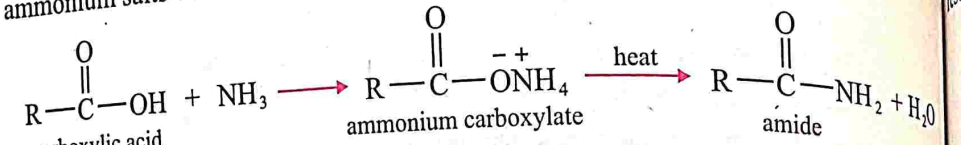


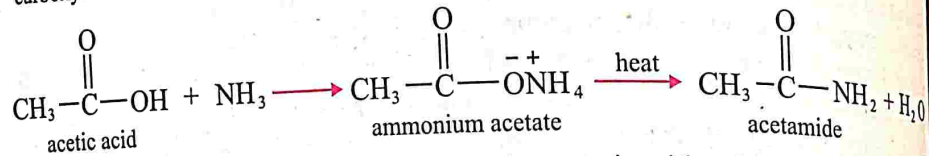


20.7.1.4 Conversion to Amides

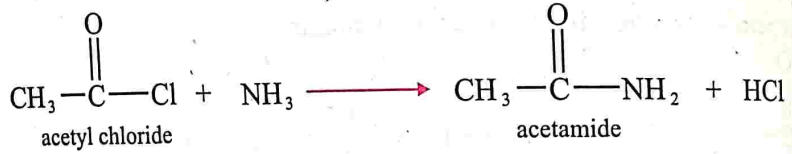
Amides are the least reactive of the derivatives of carboxylic acid derivatives. These are obtained by replacing –OH of the acid with $-N_2$ group.

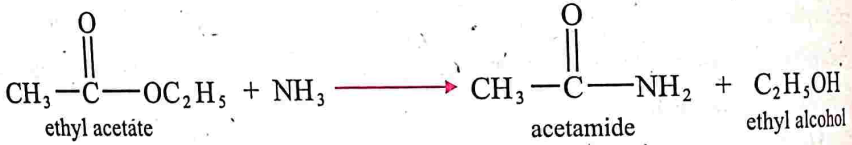
Amides can be prepared by the reaction of ammonia with carboxylic acid to form first ammonium salts which on heating produce acid amides, upon dehydration.

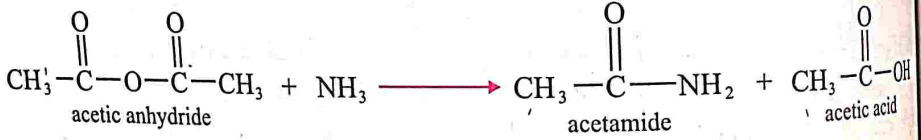




Amides can also be prepared by the reaction of ammonia with acid chlorides, esters or anhydrides (ammonolysis).

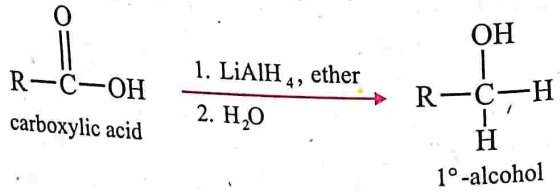






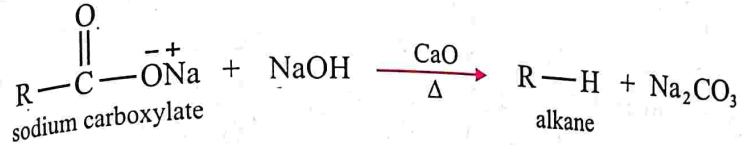
20.7.2 Reduction to Alcohols

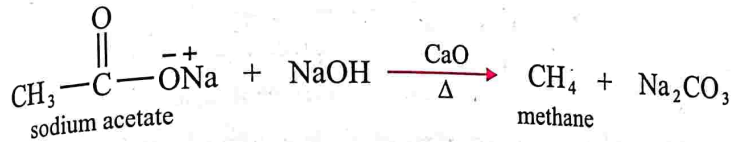
Carboxylic acids can be reduced to the corresponding primary alcohol using lithium aluminum hydride in ether **(Section 18.1.5.6)**.

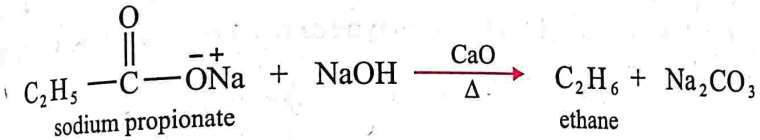


20.7.3 Decarboxylation Reactions

The removal of carbon dioxide from a carboxylic acid is known as decarboxylation. Decarboxylation of carboxylic acid takes place when its sodium salt is heated with soda lime (dry mixture of caustic soda, NaOH and quick lime, CaO) to form alkanes. The resulting alkane contains one carbon less than parent carboxylic acid.







20.7.4 Reactions of Carboxylic Acid Derivatives

20.7.4.1 Reactions of Acyl Halides

Acid halides are the most reactive of all derivatives of carboxylic acid.

(i) Friedel–Crafts Acylation Reaction

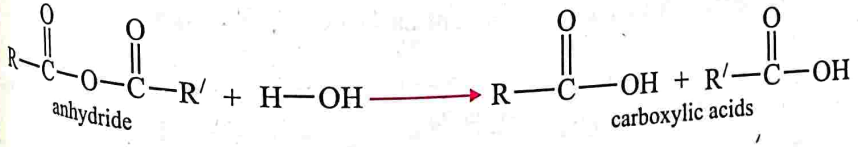
Acid halides react with benzene in the presence of Lewis acid to form aromatic ketones. **(Section 16.8.5.2.6).**

20.7.4.2 Reactions of Acid Anhydrides

Acid Anhydrides are more reactive than esters but less reactive than acid halides, toward nucleophiles.

(i) Hydrolysis

On hydrolysis, anhydrides form corresponding carboxylic acids. The hydrolysis of anhydrides can occurs in the presence of acid or base catalyst, though uncatalyzed hydrolysis can also occurs readily.



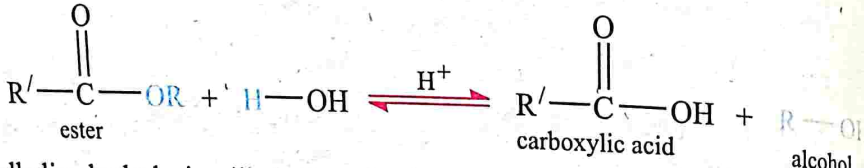
20.7.4.3 Reactions of Esters

Following are some of the important reactions of esters.

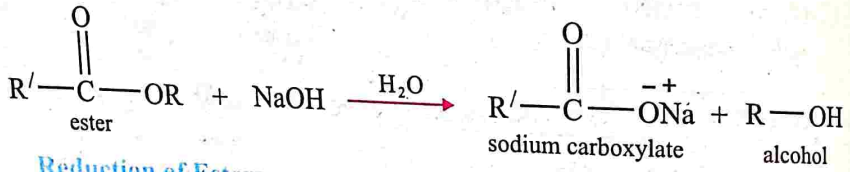
(i) Hydrolysis

Esters are commonly hydrolyzed to carboxylic acid and alcohol, on heating with water very slowly. However the hydrolysis of ester can be catalyzed by an acid or base.

The acid-catalyzed hydrolysis is reversible, and is the reverse of acid-catalyzed esterification **(Section 18.1.7.4 and 20.7.1.3)**.



The alkaline hydrolysis will yield a salt of carboxylic acid and alcohol. This reaction is also called saponification reaction, because such type of reaction is used for preparation of soap from fats.



(ii) Reduction of Esters

Ester can be reduced to alcohols in the presence of strong reducing agent such as lithium aluminum hydride in ether **(Section 18.1.5.6)**.

(iii) Reaction of Ester with Grignard Reagent

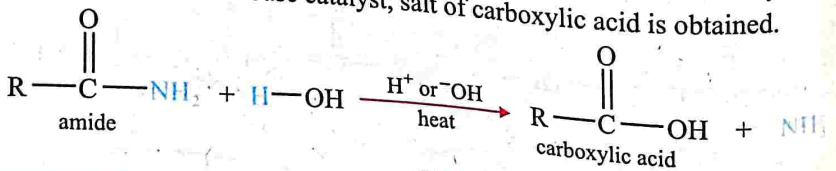
Esters react with two equivalents of Grignard reagent to give an alcohol **(Section 17.2.3.2)**.

20.7.4.4 Reactions of Amides

Amides are the least reactive of the common carboxylic acid derivatives. Like other acid derivatives, amides can also reacts with nucleophiles like water.

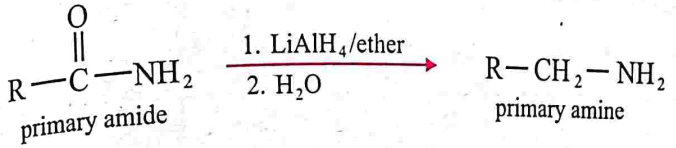
(i) Hydrolysis

Amides on hydrolysis form the corresponding carboxylic acids and ammonia. The reaction is very slow and requires the use of strong acid or base as catalyst. Both are irreversible and in case of base catalyst, salt of carboxylic acid is obtained.



(ii) Reduction

Amides can be reduced to primary amines in presence of lithium aluminium hydride **(Section 17.3.5.2.3)**.



20.7.4.5 Reactions of Nitriles

Alkyl nitriles or simply nitriles are also considered as derivatives of carboxylic acids. The following are some of the important reactions of nitriles.

(i) Hydrolysis

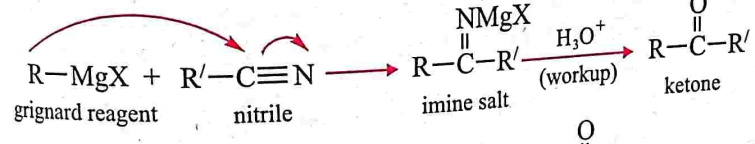
Hydrolysis of nitriles with aqueous acid or base yields a carboxylic acid. In the presence of base catalyst, the final product is actually salt of carboxylic acid **(Section 20.5.2)**.

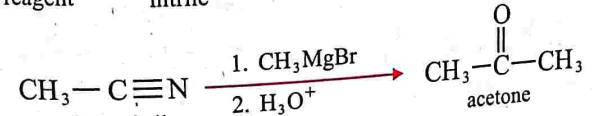
(ii) Reduction

Nitriles yield primary amines when reduced with catalytic method, or using lithium aluminium hydride in ether **(Section 17.3.5.2.1)**.

(iii) Reaction with Grignard Reagent

Nitriles on reaction with Grignard reagent produce ketones. The strongly nucleophilic Grignard reagent add to carbon-nitrogen triple bond in a similar fashion to that seen in aldehydes and ketones. The reaction proceeds via an imine salt intermediate, which is further hydrolysed to give ketones.





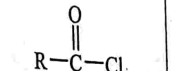
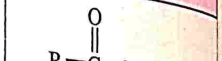
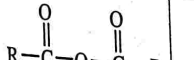
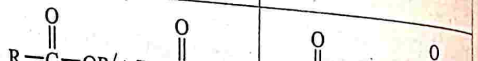
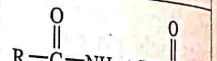
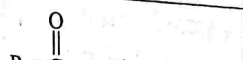
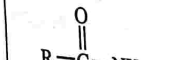
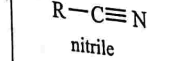
20.7.5 Summary of the Reactions that Interconvert Carboxylic Acid Derivatives

A summary of the reactions of different derivatives of carboxylic acids with certain nucleophiles, have been listed in **Table 20.5**.

The different acids derivatives are listed at the left of the chart in order of decreasing reactivities towards nucleophiles. The common nucleophiles are listed across the top. In case of hydrolysis, corresponding acid is obtained, we either start with an acyl

halides, acid anhydride, ester, amide or nitrile. Similarly alcoholysis gives an ester and ammonolysis gives an amide. All of the reactions in **Table 20.5** take place via attack of the nucleophile on the carbonyl carbon of the acid derivative, commonly called nucleophilic acyl substitution.

Table 20.5 Reactions of Acid Derivatives with certain Derivatives Nucleophile

Acid derivative	Reaction of acid derivatives with		
	H_2O (Hydrolysis)	R'OH (Alcoholysis)	NH_3 (Ammonolysis)
 acid halide	 carboxylic acid	 ester	 amide
 anhydride	 carboxylic acid	 ester carboxylic acid	 amide carboxylic acid
 ester	 carboxylic acid alcohol	 ester alcohol	 amide alcohol
 amide	 carboxylic acid	---	---
 nitrile	 carboxylic acid	---	---

Self-assessment

Write the common and IUPAC names of derivatives of carboxylic acids, which yield acetic acid upon hydrolysis.

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Some of the most common organic acids in food are found within fruits. Many people are already aware that citric acid occurs in citrus fruits such as oranges, lemons and limes, but there are lesser known acids in fruits that you may not have heard of. These include malic acid, which is found in apples and tartaric acid found in grapes. These acids provide these fruits with that distinctive sharp taste. The mixture of acid and sugar is what gives fruits their unique flavor, so foods will often be deliberately fermented in particular acids to retain or increase the flavor.

In addition to taste, acids in fruits are also used as preservatives due to their ability to reduce the onset of bacterial degradation. High acidity helps to kill bacteria so food doesn't spoil as quickly e.g. Benzoic acid and sodium benzoate have inhibitory effect on growth of fungi; major cause of food spoilage.

Many of the acids present in vegetables are also present in fruits. The key difference is that vegetables do not tend to be as acidic in their makeup, making them a potentially safer source of key acids if you struggle with acid reflux or high stomach acidity. Vegetables include citric acid, oxalic acid and benzoic acid. Oxalic acid is a naturally occurring acid found in a wide range of vegetables. Oxalates are known for binding to almost any mineral in the body. Oxalates build up insoluble compounds when binds with calcium, that can lead to kidney stones if precautions aren't taken. The principal acids found in dairy products are benzoic acid, lactic acid and a variety of fatty acids which contribute to dairy products.

Key Points

- Carboxylic acids are organic acids having carboxyl group as the functional group ("carb" from carbonyl and "oxyl" from hydroxyl).
- Acyl halides, acid anhydrides, esters, amides etc. are the derivatives of carboxylic acids obtained by replacing the –OH of carboxyl group by other functional groups.
- Some members of carboxylic acids have penetrating smells. They are water soluble and their solubility decreases with the increase in molecular mass.
- Carboxylic acids, due to strong hydrogen bonds, have high boiling points than corresponding alcohols.
- The carbon atom of the carboxyl group is sp^2-hybridized.
- Carboxylic acids are the strongest organic acids, stronger than phenol, alcohols and water.
- Substituents in a carboxylic acid molecules strongly influence the strength of the acid due to the inductive effect of the substituent.
- Carboxylic acids can be prepared from Grignard reagent by oxidation of alcohols and aldehydes and by hydrolysis of nitriles.
- Although the carboxylic group contains the carbonyl group, yet carboxylic acid do not exhibit some of the characteristic reactions of aldehydes and ketones.
- Carboxylic acids, on reaction with different species, can be converted to their derivatives.
- Among the derivatives of carboxylic acids, acyl halides are the most reactive.
- All of the acid derivatives can be converted back into the corresponding carboxylic acids on hydrolysis.

Exercise

Q1. Choose the correct one from the given options.

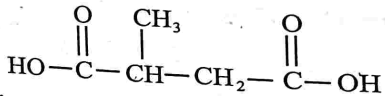
1. Which of the following represents the formula of an aromatic carboxylic acids?
   a. HCOOH b. C_6H_5OH
   c. C_6H_5COOH d. $C_6H_5CH_2OH$
2. Which of the following acids is found in rancid butter?
   a. $C_2H_4O_2$ b. $C_3H_6O_2$
   c. $C_4H_8O_2$ d. $C_5H_{10}O_2$
3. The compound with highest boiling point is
   a. acetic acid. b. water.
   c. ethyl alcohol. d. diethyl ether.
4. In which of the following compounds, the carbon atom does not show sp^2-hybridization?
   a. Methanal b. Methanol
   c. Methanoic acid d. Acetone
5. Which is the strongest acid?
   a. Ethanol b. Acetic acid
   c. Chloroacetic acid d. Fluoroacetic acid
6. Acetic acid can be prepared by the hydrolysis of
   a. methyl cyanide. b. methylmagnescium chloride.
   c. ethanal. d. ethanol.
7. Fischer esterification is the reaction between
   a. an acid and ester. b. an acid and alcohol.
   c. an acid halide and ester. d. an ester and sodium hydroxide.
8. Acyl chloride can be prepared by the reaction of a carboxylic acid with
   a. phosphorous pentoxide. b. soda lime.
   c. hydrochloric acid. d. thionyl chloride.
9. The hydrolysis of an ester in presence of alkali is known as
   a. saponification. b. decarboxylation.
   c. esterification. d. transesterfication.
10. All the acid derivatives can be converted back into the corresponding acid by one common reaction.
   a. ammonolysis b. alcoholysis
   c. reduction d. hydrolysis

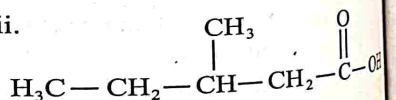
Q2. Write short answers of the following questions.

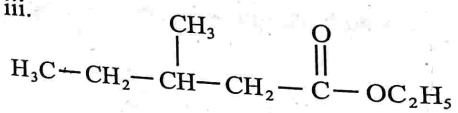
i. Why anhydrous acetic acid is known as glacial acetic acid?
ii. The boiling points of carboxylic acids are higher than corresponding alcohols. Explain briefly.
iii. How carboxylic acids are stronger acids than phenol, alcohols and water?
iv. Why methanoic acid is stronger acid than ethanoic acid?
v. Chloroacetic acid is a derivative of acetic acid. Why chloroacetic acid is stronger acid than acetic acid?
vi. How carboxylic acids can be obtained readily by the oxidation of primary alcohols?
vii. Carboxylic acids are less reactive towards nucleophile, compared to aldehydes. Why?
viii. Why amides are the least reactive derivatives of carboxylic acid, towards nucleophiles?
ix. Esters can be hydrolysed in both acidic and basic conditions. Why base hydrolysis of esters is also called saponification?
x. Acid halides are the most reactive of all acid derivatives towards nucleophiles. Explain briefly.

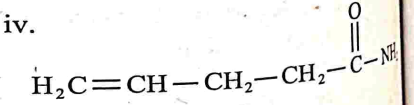
Q3. Write detail answers of the following questions.

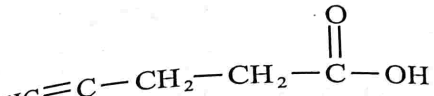
1. Explain the acidity of carboxylic acids. How their acid strength is affected by electron donating and withdrawing substitutions?
2. How will you prepare acetic acid by using?
   i. a nitrile ii. a Grignard reagent iii. an alcohol
   iv. an aldehyde v. an acid halide
3. Starting from acetic acid, how will you prepare each of the following?
   i. acetyl chloride ii. acetic anhydride iii. acetamide
   iv. ethyl acetate v. ethyl alcohol
4. Write an equation for:
   i. Hydrolysis of acetyl chloride ii. Reaction of benzoyl chloride with methanol
   iii. Esterification of butan-1-ol with acetic anhydride.
   iv. Ammonolysis of butanoyl chloride.
   v. Fischer esterfication of pentanoic acid with ethanol.
5. (a) Describe three methods for preparation of carboxylic acids.
   (b) Write the systematic names for the following organic compounds;

i. 

ii. 

iii. 

iv. 

v. 

(c) Draw the structural formula of the following organic compounds;
i. 3-ethyl-4-methylpentanoic acid ii. ethyl 3-methylbutanoate
iii. 2-chloropropanoyl bromide iv. ethanoic propanoic anhydride
v. 3,3-dimethylbutanenitrile

(d) Complete the following reactions.

i. $CH_3CH_2CH_2COOH + PCl_5 \longrightarrow$
ii. $CH_3CH_2COOH + SOCl_2 \longrightarrow$
iii. $CH_3CH_2CONH_2 + LiAlH_4 \longrightarrow$
iv. $CH_3COOCOCH_3 + NH_3 \longrightarrow$
v. $CH_3CH_2COOCH_3 + NaOH \longrightarrow$
vi. $CH_3CH_2COONa + NaOH \xrightarrow{CaO}$
vii. $CH_3CH_2COOC_2H_5 + LiAlH_4 \longrightarrow$
viii. $CH_3CH_2MgBr + CH_3CH_2CN \longrightarrow$

Project

Add few drops or a small crystal of available carboxylic acid with about 2-3 mL of aq.$NaHCO_3$ and shake well. Formation of bubbles of carbon dioxide is positive test for presence of carboxylic acid.

Unit 21

Biochemistry

Teaching	Assessment	Weightage %
6	1	6

After studying this unit, 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 enzymes as biocatalyst and relate this role to various functions such as digestion of food. (Applying)
- Identify factors that affect enzymes activity such as effect of temperature and pH. (Understanding)
- Explain the role of inhibitors of enzyme catalysed 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). (Understanding)
- 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. (Applying)
- Describe the role of iron, calcium, phosphorous and zinc in nutrition. (Applying)

Introduction

Biochemistry is the study of the chemical substances found in living organisms and the chemical interactions of these substances with one another. Living organisms consist primarily of the elements carbon, hydrogen, oxygen and nitrogen. Many other elements such as sulphur and phosphorus are essential to life but they do not comprise a large portion of living organism.

Elements combine to form the molecules that make up living cells. The substances that are associated with life are called **biochemical substances.** Biochemical substances are divided into two groups: **Figure 21.1** gives an approximate mass composition for the human body in terms of types of biochemical substances present.

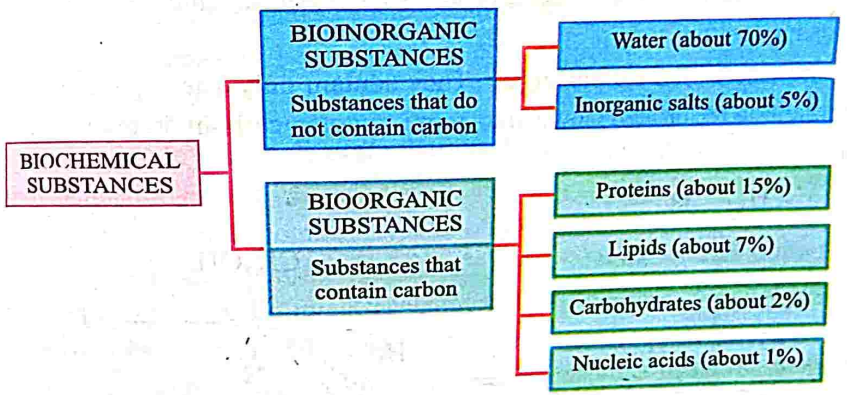


Figure 21.1 Classification of biochemical substances.

In grade–X, you have learnt the basics of biochemistry. In this unit, you will study in detail the concepts of biochemistry, biomolecules their structure and nutritional importance.

Tidbit

Bioorganic molecules make up only about one-fourth of body mass. The bioinorganic substance (water) constitutes over two-third of the mass of the human body, and another 4%–5% of body mass comes from inorganic salts.

21.1 Carbohydrates

Carbohydrates form an important class of naturally occurring organic compounds. They are widely distributed in plants and animals. Plants are the major sources of carbohydrates. Carbohydrates include glucose (grape sugar), fructose (honey, fruits), starch (potatoes), cellulose (wood) and glycogen (liver) etc. The word carbohydrate arose because molecular formulae of these compounds can be expressed as hydrates of carbon. Glucose, for example, has the molecular formula $C_6H_{12}O_6$ can be written as $C_6(H_2O)_6$. But, however, there are some compounds which are

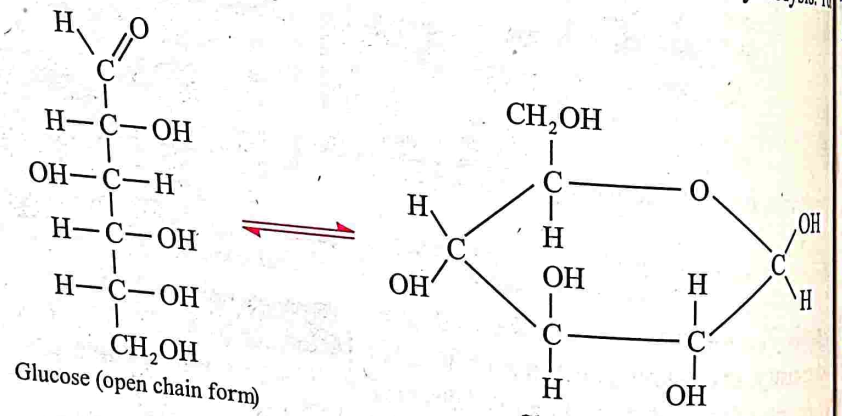
carbohydrates but they do not follow this general formula. For example, 2-deoxyribose having molecular formula $C_5H_{10}O_4$ cannot be represented by $C_n(H_2O)_n$ formula. On the other hand, there are also some compounds which follow this $C_n(H_2O)_n$ formula but they are not carbohydrates, for example formaldehyde (CH_2O) and acetic acid ($C_2H_4O_2$) [formaldehyde can be written as $C(H_2O)$ and acetic acid as $C_2(H_2O)_2$]. Hence, carbohydrates are polyhydroxy aldehydes (aldoses), or polyhydroxy ketones (ketoses) or compounds that give such compounds on hydrolysis. The hydroxyl group and the carbonyl group are the major functional groups in carbohydrates.

21.1.1 Classification

Carbohydrates are classified on the basis of the number of simple sugar units present per molecule as monosaccharides, oligosaccharides and polysaccharides.

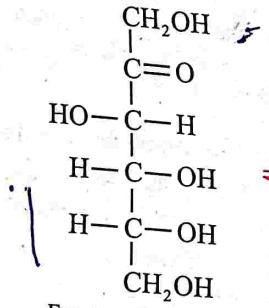
1. Monosaccharides

- They are also called simple sugars. They contain only one sugar unit per molecule. They cannot be broken down into more simpler carbohydrates on hydrolysis. For example, glucose, fructose etc.

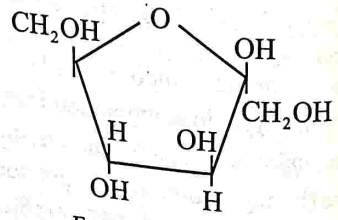


Glucose (open chain form)

Glucose (cyclic form)

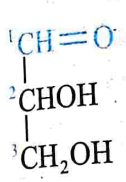


Fructose (open chain form)

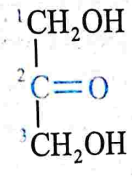


Fructose (cyclic form)

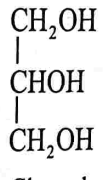
- The monosaccharides are again subdivided on the basis of the type of functional group and the number of carbon atoms in the molecule.
- On the basis of types of functional group monosaccharides may be classified as aldoses or ketoses. There are only two trioses: glyceraldehyde and dihydroxyacetone. Each has two hydroxyl groups, attached to different carbon atoms and one carbonyl group.



Glyceraldehyde (an aldose)



Dihydroxyacetone (a ketose)



Glycerol

- Similarly, on the basis of number of carbon atom in a molecule monosaccharides may be trioses, tetroses, pentoses, hexoses and so on.

2. Oligosaccharide

- An oligosaccharide is a carbohydrate that contains two to ten monosaccharide units covalently bonded to each other.
- Disaccharides are the most common type of oligosaccharide.
- A disaccharide is a carbohydrate that contains two monosaccharide units covalently bonded to each other. Like monosaccharides, disaccharides are crystalline, water-soluble substances. Sucrose (table sugar) and lactose (milk sugar) are disaccharides.
- Those oligosaccharides, which contain three and four units of monosaccharides per molecule, are called trisaccharides and tetrasaccharides respectively.
- Complete hydrolysis of an oligosaccharide produces similar or different types of monosaccharides. For example, maltose yields the same kind of two glucose units upon hydrolysis.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{2C_6H_{12}O_6}$$

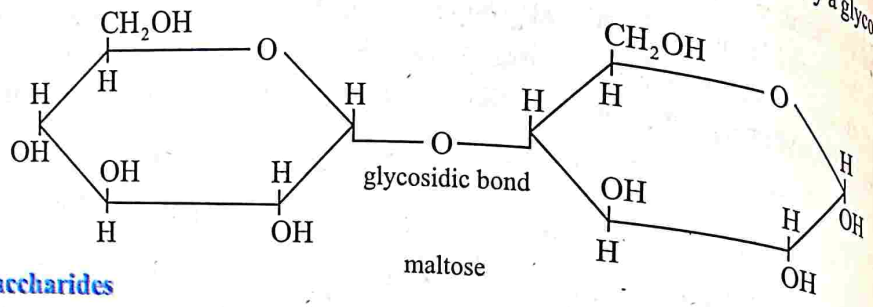
- While sucrose yields two different types of monosaccharides i.e. glucose and fructose upon hydrolysis.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Glycosidic Linkage or Bond

During the formation of disaccharides, the two monosaccharaide units combine together by an oxygen atom with the elimination of one water molecule. This type of linkage is

called glycosidic linkage or glycosidic bond e.g. two glucose units combined by a glycosi bond to form maltose as shown below.



maltose

Polysaccharides

- A polysaccharide is a complex class of carbohydrate that contains mar monosaccharide units covalently bonded to each other. The number of monosaccharid units present in a polysaccharide varies from above ten units to more than hundred units.
- Polysaccharides, like disaccharides and oligosaccharides, undergo hydrolysis unde appropriate conditions to produce monosaccharides.
- Both cellulose and starch are naturally occurring polysaccharides that are very prevalent in the world of plants.
- The paper is mainly cellulose, as is the cotton in clothing fabrics and the wood used in home construction.
- Starch is a component of many types of foods, including bread, potatoes, rice, corn beans and peas.

$$\underset{\text{sucrose}}{n\,(C_{12}H_{22}O_{11})} + nH_2O \xrightarrow{\text{Acid}} \underset{\text{glucose}}{n\,C_6H_{12}O_6}$$

21.1.2 Functions

Basic function of carbohydrates is the production of energy for the performance of vita activities in living organisms. They are also known as 'fuel of life' because they produce energy by the process of oxidation.

$$\text{Carbohydrate} + O_2 \xrightarrow{\text{(Oxidation)}} CO_2 + H_2O + \text{Energy}$$

These are chief sources of energy, therefore, they spare proteins and lipids for other important functions of the body. Some important functions are given below.

- Glucose is used as an immediate source of energy for the sick and sportsmen. It is also used in the manufacture of jams and sweets.

- Fructose is used as a sweetening agent in confectionary, in medicinal syrup. It is also used to prevent sandiness in ice-creams. It is also used as a substitute of table sugar (sucrose) for the obese and the diabetic.
- Sucrose is used as a food and as ingredient of jams, jellies, confectionaries, syrup. It is also used in the preparation of sucrose octaacetate, which is used for the denaturation of alcohols and for making anhydrous adhesives.
- Starch is principally used as a food. It is industrially used for manufacturing of ethanol by the process fermentation. It is also used as a stiffening agent in textile industry and in laundry. It is also used as an adhesive to fasten paper.
- Cellulose has no food value but is used as a roughage in our diet for promoting the peristaltic motion of digestive tract. It is used for the manufacturing of paper.
- Oligosaccharides are involved in the formation of secreted proteins like antibodies and blood clotting factors.
- The receptors on the cell membrane are the complexes of carbohydrates with certain proteins. The receptors are involved in molecular targeting or molecular recognition.

21.1.3 Nutritional Importance

Carbohydrates are the most important energy containing nutrients for living organisms. Plant contains stored carbohydrates called starch while animals contain stored carbohydrates called glycogen. Both, these polymers are broken down into the simplest monosaccharide units known as glucose, before oxidation. Then glucose is oxidized in the body cells by different types of pathways (series of enzymatic chemical reactions) to release energy. This energy is stored in the form of molecules known as ATP (adenosine triphosphate) in the different parts of the body.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow \underset{\text{(ATP)}}{6CO_2 + 6H_2O + \text{Energy}}$$

One mole of glucose on complete oxidation by citric acid cycle produces 36 ATPs.

Tidbit

Adenosine Triphosphate

Adenosine triphosphate, also known as ATP, is a molecule that carries energy within cells. It is the main energy currency of the cell and it is an end product of the processes of photophosphorylation (adding a phosphate group to a molecule using energy from light), cellular respiration and fermentation. All living things use ATP. It is also used in signal convert pathways for cell communication and is incorporated into deoxyribonucleic acid (DNA) during DNA synthesis.

Role of Various Carbohydrates in Health and Disease

There are different types of carbohydrates, which are involved in the health and disease of living beings. Some of these are given below.

1. Sucrose

Table sugar or cane sugar is the generally available form of sucrose. Sucrose is a disaccharide. Sucrose is a combination of fructose (fruit sugar) and glucose (simple plant sugar).Sucrose is a popular sweeting agent. It is used in healthy sweets, soft drinks and energy drinks. Sucrose is a caloric carbohydrate and thus is efficient to provide energy. 1 gram of sucrose produces 4 kilo calories energy when metabolised.

Excess of sucrose may cause some problems such as,

- Tooth decay
- Obesity
- Plaque formation upon our teeth
- Gum diseases

2. Lactose

Lactose is the disaccharide naturally found in milk. It is composed of glucose and galactose. Human milk contains 7.2% lactose while cow milk contains about 4.8% lactose. Milk is a universal food of new born mammals and one of the most complete human diet. Although glucose could be found in several types of foods, lactose is the only source of galactose.

Some of the important benefits of lactose (galactose) are,

- Galactose has various biological functions and serves in neural and immunological processes.
- Galactose is a component of several macromolecules, which are important constituents of nerve cells membrane.
- Galactose is also a component of the molecules present on blood cells that determine the ABO blood types.

According to recent studies, lactose may play a role in the absorption of calcium and other minerals such as copper and zinc, especially during infancy.

The main disadvantage associated with lactose (glactose) is that many human adults are unable to digest milk due to deficiency of lactase, (Lactase is an enzyme, splits lactose into glucose and galactose) which is called lactose-intolerance. Lactose intolerance is the inability to digest lactose that results in intestinal discomfort such as, cramps, flatulence, colic pains, abnormal intestinal flow, nausea and watery diarrhoea. These symptoms appear within 30-90 minutes after the ingestion of milk. It is important to remind that lactose intolerance is not a disease but a condition. To avoid this, fermented milk products such as yogurt and cheese should be used.

3. Glucose

Glucose is a simple carbohydrate. It is the most common and popular monosaccharide that can be found in sweet fruits such as grapes, which contains 20 – 30 % glucose. The carbohydrates you eat are converted to glucose in the body. The concentration of glucose in the blood, referred to as the blood glucose level, is vital to the proper functioning of the human body.

Some of the benefits and uses of glucose are,

- It is mainly used by the living bodies for the production of instant energy.
- It is an important constituent of human blood, human blood contains normally about 70 – 110mg of glucose per $100cm^3$.
- It also regulates the temperature of the body.
- The surplus glucose is converted to a polymer called glycogen in human beings. Glycogen is then stored in the liver and muscles. When the body is deficient in glucose, this liver and muscle glycogen is hydrolysed to glucose according to the body requirement.

The disadvantages related to the extra intake of glucose is,

- Human pancreas secretes a hormone known as insulin. Insulin helps in the metabolism of glucose to produce energy. In some cases, defects in the metabolism of glucose occurs due to which blood glucose level rise from the normal level. This condition results in a disease known as diabetes mellitus. The consequences of unchecked diabetes include hardening of blood vessels, dysfunction of kidney, diabetic coma that causes premature death.

21.2 Proteins

The term protein is derived from the Greek word *proteios*, which means "*first, prime or chief*". Proteins are naturally occurring polymers composed of amino acid units joined to one another by amide (or peptide) bonds. Spider webs, animal hair and muscle, egg whites and haemoglobin (the molecule that transports oxygen in the body to where it is needed) are all proteins. They are present in all animals, plants, bacteria and viruses.

- Chemically, proteins are complex nitrogenous organic compounds, which are associated with the concept of life itself.
- By chemical composition, proteins are composed of carbon, hydrogen, oxygen and nitrogen. Percentage of nitrogen is fairly constant and is about 16% of the molecular weight of protein.

- Some proteins also contain smaller quantities of sulphur and phosphorous.
- There are about 20 different amino acids, which combine in different sequence and different numbers and produce an infinite number of different types of proteins.
- The bacterium, *Escherichia coli* (E. coli) has been estimated to contain about 3000 different types of proteins. Similarly, human body contains about 100,000 different kinds of proteins. However, none of the proteins of E. coli is identical with any of the human proteins.

21.2.1 Classification

Proteins have been classified into the following three major classes.

1. Simple Proteins
2. Compounds or Conjugated Proteins
3. Derived Proteins

1. Simple Proteins

Simple proteins are made up of amino acid subunits joined together by peptide bonds. When hydrolysed by enzymes, simple proteins yield only the amino acids and their derivatives from which they are formed, examples of simple proteins include albumins, globulins, collagens, histones, glutelins, albuminoids etc.

2. Compounds or Conjugated Proteins

Conjugated proteins are complex proteins composed of simple proteins and a non-protein substance referred to as a prosthetic group or cofactor.

Most prosthetic groups or cofactors are small organic molecules formed from vitamins. When hydrolysed by enzymes, conjugated proteins yield the amino acids from which they are comprised of and some other chemical component. Examples of conjugated proteins include nucleoproteins, glycoproteins, phosphoproteins and haemoglobins.

Tidbit

Albumin

A class of simple, sulphur-containing, water-soluble proteins that coagulate when heated; occurring in egg white, milk, blood, and other animal and vegetable tissues and secretions.

Table 21.1 Different Types of Conjugated Proteins and Prosthetic Group

S. No.	Conjugated Protein	Prosthetic Group
1.	Nucleoproteins	DNA or RNA
2.	Phosphoproteins	Phosphoric acid
3.	Lipoproteins	Lipids
4.	Glycoproteins	Carbohydrates
5.	Chromoprotein	Coloured compounds

3. Derived Proteins

These are proteins derived by partial to complete hydrolysis of the simple or conjugated proteins by the action of acids, alkalies or enzymes. They may be proteins, meta-proteins, conjugated proteins etc. They include two types of derivatives, primary derived proteins and secondary derived proteins.

i. **Primary derived proteins:** They are also called as denatured proteins, in which some or all cross linkages which normally keep the molecular structure are broken. Denaturing agents may be physical or chemical such as vigorous shaking, heat, light, low pH etc.

ii. **Secondary derived proteins:** These are formed by hydrolysis of simple or conjugated proteins by acid or enzymes e.g. proteoses, peptones, etc.

21.2.2 Structure

Proteins are macromolecules having very complicated structures. Biochemists divided protein structures into four levels, to make it easier and to handle the complexity of the overall structures. In short, all the proteins appear in any of the following four different structures.

1. Primary Structure

This structure shows simply the sequence and number of different amino acids in a polypeptide chain. For example, the hormone insulin has two polypeptide chains, A and B. It also shows whether the polypeptide chain is open, branched or cyclic.

2. Secondary Structure

X-rays diffraction experiments have shown that long running polypeptide chains tend to twist or coil upon themselves in a special pattern. Secondary structure show this folding of the polypeptide chains to form a specific coiled structure held together by strong hydrogen bonding. Secondary structure may assume any of the following two different forms.

a. Alpha – helix form **b.** β– pleated sheets

3. Tertiary Structure

The long polypeptide chain of proteins molecules undergoes folding and re-folding on itself and give rise to a definite three dimensional structure. This is called tertiary structure. This structure makes proteins rounded and somewhat rigid molecules.

4. Quaternary Structure

This structure shows the association of many individual protein sub-units, each with its own tertiary structure into a complex functional unit. Examples are myoglobin (oxygen storage) and haemoglobin (oxygen carrier).

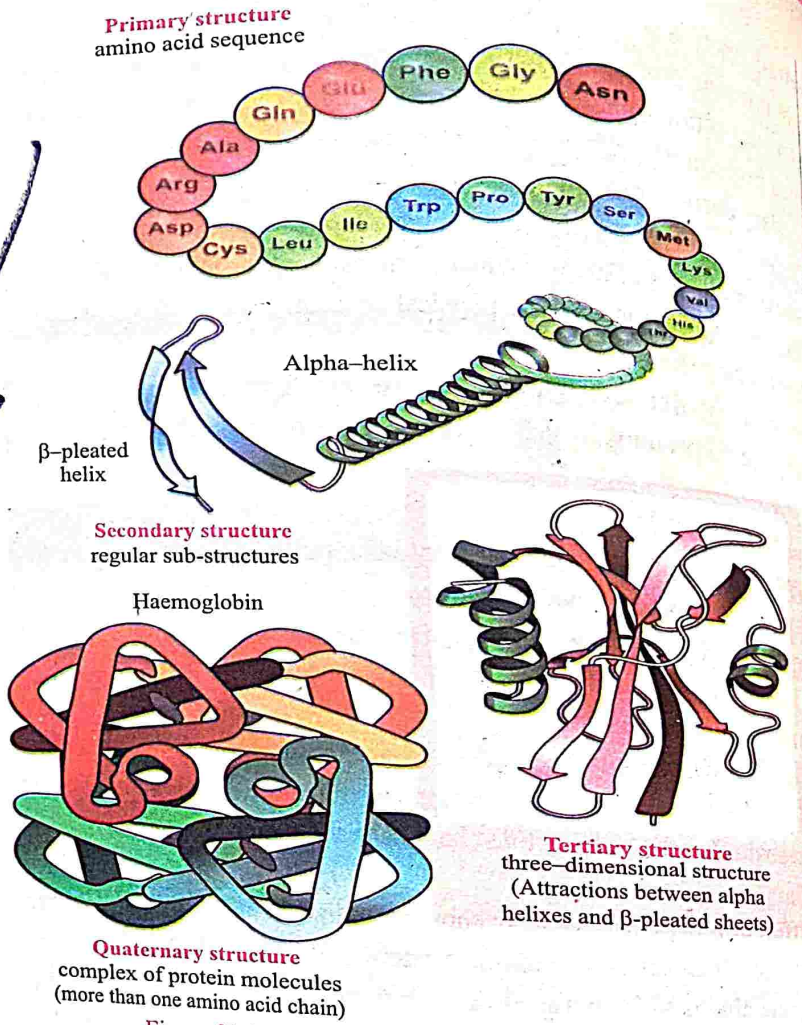


Figure 21.2 Different structure levels of proteins.

21.2.3 Properties

Proteins are complex organic compounds. The physical and chemical properties of proteins are,

1. Physical Properties of Proteins

- Proteins are colourless and usually tasteless.
- The proteins range in shape from simple crystalloid spherical structures to long fibrillar structures. Two shapes have been recognized:

(a). Globular proteins: They are spherical in shape.

(b). Fibrillar proteins: They are in thread-like structure.

- The proteins generally have high molecular weights.
- Protein denaturation is the changes in the properties of a protein or loss of biologic activity.
- Like amino acids, the proteins are amphoteric in nature because they contain both acidic (–COOH) and basic (amino) group.
- The solubility of proteins is influenced by pH.
- All protein solutions rotate the plane of polarized light to the left, i.e., these are levorotatory.

2. Chemical Properties of Proteins

The chemical properties of proteins are,

- Hydrolysis: Proteins are hydrolysed by a variety of hydrolytic agents, such as acidic agents and basic (alkaline) agents.
- They react with both acids and bases.
- They can be precipitated from their solutions by salts of heavy metals, heat and alcohols etc.
- When proteins are strongly heated or treated with certain reagents they lose their structural organization and their biological functions. This is known as coagulation of proteins.

21.2.4 Importance of Proteins

Proteins are the most significant biological compounds of living beings. They play an important role in many fundamental biological processes and functions. They are very versatile and have many different functions in the body. These are most critical to life and perform different types of functions. Some of these are,

- Proteins are the most abundant intra-cellular macromolecules and form more than 50% of the dry weight of most organisms.
- Many of the proteins act as living catalysts called enzymes. Enzymes increase the rate of biological reactions to the extent required by the body.
- They act as barrier such as skin and bacterial cell walls.
- They act as storage depots, such as ferritin for iron storage in blood.
- The nucleoproteins act as carrier of genetic information or characters. They serve as basis of inheritance of heredity characters from parents to off springs (in the form of genes).
- Hormones are proteins in nature. They regulate the growth of living organism and control a number of other physiological functions.
- Some proteins serve as carrier of different substances inside the body. For example, haemoglobin is a protein in red blood cells that acts as carrier of oxygen, ceruloplasmin, is a protein acts as carrier of copper in the blood plasma.

- Some proteins contribute to the structure of tissues for example collagen, elastin and keratin.
- They also act as receptors of chemical transmitted informations as well as the carrier of these informations in the form of substances known as *pheromones*.
- They are involved in the activities of muscles (contraction and relaxation).
- They control cell growth and diversity.
- They provide mechanical support.
- Proteins play vital role in the immune system of living organisms.

Tidbit

Ceruloplasmin is a protein made in liver. It stores and carries the mineral copper around the body. Ceruloplasmin carries 65% to 90% of the copper found in blood. Copper is vital to many processes in body. These include building strong bones and making melanin. But having too much copper in the body can be toxic.

Tidbit

Pheromones are substances which are secreted to the outside by an individual and received by a second individual of the same species.

21.3 Enzymes

The catalysis of biological reactions is probably the most important task assigned to proteins by nature. Hundreds of biological reactions are taking place every minute in different parts of the body for obtaining energy, synthesizing the protoplasmic and other structural materials, digestion, absorption and assimilation of food etc. These and so many other biological reactions are catalysed by certain special proteins known as enzymes. The word enzyme was originated from a Greek word 'en' means 'in' and 'zyme' means yeast after studying the catalytic properties of yeast. Enzyme is a *complex organic substance, which alters the rate of an already initiated biological reaction without itself being altered permanently during the reaction.* Enzymes are organic catalysts produced by living cells but they are capable of acting independently out of the cells.

Most of the enzymes are protein in nature and show all the properties of proteins. The usual proteins precipitating agent precipitate them. They are non-hydrolysable with nitrogen contents of about 16%. They are de-activated by extreme alteration of pH and high temperature. Enzymes are highly specific in nature. It means that an enzyme can work only for one type of reaction in the body. The substance upon which an enzyme acts is called substrate of that enzyme.

21.3.1 Role of Enzymes as a Biocatalyst

Enzymes are playing the decisive role in the digestion of food in different parts of the alimentary canal. For example,

In the Digestion of Carbohydrates

After ingestion food meets saliva. Saliva contains an enzyme called salivary amylase or ptyalin. This enzyme catalyzes the hydrolysis of carbohydrates of food without affecting proteins and fats. When food reaches stomach, the action of amylase comes to an end due to acidic pH of the stomach. When food enters the intestine, pancreatic juice is secreted. This juice contains pancreatic amylase, which has the same action as salivary amylase.

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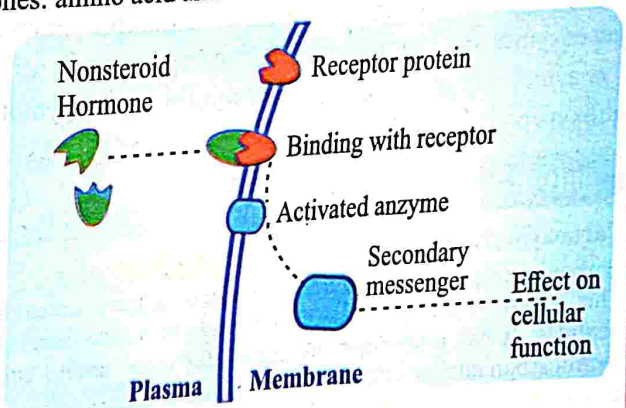
Hormones are chemical messengers that are secreted directly into the blood, which carries them to organs and tissues of the body to exercise their functions. There are many types of hormones that act on different aspects of bodily functions and processes.

The body produces many different hormones, but each hormone is very specific to its target cells. A target cell is the cell on which a hormone has an effect. Target cells are affected by hormones because they have receptor proteins that are specific to the hormone. When a hormone binds to a receptor, it causes a change within the cell.

There are two main types of hormones: amino acid and cholesterol based hormones.

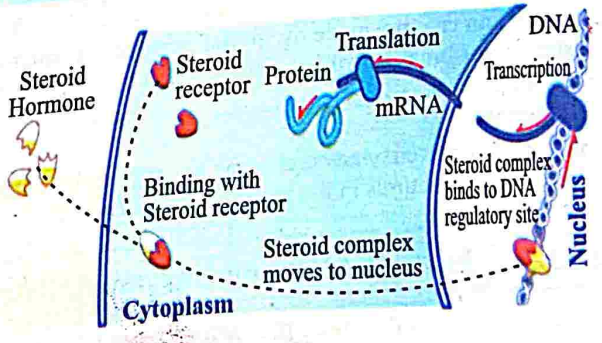
Amino Acid-Based Hormones

Amino acid-based hormones are made of amino acids. Some amino acid-based hormones are made of a few amino acids and are simple in structure, while others are made of hundreds of amino acids and are very large. These hormones are not fat-soluble and therefore cannot diffuse through the plasma membrane of their target cell. They usually bind to receptors that are found on the cell membrane.



Cholesterol-Based Hormones

Cholesterol-based hormones are made of lipids such as phospholipids and cholesterol. Hormones from this group are also called steroid hormones. Steroid hormones are fat soluble and are able to diffuse through the plasma membrane of a target cell. Steroid hormone receptors are found in the cell cytosol and nucleus.



ii. In the Digestion of Fats

There is only slight hydrolysis of fats in the mouth and stomach because no lipase is secreted by the salivary glands while the lipase of the gastric juice is weak and can hydrolysed only small fat molecules. The lingual lipase enzyme secreted by the Ebner's glands on the dorsum of the tongue remains active in stomach and can hydrolyse or digest about 30% of the ingested fats. When the fats reach the intestine, they face pancreatic juice. This juice contains a pancreatic lipase enzyme also known as steapsin. This enzyme completely hydrolyses or digests all the fats of the food.

iii. In the Digestion of Proteins

Digestion of proteins starts in stomach because the saliva contains no enzyme for the digestion of proteins. The first enzyme that acts upon the proteins of the ingested food is called pepsin present in the gastric juice of stomach. It is best active in acidic pH of 1-2 range. Pepsin has also milk-curdling properties.

When food enters the intestine, pancreatic juice comes into action. This juice contains numerous enzymes for the digestion of proteins. These enzymes include trypsin, chemotrypsin. These enzymes are secreted in their inactive forms, which are then activated, by the action of other enzymes. For example, the inactive trypsinogen is activated to active trypsin by the action of enzyme enterokinase. Besides, trypsin and chymotrypsin pancreatic juice contains carboxypeptidase's A and B, elastase, collagenase etc.

Tidbit

Carboxypeptidase

Carboxypeptidase is an enzyme synthesized in the pancreas and secreted into the small intestine. This enzyme hydrolyzes the first peptide or amide bond at the carboxyl end of proteins and peptides. It has a stronger preference for those amino acids that have aromatic or branched hydrocarbon chains.

Elastase

Elastase is an enzyme made by special tissue in the pancreas, an organ in your upper abdomen. Elastase helps break down fats, proteins, and carbohydrates after you eat. It is a key part of your digestive process.

Collagenases

Collagenases are enzymes that break the peptide bonds in collagen. They assist in destroying extracellular structures in the pathogenesis of bacteria.

21.3.2 Factors Affecting Enzyme Activity

Several factors that affect the activity of enzyme, such as temperature, pH, enzyme concentration, substrate concentration and the presence of any inhibitor or activator.

i. Effect of Temperature

The protein nature of the enzymes makes them extremely sensitive to thermal changes. Enzyme activity occurs within a narrow range of temperatures compared to ordinary chemical reactions. Each enzyme has a certain temperature at which it is more active and shows maximum activity. This temperature is called the optimum temperature. For most animal enzymes, optimum temperature is around body temperature (37°C). Some plants enzymes such as urease has optimum temperature even upto 60°C. The enzyme activity gradually lowers as the temperature rises more than the optimum temperature until it reaches a certain temperature at which the enzyme activity stops completely due to the change of its natural structure and composition (denaturation of enzyme). On the other hand, if the temperature lowers below the optimum temperature, the enzyme activity decreases until the enzyme reaches at a minimum temperature at which the enzyme activity is the least. The enzyme activity stops completely at 0C°, but if the temperature rises again, the enzyme is reactivated again. Enzymes can be stored for years in frozen state. If we plot a graph between temperature and rate of enzymatic reaction, we get the curve as shown in the **Figure 21.3.**

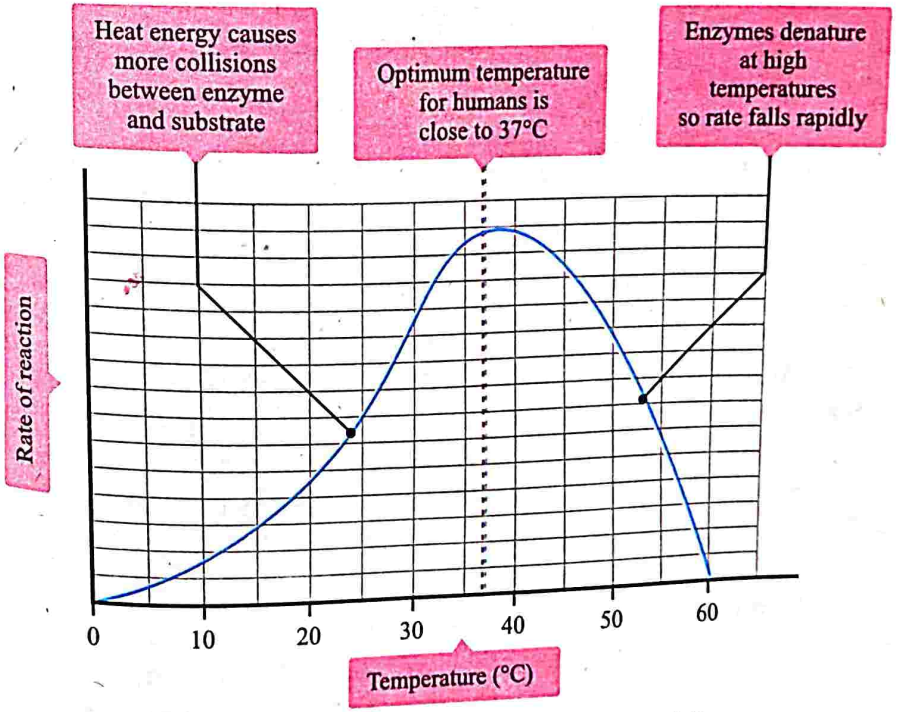


Figure 21.3 Effect of temperature on enzyme activity.

2. pH

Enzyme activity is also effected by pH. Some enzymes work best in alkaline pH while others in acidic pH. As the pH is decreased or increased, the nature of the various acid and amino groups on the side chains is altered, which results in change in the overall shape and structure of the enzyme.

Each enzyme has a pH at which it shows the maximum activity. This pH is called optimum pH. For example, the optimum pH of pepsin is around 2.0 while that of trypsin varies from 8 – 9 pH. The pH below which the enzyme loses its activity and at which the enzymes shows the lowest activity is called minimum pH. Most of the enzymes have optimum activities in the range 5–9 pH. Pepsin is an exception to this rules.

Plotting a graph between enzyme activity and pH, we get a curve as shown in the Figure 21.4.

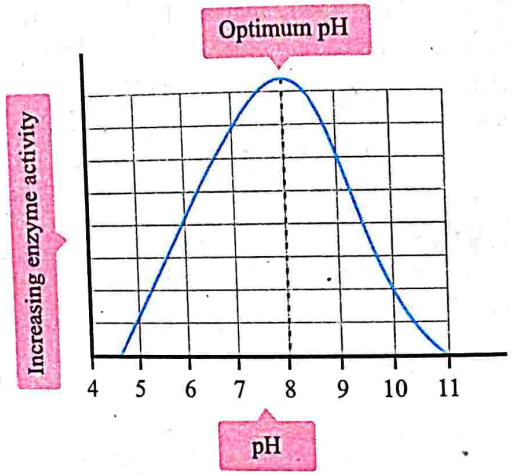


Figure 21.4 Effect of pH on enzyme.

Enzyme Inhibition

The process by which the activity of an enzyme is decreased or inhibited by the addition of certain substances to the reaction is called enzyme inhibition. The different substance, which inhibit the activity of enzymes, are known as inhibitors. Poisons and drugs are examples of enzyme inhibitors. According to the similarity between the inhibitor and the substrate, enzyme inhibition is classified into:

i. Irreversible Inhibition

When the inhibitor reacts and form a strong covalent bond with the active site of the enzyme then it termed as irreversible inhibition. The inhibitors forms a stable and irreversible complex with the enzyme. This complex cannot be broken down by physical or chemical methods to restore the active form of the enzyme.

ii. Reversible Inhibition

It is a temporary type of inhibition. In this inhibition the inhibitor binds non-covalently (weak interaction) with enzyme. If inhibitor is removed, the action of enzyme is fully restored. The activity of enzyme is fully restored on removing the inhibitor by dialysis. It is sub-divided into,

(a). Competitive Inhibition

- A competitive inhibitor has structural similarities to the normal substrate for the enzyme.
- Competitive inhibitors compete with the substrate for the active site of the enzyme and form an enzyme inhibitor complex.
- The inhibitor binds to the same active sites of enzymes to which the actual substrate binds. By this way, the active sites of the enzyme are blocked and then the substrate is unable to bind to the enzyme.

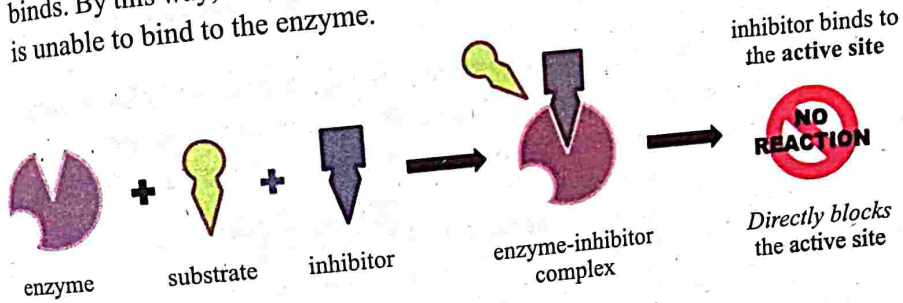


Figure 21.5 Competitive inhibition.

(b). Non-Competitive Inhibition

- The inhibitor has no structural resemblance with the substrate of the enzyme.
- They do not compete with the substrate for the active sites of the enzyme.
- The inhibitor does not bind to the active sites of enzyme.
- Inhibitor binds to the site other than active sites of the enzyme, to form enzyme – substrate inhibitor complex.

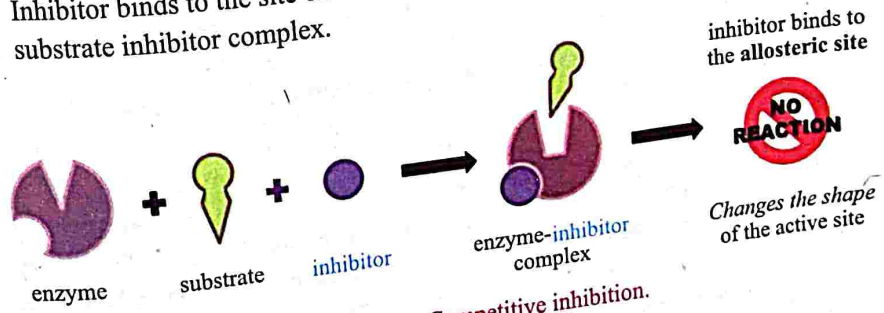


Figure 21.6 Non-Competitive inhibition.

(c). Uncompetitive Inhibition

- These are like non-competitive inhibitors.
- The uncompetitive inhibitor combines with enzyme-substrate complex rather than directly with the free enzyme to give inactive enzyme inhibitor complex.

Tidbit

Allosteric Site

Substances that bind to the enzyme at a site other than the active site. This other site is called the allosteric site.

21.3.3 Industrial Application of Enzymes

Enzymes are used in the chemical industry and other industrial applications where extremely specific catalysts are required.

Useful enzymes are obtained from both plants and animals, but most enzymes are obtained from microorganism, mainly bacteria and fungi. Some applications of enzymes are given below.

i. Biological detergents

Most of the enzymes for washing come from bacteria adapted to live in hot springs. The enzymes are used for presoak condition and direct liquid applications helping removal of proteins and starch stains. They are also able to digests fat, oil and grease stains.

ii. Fruit juice production

During the manufacture of fruit juice, the cells of the fruits have to be broken down before the bulk of the juice can be extracted. Plant cell wall is built of cellulose fibers, which are held together by pectins and hemicelluloses and they are extremely tough. When very high temperature is used to break down the fruit tissues, this will affect colour and flavour of the juice. Instead, the fruit is crushed and enzyme preparation containing cellulases and hemicellulases are added. These cause cell wall to break up and most of the juice is released.

Tidbit

Cellulases

Cellulases is an enzyme that breaks down the cellulose molecule into monosaccharaides "simple sugars". The breakdown of cellulose is on considerable economic importance.

iii. Production of ethanol

In biological industry, cellulase are used to break down cellulose into sugar which can then be fermented to produce ethanol.

iv. High fructose syrup

A sweetener that is widely used in food and drinks is high fructose corn syrup. It is manufactured from starch in corn fruit. The grains are milled to starch slurry and the enzyme amylase is added. Finally, the syrup is passed down a column of immobilized glucose isomerase enzymes. This converts much of glucose to fructose. It is added to sweeten foods without adding too many calories.

Beside this, numerous enzymes are used in other industrial processes; such as, in paper industry, enzymes like amylases, xylanases and cellulases etc. are used.

21.4 Lipids

Lipids are a heterogeneous group of organic compounds. They are greasy substances which are relatively insoluble in water and soluble in non-polar organic solvents like ether, benzene etc.

Lipids perform several important functions in living organisms.

- They act as storehouses of metabolic energy.
- They act as structural components of membranes.
- They act as protective and insulating coatings.
- Nervous tissues are rich in lipids where they play important role in their functions.
- The sub–cutaneous fat serves the role of insulating against atmospheric heat and cold.

Tidbit

Saponifiable and Non-saponifible Lipids

Saponifiable lipids are easily hydrolysed in basic condition such as, sodium hydroxide and those generally have ester linkages. Most lipids are saponifiable.

Non-saponifiable lipids cannot be hydrolysed by sodium hydroxide because they have no ester bonds.

Lipids may be saponfiable or non-saponifibale. Fats, oils and waxes are saponifible while terpenes and steroids are non-saponifible lipids.

21.4.1 Classification

Lipids have been classified into following three major classes:

1. Simple Lipids

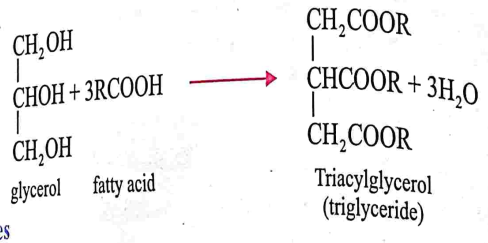
These are the esters of fatty acids with different types of alcohols. These include,

(i). Fats and oils, which yield fatty acids and glycerol upon hydrolysis.

(ii). Waxes, which yield fatty acids and long-chain alcohols upon hydrolysis.

(i) Fats and Oils

Both types of compounds are called Triacylglycerols or triglycerides because they are esters composed of three fatty acids joined to glycerol. The difference is on the basis of their physical states at room temperature. Fat is solid at room temperature while oil is liquid at room temperature. These differences in melting points reflect differences in the degree of unsaturation of the constituent fatty acids. Oils contain more un-saturation in the alkyl part of fatty acids than fats. Fatty acids are long chain carboxylic acids contain usually 12–18 carbon atoms per molecule.



(ii) **Waxes**

- Wax is an ester of long-chain high molecular weight alcohol (usually mono-hydroxy) and a fatty acid.
- The acids and alcohols normally found in waxes have chains of the order of 12-34 carbon atoms in length.
- For example, bees wax and carnauba wax etc.

2. Compound Lipids

These are the esters of fatty acids with alcohols containing some additional groups, as well. These are further divided into.

i. Phospholipids

These lipids contain fatty acids, phosphoric acid, nitrogenous bases along with some other constituents. They are also called phosphatides.

ii. Glycolipids

They contain fatty acid, alcohol and carbohydrates. They are present in large amount in the white matter of brain and in the myelin sheaths of nerves.

iii. Sulpholipids

They contain a sulphate group in addition to fatty acids, alcohol and carbohydrate.

iv. Lipo-Proteins

These are the complexes of lipids with proteins.

3. Derived Lipids

These are the substances derived by the hydrolysis of simple and compound lipids. These include fatty acids, alcohols, steroids, terpens, arytenoids etc.

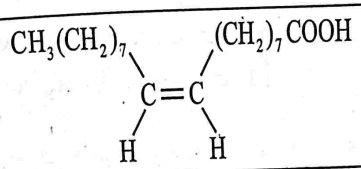
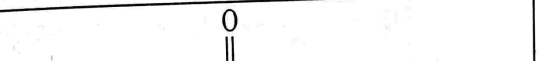
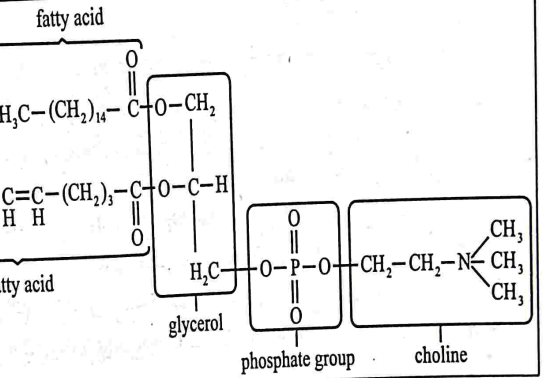
21.4.2 Structure

Lipid has no common structure. The most common occurring lipids are triglycerides and phospholipids. Triglycerides are fats and oils. Triglycerides have a glycerol backbone bonded to three fatty acids. If the three fatty acids are similar, the fats are called simple triglycerides. If the fatty acids are not similar, they are known as mixed triglycerides.

The second most common lipids are phospholipids. They are found in cell membrane of animals and plants. Phospholipids contain glycerol and fatty acids as well as phosphoric

acid and low molecular weight alcohol. Some lipids and their structure are given in Table 21.2

Table 21.2 Lipids and their Structure

Name of Lipids/ Fatty Acids	Structure
Stearic acid	$CH_3(CH_2)_{14}COOH$ (saturated)
Oleic acid	
Wax (from bee hive)	
Phospholipids	

21.4.3 Properties of Lipids

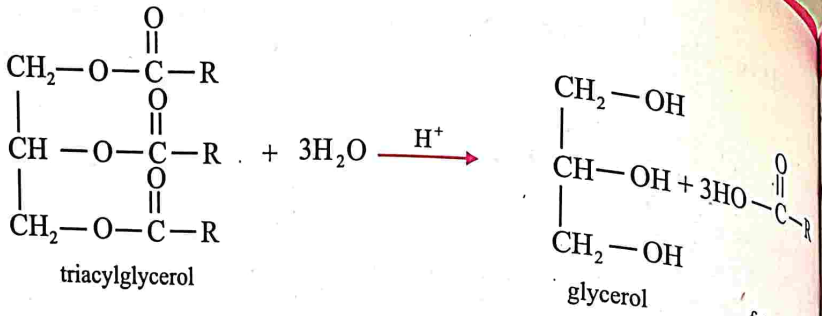
i. Physical Properties

- Natural fats are colourless, odourless and tasteless.
- They are insoluble in water but are highly soluble in organic solvents like benzene, ether, chloroform etc.
- They have well defined melting and solidifying points.
- They have low specific gravity and, therefore, float on the surface of water.

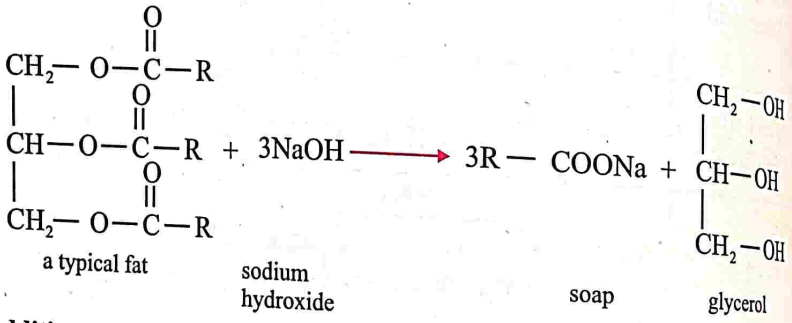
ii. Chemical Properties

- **Hydrolysis**

Natural fats undergo hydrolysis with acids or bases in boiling water where they produce free acids and glycerol.



In case of base hydrolysis, the base reacts with free fatty acids and produce salts of fatty acids called soap. This process is called saponification.



Addition reaction

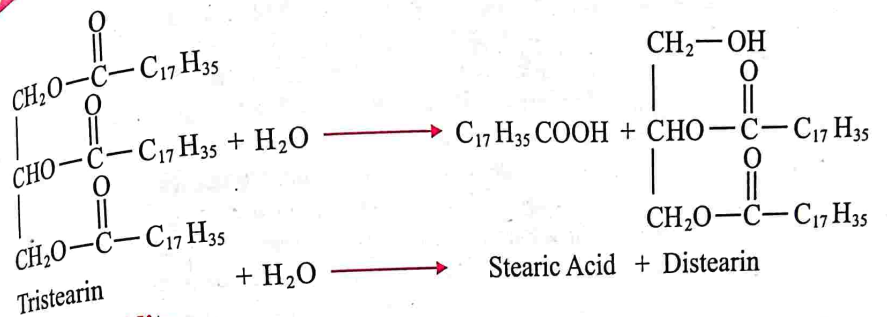
Unsaturated fatty acids of fats and oils undergo addition reactions at the points of unsaturation and produce addition products. The oils, which contain more unsaturation, are hydrogenated to produce solid ghee. By this way inedible and cheap oils such as cotton seed oils are hydrogenated and converted to solid and edible ghee.

Oxidation

Fats rich in un-saturated fatty acids (e.g linseed oil) undergo spontaneous oxidation at their double bonds and produce aldehydes, ketones and resins. They form a thin transparent coating on the surface to which the oil is applied. These are known as drying oils. They are used in manufacture of paints and varnishes.

Rancidification

Natural and specially animal fats contains lipase enzyme. By the action of atmospheric oxygen, in the presence of lipase the fats undergo partial hydrolysis and oxidation at their double bonds. This produces volatile carboxylic acids of sour taste and unpleasant smell. This process is called rancidification and the fat is said to have become rancid.



Types of Rancidity

There are three types/pathways of rancidity:

1. **Oxidative Rancidity**

Oxidative rancidity also known as autoxidation. The oxidation by the atmospheric O_2 cleave the double bonds of polyunsaturated fatty acids present in triacylglycerols by free radical reactions. This reaction causes the release of malodorous and highly volatile aldehydes and ketones.

2. **Hydrolytic Rancidity**

Hydrolytic rancidity also known as hydrolysis/enzymatic oxidation. It is due to the contamination of fat by lipase leading to the release of free fatty acids. In particular, short chain fatty acids, such as butyric acid are malodorous.

3. **Microbial Rancidity**

In which micro-organisms such as bacteria, moulds and yeast use their enzymes to break down fats, producing unwanted odours and flavours. Water needs to be present for microbial growth to occur. It can be prevented by sterilization and addition of antioxidant ingredients, such as vitamin E.

Society, Technology And Science

Insulin is a hormone released from the pancreas (an organ behind the stomach that also produces digestive enzymes). This hormone (insulin) controls the amount of glucose in the blood. Glucose in the bloodstream stimulates the pancreas to produce insulin. Insulin helps glucose to move from the blood into the cells. Inside the cells, glucose is converted to energy, which is used immediately, or the glucose is stored as fat or glycogen in the body until it is needed. The levels of glucose in the blood vary normally throughout the day. They rise after a meal and return to pre-meal levels within about 2 hours after eating. Once the levels of glucose in the blood return to pre-meal levels, insulin production decreases.
The variation in blood glucose levels is usually within a narrow range, about 70 to 110 mg per $100cm^3$ of blood in healthy people. If people eat a large amount of carbohydrates, the levels may increase more. If the body does not produce enough insulin to move the glucose into the cells, or if the cells stop responding normally to insulin (called insulin resistance),

the resulting high levels of glucose in the blood and the inadequate amount of glucose in the cells together produce the symptoms and complications of diabetes.

Diabetes mellitus is a disorder in which the amount of sugar in the blood is elevated. Doctors often use the full name diabetes mellitus, rather than diabetes alone, to distinguish this disorder from diabetes insipidus.

- Diabetes mellitus is a disorder in which blood sugar (glucose) levels are abnormally high because the body does not produce enough insulin to meet its needs.
- Diabetes insipidus is a relatively rare disorder that does not affect blood glucose levels but, just like diabetes mellitus, also causes increased urination.

21.4.4 Nutritional and Biological Importance of lipids

Lipids perform a number of different functions in living organisms. Some of these are listed below.

- Lipids provide food, which is highly rich in calorific value. One gram of lipid on complete oxidation produces 9.3 kcal of heat, which is about double the amount produced by carbohydrates and proteins.
- Lipids are insoluble in water and, therefore, they can be stored easily in the body as food reserves. The organisms then use these food reserves during hibernation periods.
- Lipids in association with different proteins form the important constituents of cell membranes.
- Fats have high insulating capacity. Great quantities of fats are deposited in the sub-cutaneous layers in aquatic mammals such as whale and in animals of cold climates. These fat deposits protect these animals from severe cold and severe temperature changes.
- Some lipids especially phospholipids play a key role in the absorption and transportation of fatty acids in the body.
- Sex hormones, adrenocorticoids, cholic acids are synthesized from a steroidal lipid known as cholesterol.
- Lipids serve as carrier of fats soluble vitamins such as vitamin A, D and E in the body.
- Squealing, a steroid present in the blood of shark has antibiotic and antifungal properties. This explains why sharks rarely contract infections and almost never get cancer.

21.5 Nucleic Acids

Nucleic acids are macromolecules that allow organisms to transfer genetic information from one generation to the next. They are present in every living organism as well as viruses. They have been found to be the essential substance of the genes and the apparatus

which the genes act or express themselves. They contain in their structure the blueprints the normal growth and development of each and every organism

- Nucleic acids are the main information-carrying molecules of the cell, and, by directing the process of protein synthesis, they determine the inherited characteristics of every living thing.
- The two main classes of nucleic acids are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).
- DNA is the genetic material found in living organisms, from single-celled bacteria to multicellular mammals.
- 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 synthesis of proteins.
- They are capable of being broken down to yield phosphoric acid, sugars, and a mixture of organic bases (purines and pyrimidines).

Nucleic acids are substances present in the nuclei of cells which are involved in the storage, expressing, transmission and processing of genetic information and mutation in living organisms. The monomer that makes up a nucleic acid is called a nucleotide.

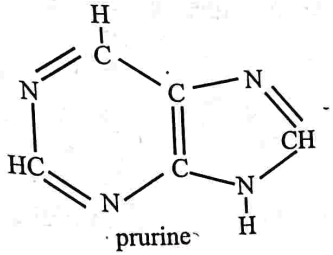
Types of Nucleic Acids

There are two types of nucleic acids.

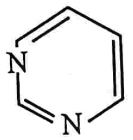
- DNA (Deoxyribonucleic acid) it is present in nuclei and in some viruses. It is the main constituent of chromosome.
- RNA (Ribonucleic acid) is present in the cytoplasm and in some viruses.

21.5.1 Structural Components of DNA and RNA

Watson and Crick determined the structure of nucleic acids. Both DNA and RNA are formed by the polymerization of large number of units known as nucleotides. That is why DNA and RNA are polynucleotides. A nucleotide is composed of a nitrogenous base, a sugar and a phosphate group. DNA differs from RNA in the type of nitrogenous base and type of sugar unit. The nitrogenous bases are of two types, purine and pyrimidine.

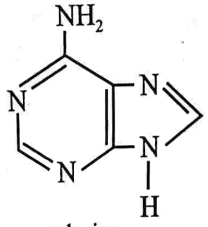


prurine

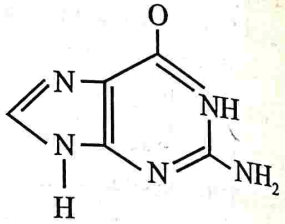


pyrimidine

- There are two different types of purine derivatives. These are adenine a guanine.

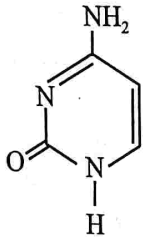


adenine

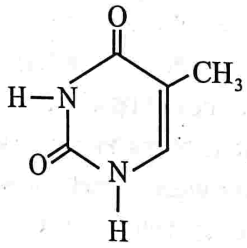


guanine

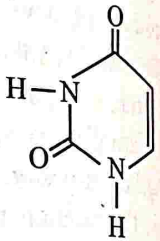
- Similarly, there are three derivatives of pyrimidine. These are cytosine, thym and uracil.



cytosine

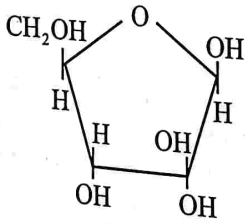


thymine
(present only in DNA)

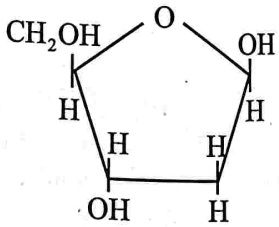


uracil
(present only in RNA)

- DNA and RNA contain two different types of sugars. One is deoxyribose and the other is ribose sugar. Both these sugars are in cyc furanose form.

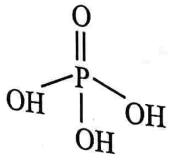


β-ribose

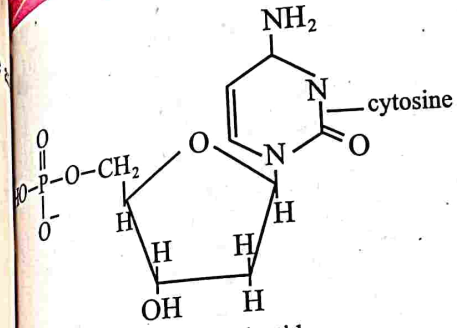


β-2-deoxyribose

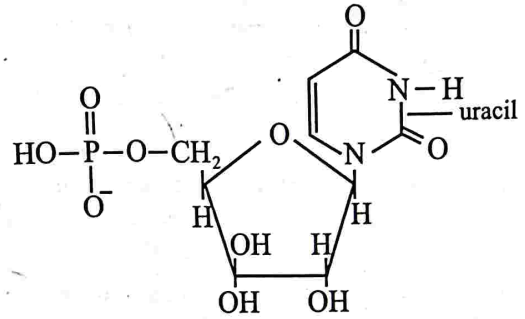
- The third component of nucleic acid is phosphoric acid.



phosphoric acid



deoxyribonucleotide



ribonuclectide

DNA molecule is formed by two antiparallel long polydeoxyribonucleotide chains, hich wind on each other. These two chains are held together throughout the whole length y hydrogen bonding present between their nitrogenous bases.

denine joins only to thymine while guanine joins only to cytosine. Adenine joins to thymine y two while cytosine joins to guanine by three hydrogen bondings. This pairing of bases is ighly specific. Adenine will never join cytosine and guanine never joins thymine.

Difference between DNA and RNA

NA and RNA differs in the following points from each other.

Comparison	DNA (Deoxyribonucleic Acid)	RNA(Ribonucleic Acid)
Location	DNA is found in the **nucleus**, while a small amount of DNA also present in **mitochondria.**	RNA is formed in the **nucleolus** and then moves to specialized regions of the **cytoplasm** depending on the type of RNA formed.
Structure	DNA consists of **two strands**, arranged in a **double helix**. These strands are made up of subunits called nucleotides.	RNA has only **one strand**, but like DNA, is made up of nucleotides.
Length	DNA is a **much longer polymer** than RNA. A chromosome, for example, is a single, long DNA molecule, which would be several centimetres in length when unravelled.	RNA molecules are variable in length, but **much shorter** than long DNA polymers.
Sugar	The sugar in DNA is **deoxyribose.**	RNA contains **ribose** sugar.

Bases	The bases in DNA are Adenine (A), Guanine (G), Cytosine (C) and Thymine (T).	The bases in RNA are Adenine (A), Guanine (G) and Cytosine (C) like DNA, but contains Uracil (U) rather than Thymine.
Base Pairs	**Adenine and Thymine pair (A-T)** Cytosine and Guanine pair (C-G)	**Adenine and Uracil pair** (A-U) Cytosine and Guanine pair (C-G)
Function	DNA **replicates** and **stores genetic** information. It is a blueprint for all **genetic information** contained within an organism	RNA **converts** the genetic information contained within DNA to a format used to synthesize proteins and then moves it to **ribosomal protein factories.**

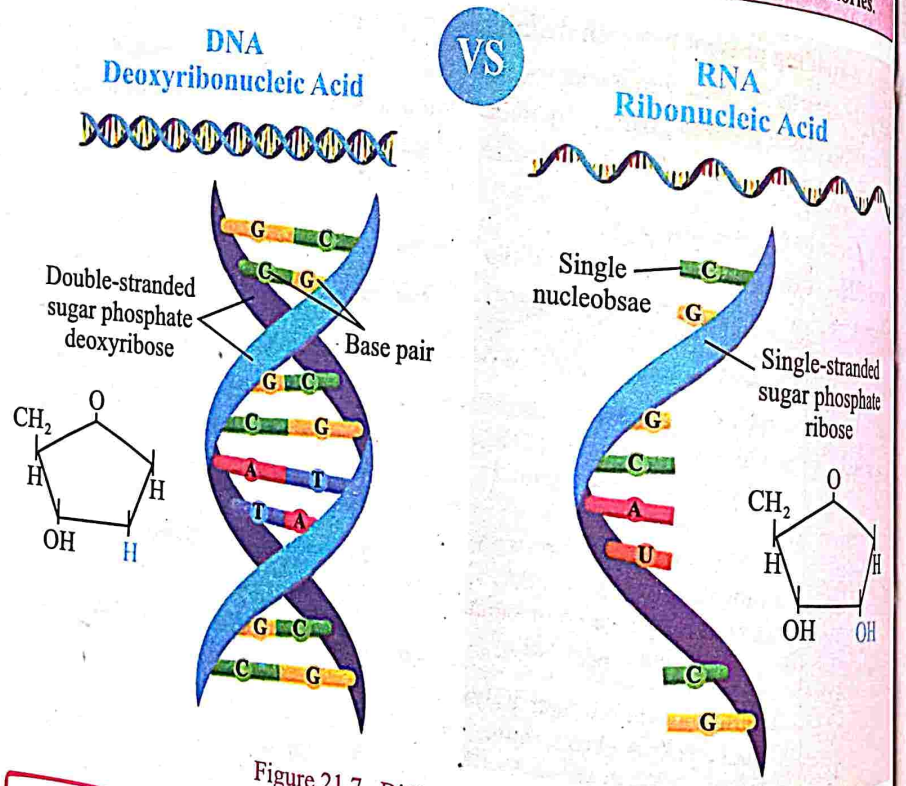


Figure 21.7 Difference of DNA and RNA.

21.5.2 Nucleic Acid Polymers

Nucleic acid polymers are DNA or RNA. The polymer DNA has 'deoxyribo nucleotide' as its monomer. While, polymer RNA has 'ribo nucleotide' as its monomers.

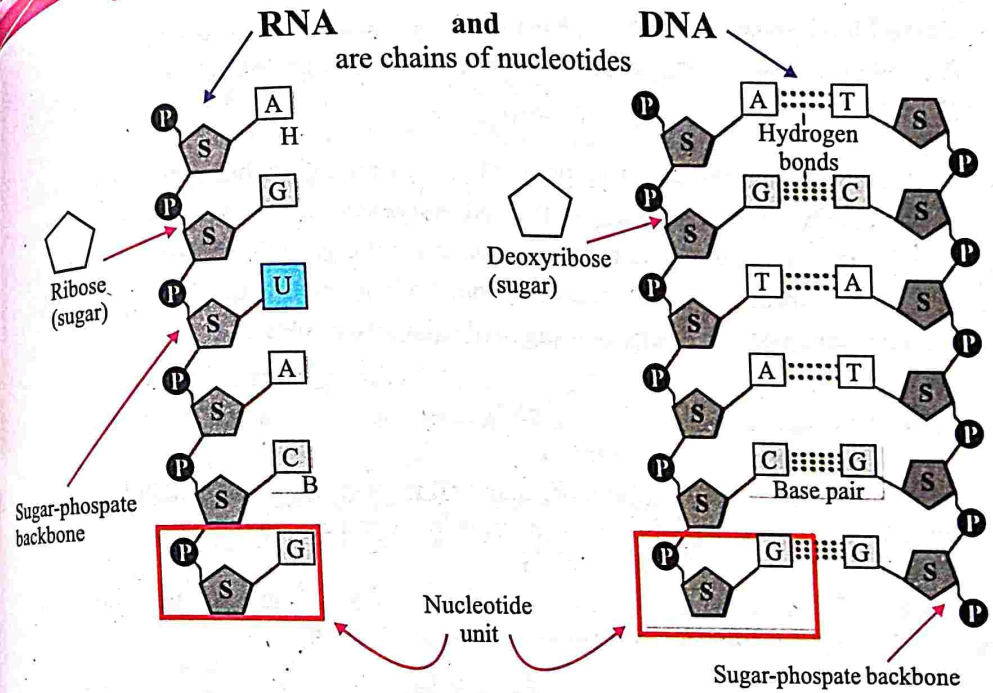


Figure 22.8 Structures of DNA and RNA polymer and nucleotide.

21.5.3 Storage of Genetic Information

DNA is the ultimate carrier of heredity in all the living organisms. Genes are composed of DNA, which contains genetic information in the form of codes. A sequence of three nitrogenous bases on DNA strands contains code for one amino acid synthesis of protein, which occurs inside ribosomes present in the cytoplasm of living cells.

The information stored in the form of genes, which are parts of DNA, are transmitted to the cytoplasm in the form of messenger RNA or mRNA. There is another type of RNA called transfer RNA (tRNA), which reads out the message of mRNA and brings the amino acids to the ribosome in the form of amino acid tRNA complexes. Then these amino acids are incorporated into the peptide chain. This process is called translation.

21.6 Minerals of Biological Significance

Minerals essential for life are the inorganic nutrients, they are needed by living organisms for vital functions but cannot be synthesized by them. The body needs many minerals; these are called essential minerals. These essential minerals include calcium, phosphorus, potassium, sulphur, sodium, chloride, magnesium, iron, zinc, copper, manganese, iodine, selenium, molybdenum, chromium and fluoride. Minerals play important roles in

maintaining blood pressure, fluid and electrolyte balance, and bone health; making new cells; delivering oxygen to cells; and contributing to normal muscle and nerve functioning.

21.6.1 Sources of Important Minerals

Minerals are widely distributed in foods, with specific minerals being found in certain foods. Minerals are naturally present in the soil and water (river water). Plants take up minerals from the soil. Animal get their minerals in drinking water and eating plants as a food. We receive these inorganic minerals from both animals and plants in our diet. Sometimes drinking water also supply appreciable quantity of minerals.

Types of minerals

Minerals can be classified according to the body needs.

1. **Macrominerals (Major Minerals)**

   Macrominerals are those we need more than 100 mg per day. These include calcium, magnesium, phosphorus, potassium, sodium, sulphur and chloride.

2. **Microminerals (Trace Minerals)**

   Microminerals are those we need less than 100mg per day. These include chromium, copper, iodine, iron, fluoride, manganese, zinc and selenium.

21.6.2 Biological Significance of Iron, Calcium, Phosphorous and Zinc

i. Iron

Iron is one of the important element because it is part of haemoglobin, a carrier of oxygen in the body.

Daily Requirement

An adult requires about 14mg of iron in daily diet. Growing children and woman requires greater concentrations of iron. The daily synthesis of haemoglobin requires about 27mg of iron but the same quantity of iron is liberated by the breakdown of body haemoglobin, therefore, only a small quantity of iron is required unless there is a loss of blood from the body.

Sources of Iron

Good sources of iron are apple, apricots, figs, wheat, green leafy vegetables, beans (including baked beans), broccoli, peas, cabbage, spinach, eggs, red meat, poultry, liver, kidney, wholegrain cereals etc.

Deficiency of Iron

Deficiency of iron produces diseases called anaemia. This may be due to the lack of iron in the diet or a deficient in its absorption by the body.

Excess of Iron

Excess of iron is stored in the form of hemosiderin in the skin, pancreas, liver, spleen etc. This leads to bronze appearance of the skin, diabetes mellitus and cirrhosis. This state is called hemochromatosis or hemosiderosis.

ii. Calcium

Calcium is essential for strong bones and teeth. It also plays an active role in the body's immune system. Calcium is present in largest quantity in the body, because of being the main constituent of bones and teeth. Calcium accounts for 1 to 2 percent of adult human body weight, 99% of which is present in bones in the form of hydroxyapatite crystals. Small amount of calcium is also present in blood.

Daily Requirement

The recommended daily amount of calcium for an adult is around 800mg.

Calcium is required for the regulation of a large number of cellular activities, muscle and nerve functions, hormonal action, blood coagulation and cell motility.

Sources of Calcium

- High amount of calcium is found in dairy products such as milk and yogurt. On average 250mL of cows' milk or 150g yogurt contains 300mg of calcium.
- The main sources of calcium are milk and milk products, egg yolk, legumes, green leafy vegetables, almonds, hazelnuts, broccoli, okra, spinach, apricot, figs, pulses, sesame seeds.

Deficiency of Calcium

- Decrease of calcium in the diet is contributing to a factor known as osteoporosis, a condition that causes brittle bones in adults.
- Decrease of calcium level in plasma leads to a condition known as hypocalcemia.

Excess of Calcium

Increase in the concentration of calcium in plasma leads to a condition known as hyperparathyroidism.

iii. Phosphorus

Phosphorous is also the major constituent of bones and teeth. It is present in all the body cells in association with proteins, lipids and carbohydrates in the form of phosphoproteins, phospholipids and similar compounds.

The major function of phosphorus is in the formation of the bone component hydroxyapatite with calcium. 80% of the phosphorous in the body is present as calcium salts in the skeleton and, therefore, is essential for healthy bone and tooth structure. It has unique role in the storage and transformation of energy in the body.

Daily Requirement

An adult requires about 800mg per day of phosphorous.

Sources of Phosphorous

Most foods contain phosphorus. It is present in association with calcium in its sources.

- Foods that are rich in protein are also excellent sources of phosphorus. They include meat and poultry, fish, eggs, milk and other dairy products.
- Some non-protein food sources also contain phosphorus. For example, whole grains, potatoes, garlic, dry fruits and carbonated drinks .

Deficiency of Phosphorous

- Deficiency of phosphorous in the body leads to various problems such as, joint or bone pain, loss of appetite, irritability or anxiety, fatigue and poor bone development in children.
- Deficiency of phosphorous in children leads to renal rickets.

Excess of Phosphorous

Too much phosphate can be toxic.

- An excess can cause diarrhoea, as well as a hardening of organs and soft tissues.
- An increase in the plasma phosphate level due to decrease in its excretion leads to kidney dysfunction.

iv. Zinc

Zinc is antioxidant and important for the maintenance of a healthy immune system. Zinc is an important element for the normal growth, reproduction and longevity of animals.

Daily requirement

- The recommended daily amount of zinc for an adult is 10 mg.
- It is a constituent of several types of enzymes such as alkaline phosphatase, carbonic anhydrase etc.
- It also forms a complex with insulin and helps in its storage and release according to the needs of the body. It is also required for maintaining the plasma concentration of vitamin A.

Sources of Zinc

The different sources of zinc include meat, liver, eggs, fish, milk and cereals.

Deficiency of Zinc

Deficiency of zinc results in slow healing of wounds, impairment of acuity of taste and skin problems.

Excess of Zinc

Excess intake of zinc can cause gastrointestinal discomfort and when chronic, may disrupt the balance of other chemicals in the body, including copper and iron.

Key Points

- Biochemistry studies the chemistry of life.
- Carbohydrates, proteins, lipids, nucleic acid are called biomolecules.
- Carbohydrates are polyhydroxy aldehydes (aldoses) and polyhydroxy ketones (ketoses) or compounds formed by linking aldoses and ketoses.
- Glucose is known as "aldose" and has an aldehyde structure at carbon atom number one.
- Fructose is known as "ketose" and has a keto structure at carbon atom number two.
- The main classes of carbohydrates are monosaccharide, oligosaccharide and polysaccharide.
- Monosaccharides and oligosaccharides are collectively called sugars. Polysaccharides are non-sugars.
- When two monosaccharide units combine together by an oxygen atom with elimination of one water molecule, this type of linkage is called glycosidic linkage or glycosidic bond.
- Amino acids are monomers of proteins and they are connected by peptide bond in proteins.
- The structure of protein is considered at four levels, primary, secondary, tertiary and quaternary.
- Lipids are heterogeneous class of organic compounds. They may be saponifiable or non-saponifiable.
- The oils, which contain more unsaturation, are hydrogenated to produce solid ghee.
- DNA and RNA are two examples of nucleic acid and their function is replication and protein synthesis.
- The building blocks of nucleic acids are nucleotides.
- The three components of a deoxyribonucleotide are a five-carbon sugar called deoxyribose, a phosphate group and a nitrogenous base.
- Enzymes are protein in nature, which can speed up a chemical reaction.
- Enzyme inhibition may be irreversible or reversible.
- Most animal enzyme's optimum temperature is body temperature (37°C).
- A pH, at which an enzyme shows the maximum activity, is called optimum pH.

- The substances, which decrease the activity of an enzyme, known as enzyme inhibitor and this process is known as enzyme inhibition.
- Lipids have three major subclasses: simple lipids, compound lipids and derived lipids.
- The monomer that makes up a nucleic acid is called a nucleotide.
- Nucleotide has three parts: an inorganic phosphate group, a five-carbon monosaccharide sugar, and a nitrogen containing structure known as a nitrogenous base.
- DNA contains genetic information in the form of codes.
- Minerals essential for life are the inorganic nutrients.
- Iron is a part of haemoglobin, a carrier of oxygen in the body.
- Calcium is the main constituent of bones and teeth.
- Living organism cannot synthesized the essential minerals.

Exercise

Q I. Choose the correct one from the given options.

1. The optimum pH of pepsin is around
   a. 3.0 b. 3.5 c. 2.0 d. 2.5
2. The most abundant carbohydrate found in nature is
   a. cellulose b. glycogen c. pectin d. chitin
3. The glycosidic linkage is present between the molecules of
   a. glucose b. glycine
   c. fatty acid d. none of these
4. Steroid belong to family of
   a. carbohydrates b. proteins
   c. lipids d. enzymes
5. Protein present in haemoglobin has the structure known as
   a. primary structure. b. secondary structure.
   c. tertiary structure. d. quaternary structure.
6. Which carbohydrate does not conform the general formula $C_n(H_2O)_n$?
   a. Deoxyribose b. Ribose c. Glucose d. Fructose
7. Ethanol is produced from starch by the process of
   a. hydrolysis b. hydrogenation
   c. decomposition d. fermentation

8. Human are unable to digest
   a. glucose b. cellulose
   c. starch d. denatured protein
9. Which one of the following term is not related to term aldohexose?
   a. Aldehyde b. Ketone c. Six d. Sugar
10. Slow healing of wounds is due the deficiency of
    a. Ca b. P c. Zn d. Fe
11. RNA is primarily seen in
    a. nucleus b. cytoplasm
    c. cell wall d. cell membrane
12. In which of following disaccharides both the basic structural units are the same?
    a. Maltose b. Lactose c. Sucrose d. All of these
13. In competitive inhibition, the inhibitor
    a. competes with enzyme. b. irreversibly binds with the enzyme.
    c. binds with substrate. d. competes with substrate.
14. In DNA, adenine forms a complementary pair with which other nitrogen base?
    a. Uracil b. Cytosine c. Thymine d. Guanine
15. Proteins are polymers of
    a. glucose b. disulphide bridges
    c. amino acids d. peptide bonds

Q2. Write short answers of the following questions.

i. Why vegetable oil is sensitive to rancidity?
ii. Why melting point of saturated fatty acid is higher than unsaturated fatty acid?
iii. Make at least one point difference in each compound in the given pairs. Differentiate between the following compounds.
   a. Glucose and fructose b. Sucrose and maltose
   c. Cellulose and starch
iv. Write down at least three important functions of nucleic acids.
v. Write down the products of hydrolysis of sucrose with reaction.
vi. What happens when protein is denatured?
vii. What are chemical components that compose the nucleic acid?
viii. Describe briefly the primary, secondary, tertiary and quaternary structure of protein.
ix. Differentiate between non-competitive and uncompetitive inhibitions.
x. Write down the physical and chemical properties of lipids.

Q3. Write detail answers of the following questions.

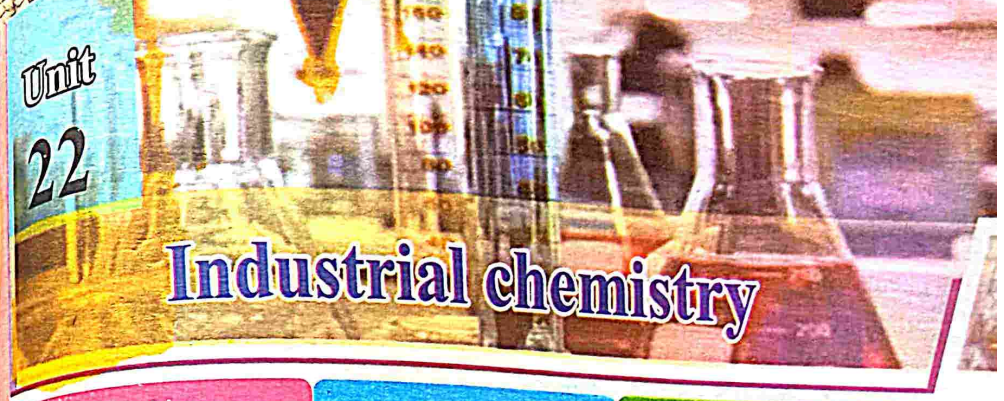
1. (a). What are carbohydrates? Explain the basis of classification of carbohydrate.
   (b). How would you evaluate the role of various carbohydrates in health and diseases?
2. (a). Describe various classes of protein along with examples.
   (b). Enlist the properties of protein.

3. (a). What are lipids? Explain the basis of classification of lipids.
   (b). Discuss in detail the structure and nutritional and biological importance of lipids.
4. (a). Explain the role of inhibitors of enzyme catalysed reactions.
   (b). Identify the different structural components of DNA and RNA.
5. (a). Assess the role of enzyme as biocatalyst and relate this role to various functions such as digestion of food.
   (b). Evaluate the factors that affect enzyme activity such as effect of temperature and pH.
6. (a). Why zinc is important for human being?
   (b). State the medical problems that may relate to calcium and phosphorus.

Project

Take 250cm^3 milk in a beaker. Gently warm the milk (not boil), add small amount of lemon juice or vinegar (acetic acid) in it and observe it. Report your observation by answering the following questions.

1. What happen to the state of the milk?
2. Is there any chemical change occur in it?
3. Does the change in pH affect the milk?
4. Name the product obtained during the process.
5. Is this product has any nutritional importance?
6. Name some products in which it is used.



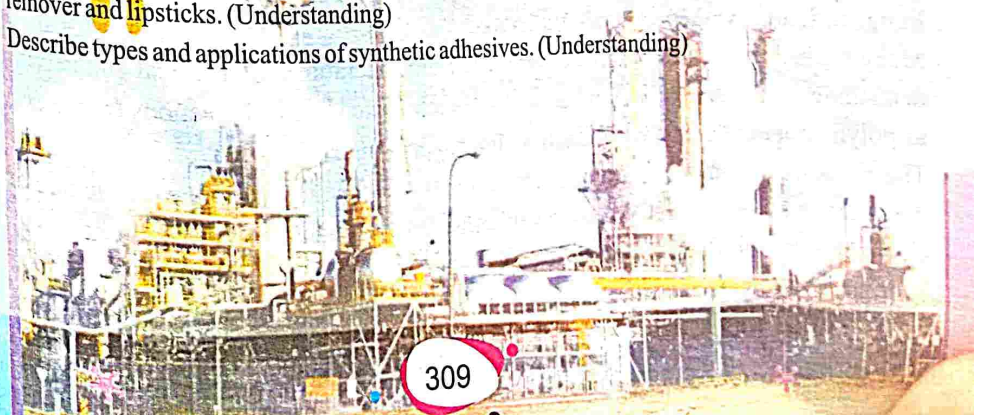
Unit 22

Industrial chemistry

Teaching	Assessment	Weightage %
8	1	6

After studying this unit, students will be able to:

- Discuss the importance of the chemical industries in the economy of Pakistan. (Analysing)
- 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. (Analysing)
- Identify the important fractions. (Analysing)
- 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)



Introduction

Industrial chemistry is concerned with chemical processing of raw materials to useable and profitable products. Certain of these marketable products will be consumer goods and enter directly into economic life of the country. Others will be intermediates or chemical for the manufacture of consumer's items. The consumer purchases these products because they have the required properties, which make them suitable for particular applications.

Chemical processing may be defined as the industrial processing of the chemical raw materials leading to the products of enhanced industrial value. Generally, this involves the chemical conversion and production by complicated chemical reactions. In all these chemical changes, physical operation are intimately involved such as heat transfer and temperature control etc.

In grade–X, you have studied the basic chemical operations and some chemical industries. In this unit, you will learn the importance of chemical industry, petroleum and petrochemicals, PVC and adhesives in detail.

22.1 Introduction to the Chemical Process Industry and Raw Materials used

The Chemical Process Industry

The chemical process industry includes those manufacturing facilities whose products result from,

(a) Chemical reactions between organic materials or inorganic materials or both;

(b) Extraction, separation, or purification of a natural product, with or without the aid of chemical reactions;

(c) The preparation of specifically formulated mixtures of materials, either natural or synthetic. Examples of products from the chemical process industry are plastics, resins, dyes, pharmaceuticals, paints, soaps, detergents, petrochemicals, perfumes, inorganics, and synthetic organic materials.

Many of these processes involve a number of unit operations of chemical engineering depending on the size of a plant, as well as such basic chemical reactions (processes) as polymerization, oxidation, reduction, hydrogenation etc.

The processes of the chemical industry convert the chemical structure and nature of materials in order to develop products of value to other industries or in daily life.

Chemicals are produced from these raw materials (principally minerals, metals and hydrocarbons) in a series of processing steps. Further treatment, such as mixing and blending, is often required to convert them into end-products (e.g., paints, adhesives, medicines and cosmetics).

Thus, the chemical industry covers a much wider field than we usually called "chemicals" since it also includes such products as artificial fibres, resins, soaps, paints, photographic films etc.

Chemicals fall into two main classes: organic and inorganic.

Organic chemicals have a basic structure of carbon atoms, combined with hydrogen and other elements. Oil and gas are today the source of 90% of world organic chemical production.

Inorganic chemicals are derived chiefly from mineral sources. Examples are sulphur, and chlorine etc.

The products of the chemical industry can be broadly divided into three groups, which correspond to the principal steps in manufacture:

Base chemicals (organic and inorganic) are normally manufactured on a large scale and are normally converted to other chemicals;

Intermediates are derived from base chemicals. Most intermediates require further processing in the chemical industry, but some, such as solvents, are used as they are;

Further chemical processing makes finished chemical products. Some of these are consumed as such for example, drugs, cosmetics and soaps. Others are further processed such as fibres, plastics, dyes and pigments.

The main sectors of the chemical industry are as follows:

- Basic inorganics: acids, alkalies and salts, mainly used elsewhere in industry and industrial gases, such as oxygen, nitrogen and acetylene.
- Basic organics: feedstocks for plastics, resins, synthetic rubbers and synthetic fibres; solvents and detergent raw materials; dyestuffs and pigments.
- Fertilizers and pesticides (including herbicides, fungicides and insecticides).
- Plastics, resins, synthetic rubbers, cellulosic and synthetic fibres.
- Pharmaceuticals (drugs and medicines).
- Paints, varnishes and lacquers.
- Soaps, detergents, cleaning preparations, perfumes, cosmetics and other toiletries.
- Miscellaneous chemicals such as polishes, explosives, adhesives, inks, photographic film and chemicals.

Raw materials in Pakistan for various Chemical and Petrochemical Industries

- Raw materials for chemical industries are oil, natural gas, metals, minerals, coal and salt etc.

- Raw materials for petrochemical industries are methane, ethane, propane and butanes. These are obtained primarily from natural gas processing plants. Gas oil and naphtha are obtained from petroleum refineries. Benzene, toluene and xylene are also primarily obtained from petroleum refineries.
- Methane, benzene, toluene and xylene are used directly as feedstocks for producing petrochemicals.

Economy of Pakistan

Chemical Industry refers to the industry, which is involved in the business of making different products from raw materials through chemical reactions. Chemical sector plays a fundamental role in economic development of any nation. It converts the essential raw materials into more than seventy thousand variety products for industry as well as the goods of consumers that people depend upon their daily lives.

Pakistan trades in chemicals with other countries to earn foreign exchange in the field of chemical industry such as a fertilizer, plastics, rubber, medicine, cement, dyes and pigments soaps and detergents.

Chemical industries are very important for the economy of any country.

- Chemical industries supply the farmers the pesticides and fertilizers, which are essential for crop growing. Chemical industries contribute to agriculture and food self-sufficiency of every country.
- In our everyday life, we use many industrial products and most of them are related to chemical industry in some way or the other. Chemical industry produces the synthetic fibres and dyes, which are used in textile industry.
- It supplies the synthetic sweeteners and synthetic flavours, which are used by food manufacturing companies.
- Chemical industry indirectly helps the pharmaceutical industry and health care industry by providing the essential chemical components.

In short, chemical industry contributes indirectly to almost every sector of economy.

22.2 Safety Considerations in Process Industries

The following safety consideration in the process industry must be kept in view before launching an industrial activity.

- To keep away the factory itself from corroding away, proper material of construction should be selected by the designing chemical engineers.
- To avoid harmful impurities in raw materials, to follow the course of chemical reactions and to secure the requisite yield and purity of products, careful process control by periodic analysis is required as well as modern instrumentation and automatic control.
- To transmit goods in a clean and economical manner from the manufacturer to the customer, suitable containers must be used.
- To ensure the safety of workers and the plant all procedures, must be carried on in a non-hazardous manner.
- To guarantee progress to continue profits and to replace obsolescent processes and equipments much attention and money must be spent upon containing research and development.
- To prevent the contamination of water and air, factories must avoid discharge of toxic material into the air and water of their localities.
- To label the chemicals that can help in identifying the more hazardous chemicals.

22.3 Dyes

Dyes are substances that are used to impart colour to various substrates, which adds value to products for their cost, including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials.

- A dye is a coloured compound, normally used in solution, which is capable of being fixed to a fabric.
- The dye has a colour due to the presence of chromophore and its fixed property is due to the acidic or basic groups such as $-OH$, $-SO_3H$, $-NH_2$, $-NR_2$, etc.
- The polar auxochrome makes the dye water-soluble and binds the dye to the fabric by interaction with the oppositely charged groups of fabric structure.

Properties of Dye

Dyes must possess the following four properties:

1. Colour
2. Solubility in water
3. Ability to be absorbed and retained by fibre (substantivity) or to be chemically combined with it (reactivity).
4. Ability to withstand washing, dry cleaning and exposure to light.

Chemical Composition of a Dye

A dye consists of a colour producing structure called the 'chromogen' and a part

Tidbit

Pigment and Dye

Pigments and dyes are called colorants. The ways in which colorants are used determines whether they are pigments or dyes.

Pigments are water and oil-insoluble, natural and synthetic products that impart colour to materials such as paper and plastics. Whereas,

Dyes, are water-soluble colorants, although some are converted into insoluble lake pigments by co-precipitating onto an inorganic base. Artists' colours are pigments that are spread on a surface suspended in a suitable medium, such as oil.

to regulate the solubility and dying properties called the 'auxochrome'. The chromogen is an aromatic body containing a colour-giving group, commonly called the 'chromosphore'. **Chromophore** is that part of the molecule which when exposed to visible light will absorb and reflect a certain colour. Some common chromophores are given in the **Table 22.1**.

Table 22.1 Some Common Chromophore Groups

S. No	Chormophore	Structure
1.	Nitroso group	$-NO$ (or $=N-OH$)
2.	Nitro group	$-NO_2$ (or $-NOOH$)
3.	Azo group	$-N=N-$
4.	Ethylene group	$-C=C-$
5.	Carbonyl group	$\begin{matrix}O\\\|\\-C-\end{matrix}$
6.	Carbon nitrogen group	$\begin{matrix}N\\\|\\-C\equiv N-C-\end{matrix}$
7.	Carbon Sulphur Groups	$-CH_2-SH$

Auxochromes are commonly called as 'colour helpers' or 'colour intensifiers'. The auxochrome, the part of the dye which causes it to adhere to the material which it colours (usually textiles) are $-NH_2$, $-OH$, $-NR_2$, $-COOH$ and $-SO_3H$ of these groups. $-NH_2$ and $-NR_2$ cause solubility in acids while $-OH$, $-COOH$ and $-SO_3H$ cause solubility in basic solutions.

Classification of Dye: There are several ways for classification of dyes. One of the prominent ways of classification is the classification based on the source of materials. It is further divided into two main types:

i. Natural Dyes ii. Synthetic Dyes

i. Natural Dye

Natural dyes are dyes or colorants derived from plants, invertebrates, or minerals. The majority of natural dyes are vegetable dyes from plant sources e.g. roots, berries, bark, leaves and wood. Other organic sources include fungi and lichens.

ii. Synthetic Dyes

Almost all the colours in use today are synthetic dyes. Synthetic dyes are used everywhere in everything from clothes to paper, from food to wood. This is because they are cheaper to produce, brighter, more colour-fast and easy to apply to fabric. For example, acid dyes, azo dyes, basic dyes, mordant dyes, etc.

Tidbit

Differences between dyes and pigments

Dyes and pigments are substances that impart colour to a material. The major difference between dyes and pigments is the particle size. Dyes are much finer than pigments. **Dyes,** also known as colourants in which the colouring matter is dissolved in liquid, are absorbed into the material to which they are applied. **Pigments,** on the other hand, consist of extremely fine particles of ground colouring matter suspended in liquid which forms a paint like film that actually bonds to the surface.

22.4 Pesticides

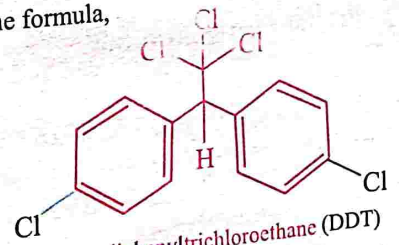
Pesticides are chemicals that are used to destroy, repel or otherwise lower pest infestations to protect crops from damage or simply we can say a substance that kills a pest (insect, weed, bacteria, nematode etc.), for example lead arsenate, $Pb_3(AsO_4)_2$, nicotine sulphate etc.

Characteristics of an Ideal Pesticide

An ideal pesticide should possess the following characteristics:

- It should be effective only against the specific target organism.
- It should be non-toxic to other living organisms.
- It should be non-persistent.
- It should be biodegradable.
- It should break down in nature into harmless products and cause no damage to environment.
- It should be inexpensive and easily available.

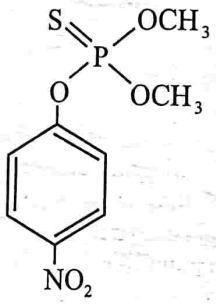
Pesticides are the chemical substances that are used to control the pests such as DDT, heptachlor etc. DDT has the formula,



dichlorodiphenyltrichloroethane (DDT)

DDT acts directly on insects. It is a very stable chemical, it's half-life is estimated to be 10 – 15 years. DDT is insoluble in water, therefore, it accumulates in animals and in particular in their fatty tissues. Therefore, the environmentalists banned the use of DDT in the world.

Nowadays, parathion is used instead of DDT.



Parathion

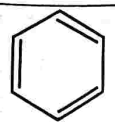
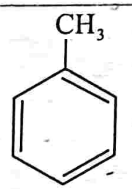
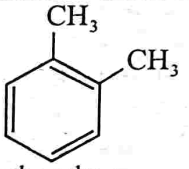
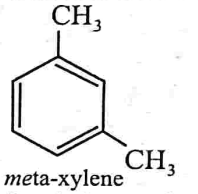
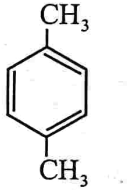
This compound breaks down fairly readily to products that appear to cause no biological damage. So, it has no long term damages but carefully handling is necessary. In short, the ideal pesticide is clearly not yet available.

22.5 Petrochemicals

Petroleum is a complex mixture of hydrocarbons formed by the decomposition of fossil remains. It exists as a gas (natural gas), liquid (crude oil) or as solids (oil shales) and is found deep underground or below seabed. About 10% of the petroleum is used to prepare a range of chemicals called petrochemicals. Petrochemicals as a group of chemicals produced directly or indirectly from the hydrocarbons of petroleum or natural gas. Examples of petrochemicals are plastics, rubbers, fibres, paints, solvents, and detergents.

Since every area of human activity makes use of petrochemicals or the materials made from them, our life without petrochemicals would be very different and less comfortable. The different petrochemicals are compiled in **Table 22.2**.

Table 22.2 Some Important Petrochemicals

S. No.	Feedstock	Primary petrochemicals	Formulae
1.	Natural gas	Ethene	$CH_2 = CH_2$
		Propene	$CH_3 - CH = CH_2$
		Ethyne	$CH \equiv CH$
2.	Naphtha	Ethene	$CH_2 = CH_2$
		Propene	$CH_3 - CH = CH_2$
		Butadiene	$CH_2 = CH - CH = CH_2$
3.	Reformed Naphtha	Benzene	
		Toluene	
		o – xylene	 *ortho*-xylene (1,2-dimethylbenzene)
		m – xylene	 *meta*-xylene (1,3-dimethylbenzene)
		p – xylene	 *para*-xylene (1,4-dimethylbenzene)

The Basic Building Block Processes

The basic building block petrochemical processes are divided into two. These processes are cracking and reforming process.

i. Cracking Process

Cracking is a process in which molecules of raw material are dissociated into smaller ones. There are two types of cracking process, thermal steam cracking and catalytic cracking.

a. Thermal Steam Cracking

Steam cracking is the breaking of raw material such as ethane and propane yielding important petrochemical products, such as ethene and propene. Methane and hydrogen are also some of the major by-products.

b. Catalytic Cracking

Breaking of larger, stable molecules requires catalysis. Refinery products such as gas oil and fuel oil is passed through catalytic cracker to obtain gasoline and kerosene oil as major products and by-product, propene.

ii. Reforming Process

The process of reforming of hydrocarbon is carried out by using heat, pressure and/or catalyst in order to obtain desired products. In this process, heavy naphtha is converted into aromatics such as benzene, toluene and xylene as well as hydrogen as by-product. Reforming process breaks down the molecules of low octane rating naphtha into high octane gasoline blending components (reformates). It is one of the most important processes in oil refineries.

Fractional Distillation of Petroleum

Petroleum in the unrefined form is called crude oil. It is a naturally occurring thick viscous brown or greenish black liquid, which is obtained from earth crust. The crude oil consists of different substances. These substances in crude oil are miscible. Therefore, they do not separate out into layers. Thus, fractional distillation, which is carried out in the fractionating towers, is used in refining petroleum. Fractional distillation is the process of heating up a mixture containing different substances with different boiling points and after condensation drawing the different fractions off. Each fraction is not a pure compound but is a mixture of different hydrocarbons with similar boiling points. Crude oil is first treated to remove the sulphur or sulphur compounds that may be present. The cleaned hydrocarbon material is then distilled and fractions with various boiling ranges are collected. (Figure 22.1).

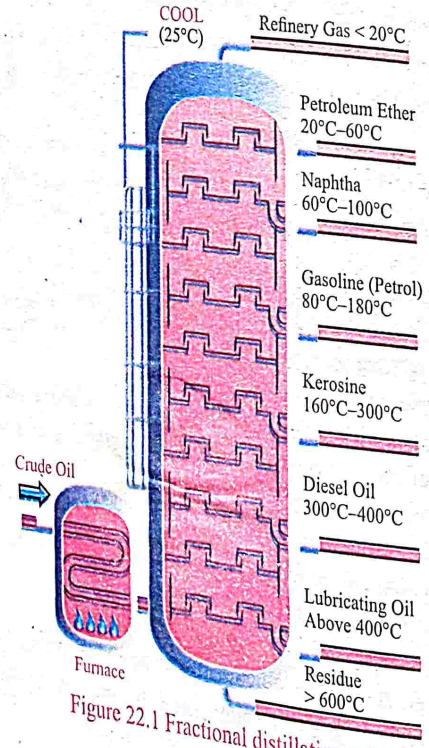


Figure 22.1 Fractional distillation column.



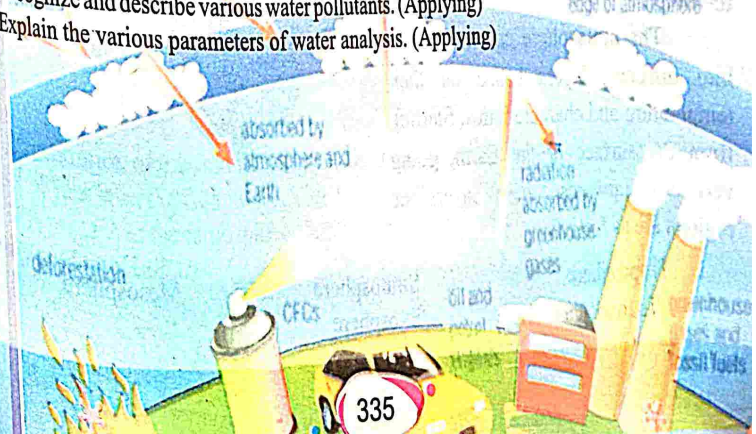
Unit 23

Environmental Chemistry

Teaching	Assessment	Weightage %
9	1	6

After studying this unit, students will be able to:

- Recognize various chemical reactions, occurring in the atmosphere. (Understanding)
- Recognize that the release of CO_x, SO_x, NO_x, 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-up 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)



Introduction

In this unit, we will turn our attention to environmental issues, associated with Earth's atmosphere. Air and water pollutions are the major problems in most of the World's cities. The atmosphere, a part of the environment, acts as repository for emissions from combustion and from many other human activities. The air can be cleansed by natural mechanisms but these can be overwhelmed by the amount of pollutants being produced. Human activities are increasing the atmosphere concentration of carbon dioxide and other greenhouse gases. In addition, the stratospheric ozone shield, which protects us from the ultraviolet rays, is threatened by the emission of ozone-destroying chemicals.

Likewise, water quality is as important issue. Although most of the water supply is returned to the stream flow after use, its quality is necessarily degraded. The quality of surface and ground water is of concern due to two distinct points of view, that is, human health and welfare and the health of aquatic ecosystems.

Atmosphere is the envelop of gases, surrounding the Earth's surface. It plays a key role to sustain life on Earth and save it from the hazardous environment of the outer space. The atmosphere absorbs most of the cosmic rays from the outer space and harmful radiation such as U.V. through ozone (O_3) layer. In addition, the atmosphere maintains the heat balance of the earth through absorption of energy from the sun and re-emitted.

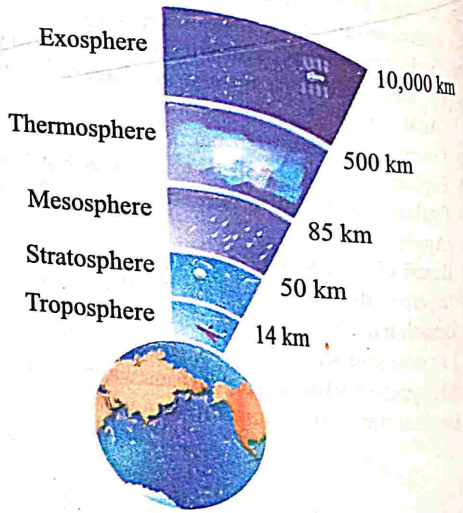


Fig: 23.1: Layers of atmosphere.

The atmosphere can be divided into different layers based on their temperature and characteristics. Starting from the surface of the Earth, going vertically upwards, these layers or regions are as follows:

i. Troposphere
ii. Stratosphere
iii. Mesosphere
iv. Thermosphere
v. Exosphere

Table: 23.1 The Regions of Atmosphere

S. No.	Zone/Sphere	Altitude (in km)	Temperature range (^{0}C)	Important Chemical Species
1.	Troposphere	0–14	15 to –56	N_2, O_2, CO_2, H_2O, Ar
2.	Stratosphere	10–50	–56 to –2	O_3 (ozone), N_2, O_2
3.	Mesosphere	50–85	–2 to –92	NO^+, O_2^+
4.	Thermosphere	85–500	–92 to 1200	O_2^+, NO^+, O, O^+
5.	Exosphere	500–10,000	Above 1500	H, He, N_2, O_2, CO_2

23.1 Chemistry of the Troposphere

Troposphere is the part we live in. It extends from the surface of the Earth up to 11 kilo meters. It constitutes about 10% of the atmosphere's height but contains 80% of its mass. The temperature in this sphere ranges from 15 °C to –56 °C **(Table 23.1)**. Nearly all atmosphere water vapours is found in the troposphere so it is the layer where most of the Earth's weather phenomena occurs. The important chemicals that exist in this sphere are N_2, O_2, CO_2 and $H_2O_{(Vapours)}$. It is also a region of much turbulence, due to the global energy flow that results from the imbalances of heating and cooling rates between the equator and the poles. The temperature in troposphere falls off uniformly with increase in altitude. Thus, the air it contains is mixed rapidly by convection.

23.1.1 Chemical Reactions in the Atmosphere

Apart from the chemicals mentioned earlier, in some areas (particularly the industries zones), the atmosphere (troposphere) may also contain SO_x and NO_x gases which are responsible for the acid rain. For example, NO_2 or SO_2 react with oxygen in the presence of rain water and produce acids.

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

$$SO_2 + H_2O + \frac{1}{2}O_2 \longrightarrow H_2SO_4$$

The concentration of the acid thus formed can be quite higher, which ultimately reduces the pH of rain water substantially. This results in producing, what is called, acid rain. The CO_2 present in the atmosphere (0.036%) also reacts with the rain water, making it slightly acidic (pH≅5.6).

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Carbonic : ...

The lightening in air and also in combustion engine of motor vehicles may also cause reaction between stable molecules of N_2 and O_2, producing NO.

$$N_2 + O_2 \longrightarrow 2NO$$

Incomplete combustion of the carbonaceous compounds (hydrocarbons, coal etc.) results in the formation of carbon monoxide; e.g.

$$\text{Hydrocarbon} + O_2 \xrightarrow{\text{(limited } O_2\text{)}} CO + H_2O + \text{Energy}$$

CO, like other pollutants such as SO_x, NO_x etc, pollute the fresh air. At concentration higher than 750 ppm, CO may cause loss of consciousness or death.

Some chemical reactions, occurring in the atmosphere, are involved in the formation of industrial and photochemical smog.

23.1.2 CO_x, NO_x, VOCs, SO_x, O_3 as Air Pollutants

The term air pollutant generally refers to substances that on local and regional scales directly harm animals, plants and people and their artifacts. Clean and dry air contains 78.09% nitrogen, 20.94% oxygen by volume. The remaining 0.97% is comprised of gaseous mixture of CO_2, He, Ar, Kr, Xe and nitrous oxide (N_2O). A wide range of chemicals can pollute the air. They include carbon monoxide, sulphure dioxide, toxic organics, nitrogen oxides and volatile organic compound (VOCs).

Carbon Monoxide

Carbon monoxide mainly results from the incomplete combustion of carbonaceous compounds. It is colourless, odourless, toxic gas. It is termed as asphyxiating (suffocating) pollution because it can displace (O_2) bound to hemoglobin (Hb).

$$\underset{\substack{\text{Oxyhaemoglobin}\\\text{complex}}}{HbO_2} + CO \longrightarrow \underset{\substack{\text{Carboxyhaemoglobin}\\\text{complex}}}{COHb} + O_2$$

The iron (Fe) binding sites in hemoglobin bind carbon monoxide (CO) 320 times more tightly than O_2. The main source of CO to the environment are the vehicle emission, combustion of fuel such as natural gas, coal, or wood. When the concentration of the CO inhaled, reaches 100 ppm, particularly in the closed spaces like tunnels, parking garages etc., it may result in headache and shortness of breath. The severity of the effects depends on the duration of the exposure and level of exertion. At a concentration higher than 750 ppm, loss of consciousness or death may occur.

Sulphur Dioxide (SO_2)

The main sources of sulphur dioxide (SO_2) emission to contaminate air, are combustion of coal and the smelting of metals (metallurgy) particularly copper. The sulphur content

of the refined petroleum is generally quite low but the sulphur content of coal is quite high. The sulphur in coal is converted to SO_2 during combustion. SO_2 itself is a lung irritant and is harmful to people suffering from respiratory diseases. However, the most damaging health effects in urban atmosphere are not by SO_2 but by the sulphuric acid aerosol formed from its oxidation. Sulphuric acid not only irritates the fine vessels of the pulmonary region, causing them to swell and block the passages, but is also the major contributor to the acid rain.

Nitrogen oxides NO_x and Volatile Organic Compounds (VOCs)

NO_x is a common designation of nitrogen oxides, NO and NO_2. Nitrogen oxide, particularly nitrogen dioxide, is emitted from high temperature combustion processes and is also produced during thunderstorm by natural electric discharge. NO_x can cause serious health damage to humans, including respiratory diseases. NO_x is also responsible for smog formation and typical brown clouds or haze that covers large cities which results in poor air quality. NO_x emission also contributes to acid rain and formation of ground level ozone that can damage animal and plant life. NO_x reacts with volatile organic compounds in the presence of sunlight and forms ground level ozone which can be transported with wind over longer distance. High level NO_x concentration can have negative effects on vegetation and causes forest damage.

Volatile organic compounds (VOCs) include methane, CH_4. It is an efficient greenhouse gas which contributes to enhance global warming. The major sources of VOCs emission are the industrial processes, solvent utilization and vehicular emission.

Ozone (O_3) as Pollutant

Some VOCs are responsible for ozone production in lower atmosphere at the ground level. Ozone at ground level is quite harmful, producing cracks in rubber, destroying plants, and causing respiratory distress and eye irritation in humans. These effects set in at quite low concentrations, around 100 ppb.

The naturally produced ozone in upper troposphere is useful for life as it prevents us from harmful ultraviolet (U.V.) radiations, however, some man-made chemicals like chlorofluorocarbons (CFCs) are harmful to this protective ozone layer. The CFCs are emitted from air conditioners, refrigerators, aerosols sprays, etc. On release into air, CFCs rise to stratosphere where, they come in contact with other gases and through chemical reaction damage the ozone layer. This allows harmful U.V. rays to reach the Earth's surface and have adverse effects.

23.1.3 Automobile, Pollutants and the Catalytic Converter

The major pollutants, present in the exhaust gases emitted by automobiles, are carbon monoxide (CO), nitric oxide (NO) and the hydrocarbons (HCs). These gases disturb the composition of the clean air and thus cause air pollution. When present in considerable amount, they cause damage to human health and plants life.

Tidbit

A 3-way catalytic converter is a device used in the exhaust system of the engine of the vehicles to reduce emission of hydrocarbon (HCs), carbon monoxide (CO) and nitric oxide (NO)

One way of reducing emissions is to remove the pollutants from the exhaust gases. In automobiles, this is accomplished with a three-way catalytic converter.

It converts harmful gases in the engine exhaust to relatively harmless gases; nitrogen (N_2), carbon dioxide (CO_2) and water.

Working: A 3-way catalytic converter makes use of two catalysts to convert harmful gases to harmless gases in two chambers in succession. They are:

i. **Reduction catalyst:** Reducing chamber is made up of platinum and rhodium. The exhaust gases are first sent over the reduction catalyst. It converts oxides of nitrogen (NO_x) to nitrogen (N_2) and oxygen (O_2). The following reaction take place when the exhaust gases pass over the reduction catalyst.

$$2NO \longrightarrow N_2 + O_2$$

$$2NO_2 \longrightarrow N_2 + 2O_2$$

Thus, the reduction catalyst removes oxides of nitrogen and convert to oxygen and nitrogen, the harmless gases.

ii. **Oxidation catalyst:** The oxidation chamber is made up of platinum and palladium. The exhaust gases that are free of oxide of nitrogen (NO_X) are then sent over the oxidation catalyst which converts carbon monoxide (CO) and hydrocarbon (HC) in the gases into carbon dioxide (CO_2) and water. The following reaction takes place when the exhaust gases pass over the oxidation catalyst

$$2CO + O_2 \xrightarrow{Pt/Pd} 2CO_2$$

$$HC + O_2 \xrightarrow{Pt/Pd} CO_2 + H_2O$$

(HC are hydrocarbon, may be methane, ethane, or other hydrocarbons)

The gases that finally come out of the catalytic chamber are N_2, CO_2, and H_2O.

3-way catalytic converters are so named because they are capable of eliminating three pollutants-NO_x, CO and HC.

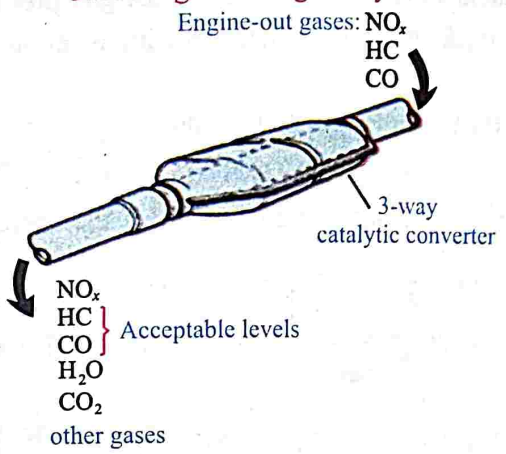


Fig: 23.1: The three-way catalytic remover for HCs, NO and CO, from automobile exhaust.

23.1.4 Industrial Smog

The word smog is combination of smoke and fog. It produces a yellow-brown colour in the atmosphere near the ground level which results in poor visibility in the area. There are two major types of smog: 'industrial smog' and 'photochemical smog'. Industrial smog forms in the areas with high water vapours. It is caused by the burning of coal, vehicular emission and industrial fumes. Smog contains carbon particles like smoke, sulphur dioxide (SO_2) and other compounds. Burning of fossil fuel produces SO_2 which is produced due to the presence of sulphur in the fossil fuel. SO_2 gradually reacts further to form sulphur trioxide SO_3. Then in the presence of water or water vapours, droplets of H_2SO_4 are formed as a result of this reaction.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

H_2SO_4 is corrosive to materials as building stones and the human respiratory tract. Another coal-burning power station pollutant is soot, (primarily particles of carbon) which gives smoke its persistent dark colour. The soot also plays its role in the industrial smog.

23.1.5 Photochemical Smog

Photochemical smog forms when pollutants from automobile and industrial exhausts, such as nitrogen oxides and organic compounds react together in the presence of sunlight and produce ozone gas. (Which is one of the primary components of the photochemical smog).

Nitrogen dioxide + hydrocarbon + sunlight = ozone

It is characterized by an accumulation of brown, hazy fumes over the horizon. Ozone in the stratosphere protects Earth from harmful UV radiations, while ozone in the ground level

is hazardous to human health and being a greenhouse gas, produces global warming. Various reactions that take place in connection with the photochemical smog formation are as under.

$$NO + VOC \text{ (volatile organic compound)} \longrightarrow NO_2$$

$$NO_2 + UV \longrightarrow NO + O$$

The oxygen atoms (O) react immediately with the surrounding O_2 molecules to produce ozone.

$$O + O_2 \longrightarrow O_3$$

$$NO_2 + VOC \longrightarrow PAN \text{ etc. (PAN = Peroxyacetyle nitrate)}$$

Net Reaction

$$NO + VOC + O_2 + UV \longrightarrow O_3 + PAN$$

Peroxyacetyl nitrate (PAN) is relatively common smog constituent, it irritates the lungs and eyes.

23.1.6 Global Warming and Climate Change

Several climatic changes are attributed to the large emissions of pollutants into the atmosphere. Generally, the global climate changes are studied from two aspects.

i. Global warming caused by the greenhouse effect.
ii. Destruction of the ozone layer in the stratosphere. The later will be discussed in detail in "the chemistry of stratosphere"

Global warming

Global warming is the term used to described a gradual increase in the average temperature of the Earth's atmosphere and its oceans, a change that is believed to be permanent in the Earth's climate.

The Earth maintains its long-term average temperature as a result of a balance between the heat received from the sun and the heat emitted to space by the Earth. The Earth receives mostly visible radiations from the sun and gets heated. The Earth emits most of its heat in the form of infrared (IR) radiation **(Figure 23.2)**. This heat is absorbed by some of the gases present in the atmosphere and redirect it back to the Earth as heat. These gases trap the heat into the atmosphere which results in increase in the Earth's temperature and is called "the greenhouse effect". These gases are called the greenhouse gases because they behave like glass cover of the green house which is responsible for maintaining the temperature of the greenhouse used to cultivate vegetation in cold climate regions.

The main greenhouse gases are CO_2, CH_4, SO_2, N_2O, O_3 and some other gases emitted from variety of industrial processes.

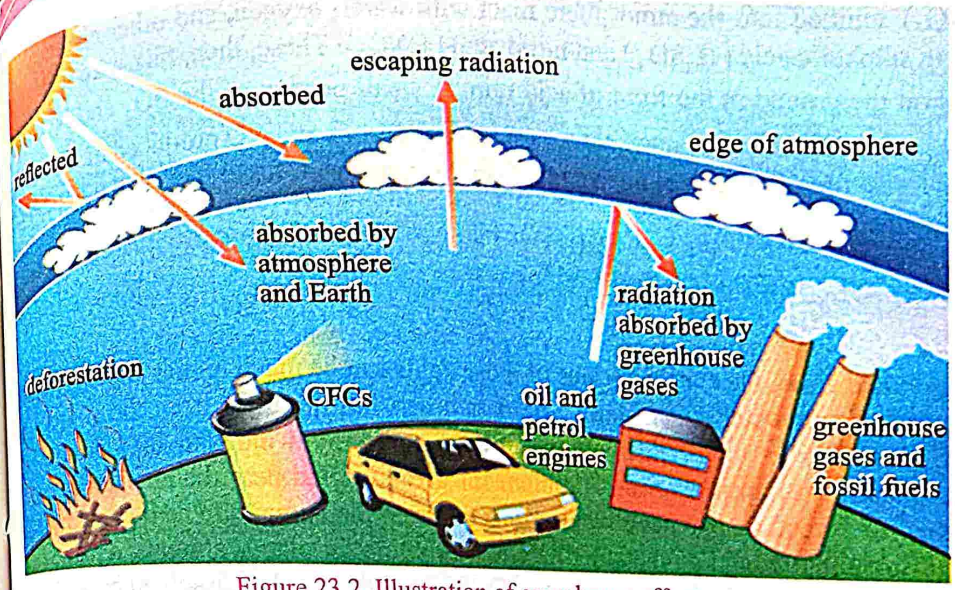


Figure 23.2 Illustration of greenhouse effect.

The major gas contributing 50% to greenhouse effect is CO_2. Other gases (CH_2, CFCs, SO_2 and NO_x) together contribute the rest of 50%.

Human activities are increasing the atmospheric concentration of CO_2 and other greenhouse gases, thereby altering the way the sun's heat is distributed on the Earth's surface and in the atmosphere. In addition, the stratospheric ozone shield, which protects us from the sun's UV radiations, is threatened by the emission of ozone-destroying chemicals. The Earth's average temperature is being increased (global warming) which ultimately changes our climates. The most serious outcome would be rise in sea level, floods and pattern of rain fall.

23.1.7 Acid Rain

The concept of acid rain is also associated with polluted air. Acid rain, also called acid precipitation or acid deposition, precipitation possessing a pH of about 5.6 or below primarily produced from the emission of sulfur dioxide (SO_2) and nitrogen (NO_x; the combination of NO and NO_2) from human activities. Rain water is generally, slightly acidic (pH = 5.6) due to the dissolved CO_2 which is a common constituent (0.036%) of the Earth's atmosphere making carbonic acid.

$$H_2O + CO_2 \longrightarrow \underset{\text{Carbonic acid}}{H_2CO_3}$$

Therefore, any precipitation (rain, dew and snow) having a pH of less than 5.6, would be classified as acid rain. Apart from the acidifying effect of CO_2, there are other pollutants which are also responsible of acid rain. Sulphur dioxide and nitrogen oxide

(NO_x), emitted into the atmosphere react with water, oxygen, and other chemicals to form sulphuric acid (H_2SO_4) and nitric acid (HNO_3). These, then, mix with water and fall on the ground in the form of acid rain. A small portion of the SO_2 and NO_x that cause acid rain is from natural sources such as volcanos and NO produced in lightening and forest fires, but most of them come from the burning of fossil fuels and other human activities.

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

$$SO_2 + H_2O + \frac{1}{2}O_2 \longrightarrow H_2SO_4$$

In polluted areas, the concentrations of these acids can be much higher and can reduce the pH of rain water substantially. Acid rain can fall quite far from the sources of pollution, due to long-range atmospheric transport by wind and air currents. In particular, acid rain is a serious problem for areas located near the coal-fired power plants. Acid rain, on one hand, is a serious threat to the human life as it contaminates the drinking water and on the other hand is a problem for plants, animals, aquatic life, and building material. Heavy metals e.g. Cu, Hg and Pb are also dissolved by acid rain producing various toxic effects.

Acidic streams and lakes or rivers affect the aquatic life. High acidity may result in killing of fish, reduces their growth and causes reproductive failure. Hatching of fish eggs is prevented due to change in pH of water. Moreover, green algae and many forms of beneficial bacteria, which are essential to aquatic life are also killed as a result of acidity in water. Plant growth is seriously inhibited due to acid rain. In addition, the acid rain also corrodes buildings, monuments, statues, and metals. For example, H_2SO_4 destroys the $CaCO_3$ of the building material according to the following reaction.

$$CaCO_{3(s)} + H_2SO_{4(aq)} \longrightarrow CaSO_{4(ppt)} + CO_2 + H_2O$$

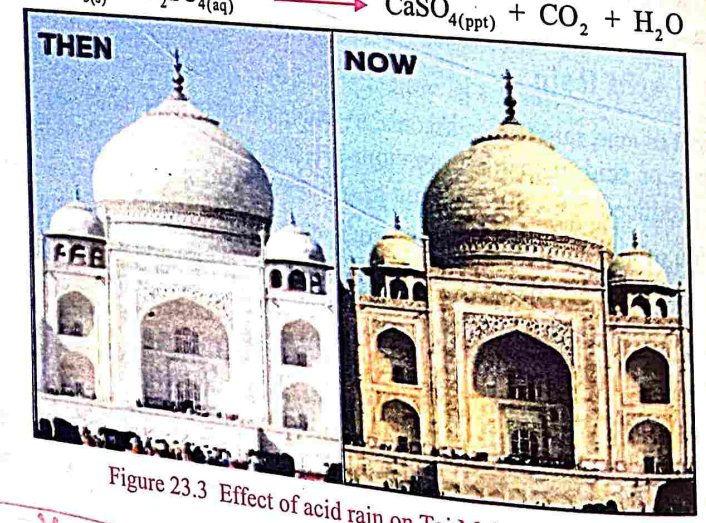


Figure 23.3 Effect of acid rain on Taj Mahal (India).

23.2 Chemistry of the Stratosphere

As mentioned earlier in this unit (Table 23.1) stratosphere is the part of atmosphere which extends from 11–50 km above the Earth's surface. The temperature of the stratosphere ranges from –56°C to –2°C. The important chemical species that exists in this sphere is ozone (O_3), which acts as a protective shield (layer) for the survival of life on the Earth from the harmful effects of sun's UV radiations. The temperature of this sphere increases with increasing altitude.

Production and Destruction of Ozone

The production of ozone in the stratosphere results from the breaking of the chemical bond of oxygen molecule (O_2) by high energy solar radiations (UV radiations). This process, called photo dissociation, results in the release of single oxygen atoms.

$$O_2 + h\upsilon \xrightarrow{\lambda < 242\ nm} 2O$$

The oxygen atoms produced in the reaction, then combine with oxygen molecules to form ozone.

$$O + O_2 \longrightarrow O_3$$

Conditions most suitable for ozone formation are found at intermediate altitude (between 25 and 30 km where both oxygen molecules and free oxygen atoms are present.)

Ozone layer in the stratosphere absorbs UV radiations from the sun and does not allow them to reach the Earth's surface thus it protects us from the harmful effects of these radiations.

Ozone is also destroyed by solar radiation. When O_3 absorbs a solar UV photons it dissociates into O_2 and O.

$$O_3 + h\upsilon \longrightarrow O_2 + O$$

Also, when O_3 encounters a free oxygen atom (O), the two can combine to form two O_2 molecules.

$$O_3 + O \longrightarrow 2O_2$$

The concentration of O_3 depends on the relative rates of the formation and destruction reactions.

Depletion of Ozone layer

Ozone depletion is the gradual thinning of Earth's ozone layer in the upper atmosphere due to the release of chemical compounds containing chlorine or bromine from industries and other human activities. Ozone depletion is a major environmental

problem because it increases the amount of U.V.radiations that reach Earth's surface which create human health problems.

The global decrease in stratospheric ozone is correlated with rising level of chlorine and bromine in the stratosphere from the manufacture and release of chlorofluorocarbons (CFCs) and other halocarbons. Halocarbons are produced by industries for a variety of uses, such as refrigerants (used in refrigerators, air-conditioners, chillers etc.) propellants for aerosol, blowing agent for making plastic foams, firefighting agents and solvents for dry-cleaning and degreasing.

CFCs are very stable molecules, they rise into the stratosphere where they are eventually broken down by UV rays from sun. This causes release of free halogen atom or free radical ($X^{\bullet}$). The free halogen atom, $X^{\bullet}$, reacts with oxygen which leads to chemical process of destroying ozone molecules.

$$X^{\bullet} + O_3 \longrightarrow XO + O_2$$

$$XO + O \longrightarrow X^{\bullet} + O_2$$

Overall reaction is $O_3 + O \longrightarrow 2O_2$

Society, Technology And Science

- The effect of radiation pollution can include increase risk of developing cancer. Such as lung cancer, skin cancer and thyroid cancer etc. and skin burns, genetic changes (mutation), change in physical characteristics in animals and human.
- The water is purified commonly by distillation, sand filtration, charcoal filtration, reverse osmosis and also by ultraviolet light.
- CFCs play a major role in ozone depletion. However, apart from this the CFCs are also greenhouse gases; more effective than CO_2.
- Smog is a kind of air pollution. Classic smog results from large amounts of coal burning in an area caused by a mixture of smoke and sulfur dioxide. Modern smog does not usually come from coal but from vehicular and industrial emissions that are acted on in the atmosphere by ultraviolet light from the sun to form secondary pollutants that also combine with the primary emissions to form photochemical smog.

23.3 Water Pollution and Water Treatment

The quality of water is very important because of its role in human health and benefits of aquatic ecosystem. *Water pollution is any change in the physical chemical or biological properties of water that will have harmful effects on humans, environment and ecosystem.* Water pollution is the contamination of water bodies (lakes, oceans, seas, rivers, and groundwater) usually caused by the human activities, agricultural, industrial, mining and other activities.

Some of the most commonly occurring water pollutants are:

- Domestic waste
- Industrial effluents.
- Insecticides and pesticides.
- Detergents and fertilizers.

Some of the water pollution is caused by direct sources, such as factories, waste management facilities, refineries etc. that directly release waste and harmful by-products into the nearest water source. Indirect sources include pollutants that enter the water bodies via ground water or soil or via the atmosphere as acid rain. Discharge of sewage from homes and commercial establishments, reduces the dissolved oxygen content, again upsetting the biological balance of surface water. All of these activities make water unfit for drinking and public use. Such water is said to be polluted water which needs treatment before it is made fit for public use.

23.3.1 Types of Water Pollutants

Water that we either use or discard generally contains the following categories of undesirable substances (pollutants).

1. Suspended Solids and Sediments

Two sub-categories of the undissolved solid material present in water can be recognized. One consists of particles large enough to be removed by running the water through a filtering apparatus. The second, consists of particles so small that they cannot be removed by such treatments. Those in the second category are called colloids, which are too small to be seen, even with a microscope. They can, however, be detected, because they give water a turbid or cloudy appearance. They are most easily detected by passing a beam of light through the water and observing the scattering of light they produce like a beam of light passing through smoky or foggy air.

2. Dissolved Solids

The dissolved solid material, present in water, may either be organic or inorganic. The dissolved organic compounds, acting as impurities, enter into water as a result of the growth and the death of aquatic plants, such as algae. Others are contributed by sewage from domestic sewage systems and by industrial wastes. The combined total amount of all the organic and inorganic substances found in water are represented by a term, "total dissolved solids" (TDS). The dissolved inorganic materials present in water are mostly salts. The common cations of the inorganic salts are calcium, iron, zinc, magnesium, potassium and sodium etc. and the common anions are carbonates, chlorides, fluorides, nitrates, bicarbonates, phosphates and sulphates etc. Some of these are minerals and

nutrients that are beneficial to the human body, but if their concentrations are greater than about 500 ppm, they make water unfit for drinking and such water is considered to be polluted. Hardness of water is due to salts of calcium and magnesium.

Source of Water Pollution

Some of the important sources of water pollutions are:

i. Domestic effluents and sewage
ii. Industrial effluents
iii. Agricultural effluents
iv. Radioactive waste and mining
v. Thermal pollution
vi. Oil pollution.

Some of these are discussed below.

i. Domestic effluents and sewage.

Domestic water contains mainly soaps and detergents. In urban areas, municipal sewage is discharged into the nearby canals, thus polluting the canal and also deteriorating the ground water. Municipal sewage includes wastewater from houses, commercial buildings and institutions. The important pollutants present are soap and detergent remains, bio-degradable organic matter, coliforms bacteria and pathogens which cause a bad and foul smell to fresh water (eutrophication). Moreover, the turbidity of water due to the presence of suspended particles may affect the aquatic life by screening off the sunlight.

ii. Industrial sewage.

Industries are the major contributors of water pollution. Industries such as sugar mills, pulp and paper mills, textile, oil refineries, tanneries, etc. generate a large quantity of wastewater having pollutants like non-degradable organic substances etc. which is discharged into natural water-ways either without treatment or after partial treatment. Other pollutants from industrial facilities include asbestos, lead, mercury, arsenic, cadmium, nitrates, phosphates, sulphate and oil etc. Arsenic in drinking water is a slow poison. It decolorizes the skin which leads to cancer. Mercury causes numbness of limbs and blurring of vision, lead exposure produces anemia.

iii. Agricultural sources

Pollutants discharged into water due to agricultural activities include, soil and silt removed by erosion, agricultural pollutants run-off, synthetic fertilizers, herbicides and pesticides, insecticides and plants residues. Drainage from poultry farms creates an extremely high potential for water pollution.

iv. Mining and radioactive source

Ore-washings disposed into water may be transferred to natural water bodies to pollute them. Mining operation also produces soluble toxic materials. Acid drainage from different mines and arsenic residues from gold mines are some of

the sources of environmental pollution. Radioactive waste from mining and refining of uranium and thorium may produce serious threats to human health if proper care is not taken.

Thermal Pollution

Heavy industries, such as power plants, paper, nuclear etc. use water as coolant. These industries take water from the nearby natural water bodies and discharge hot water back into the natural sources after use. When this hot water mixes with the natural water bodies, their temperature rises and as a result the level of dissolved oxygen in water is decreased. This affects the ecosystem and influences the biological activity and growth of organism that live in natural water bodies and cause difficulty in their survival. The high-temperature water, when mixed with cold water, increases the solubility of many pollutants (organic and inorganic, salts, ions) causing the water to be more easily polluted, thus affecting the quality of water and making it unfit for drinking and public use.

Parameters of Water Analysis

Water quality parameters include chemical, physical, and biological properties and can be tested or monitored based on the desired or recommended parameters values. The parameters that are frequently used for water quality monitoring include colour, odour, turbidity, conductivity, TSS, TDS, BOD, COD, pH and DO. These parameters are used to decide whether the water is fit for drinking or not. These are briefly described as follows:

Odour: Odour in the drinking water may be defined as the sensation that is due to the presence of substances that have an appreciable vapour pressure and that stimulate the human sensory organs in the nasal and sinus cavities. Odour in the water may be due to the chemicals which are produced during the biological activities on the pollutants present in the water.

Colour: Colour is due to the presence of natural organic matter or other solid particles.

Turbidity: It is related to the presence of fine suspended particles of inorganic or organic nature in water. The recommended turbidity value is not more than 10 ppm.

Taste: It is often due to dissolved organic impurities, such as phenol, chlorophenol, and sewage compounds. Algae can produce taste and odour problems.

Temperature: It affects a number of water quality parameters such as dissolved oxygen and it is also responsible for solubility of some un-desired compounds and salts due to increased temperature.

Conductivity: It is a measure of water capacity to pass an electric current showing the presence of dissolved ions in water.

Total suspended Solids (TSS): It gives the amount of filterable solid in water sample.

Total Dissolved Solids (TDS): It shows the presence of non-filterable material in water sample that pass through the filtering apparatus.

pH: It shows the intensity of acidity or alkalinity of water. The recommended pH range is slightly alkaline (pH = 7.0 – 8.5).

BOD: Biological Oxygen Demand, represents amount of oxygen required by living organism to survive and for oxidation of biodegradable organic matter present in water under aerobic condition. It is an indirect measurement of quantity of bio-degradable organic matter in water.

Chemical Oxygen Demand (COD): It is amount of oxygen needed for oxidation of toxic organic matter present in water by strong chemical oxidizing agents such as $K_2Cr_2O_7$.

Dissolved Oxygen (DO): Dissolved oxygen provides a source of oxygen for aquatic aerobic (oxygen requiring) organism like fish, aerobic bacteria.

Total Organic Carbon (TOC): Water purity is critical for a number of industries such as pharmaceutical and semiconductor manufacturing etc. The presence of bacteria and other organic compounds in water can create significant challenges like negative impact on product quality and profitability. The total organic carbon (TOC) analysis is the standard test for quality and purity of water. It simply measures the carbon found in any organic compound in water , it is not able to indicate the type of organic molecule present.

23.3.2 Wastewater Treatment

The wastewater is full of contaminants such as chemicals, bacteria, and other pollutants. The wastewater treatment is a process used to remove contaminants from wastewater or sewage and convert it into an effluent that can be returned to water cycle with minimum impact on the environment. The following treatment process takes place in wastewater treatment plant.

Stage–I: Screening: Screening or filtering removes large floating solid objects like broken bottles, plastic objects, shopping bags, cloth pieces, stones etc. that may block or damage the equipment.

Stage–II: Primary Treatment: It involves the treatment of solid organic matter from the wastewater by putting the wastewater into large settlement tanks. The finer, colloidal particles that make water turbid, cannot be removed by simple filtration. So, a flocculating agent that is a substance which forms large gelatinous particles, is added. The common flocculating agent is aluminum sulphate, $Al_2(SO_4)_3$, often referred to as

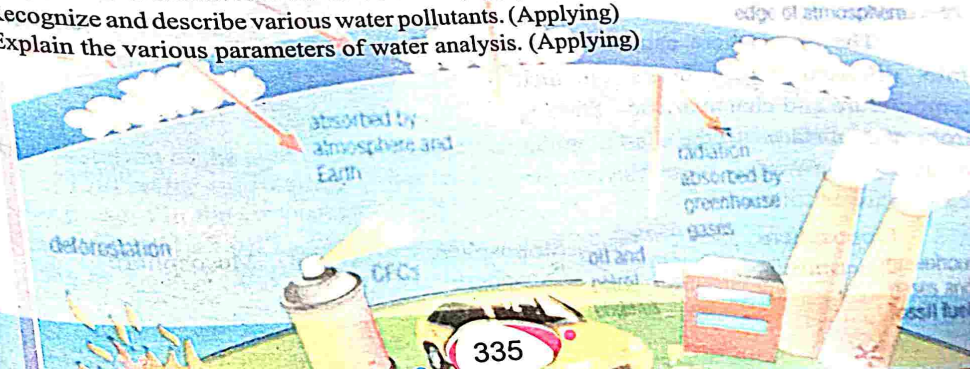
Unit 23

Environmental Chemistry

Teaching	Assessment	Weightage %
9	1	6

After studying this unit, students will be able to:

- Recognize various chemical reactions, occurring in the atmosphere. (Understanding)
- Recognize that the release of CO_x, SO_x, NO_x, 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-up 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)



Total suspended Solids (TSS): It gives the amount of filterable solid in water sample.

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$$Al_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Al(OH)_{3(ppt)} + 3CaSO_4$$

This precipitate traps both inorganic solid particles and bacteria in the large curd like particles. These particles are then easily removed by filtration through a sand-bed or charcoal. Some heavy particles sink to the bottom, which is called 'sludge'. It is further treated separately.

Stage–III: Secondary Treatment: The water at this stage is put into large rectangular tanks, where air is pumped into the water so that the bacteria break down the tiny bits of sludge.

Stage IV: Tertiary or Final Treatment: Next, the almost treated wastewater is passed through a settlement tank. Here, more sludge is formed at the bottom of the tank from the settlement of the bacterial action. Again, the sludge is scraped and collected for treatment. The water at this stage is almost free from harmful substances and chemicals. The water is filtered to remove additional particles.

After that the filtered water is discharged into river. If water is treated for drinking purposes then it is passed through a process of disinfection using chlorination, ozone treatment and ultraviolet light etc. to eliminate disease causing organisms. Chlorination is the widely used method to disinfect water.

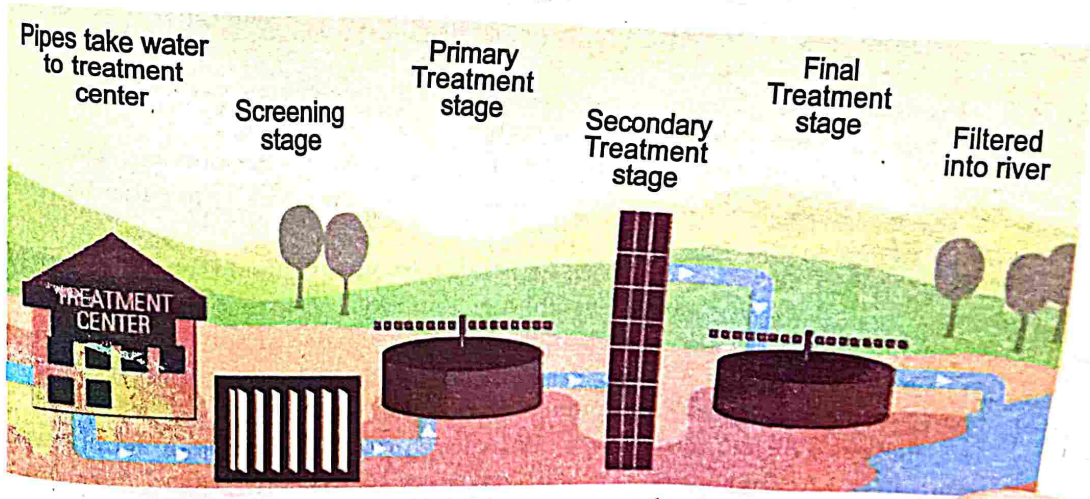


Figure 23.4 Water treatment plant.

Air is sometimes blown through the water to improve its odour and taste. A fluoride compound is added in some plants, to help fight tooth decay. The result of thorough "water treatment" operation is a water, that is as good as new.

23.4 Green Chemistry

The green chemistry or sustainable chemistry is defined as: *"the invention, design and application of chemical products and processes to reduce or eliminate the use or generation of substances hazardous to humans, animals, plants, and the environment."*

The aim of the green chemistry is to reduce chemical related impact on human health and virtually eliminate contaminants of the environment through dedicated sustainable prevention programs. Green chemistry searches for alternative, environmental friendly reaction media and at the same time strive to increase reaction rate and lower reaction temperature.

Green Chemistry is based on 12 principles proposed by Anastas and Warner. These 12 principles of green chemistry are considered fundamentals to contribute to sustainable development. The principles comprise of instructions to implement new chemical products, new synthesis and new processes as given below:

1. **Atom Economy:** Design syntheses so that the final product contains the maximum proportion of the starting material. Waste few or no atoms of the reactant i.e. to maximize the incorporation of all materials, used in the process, into the final product.
2. **Prevent Waste:** Design a process to prevent the generation of waste instead of later on treating and cleaning up the waste.
3. **Design less Hazardous Chemical Syntheses:** Wherever possible design to use and generate substances, that possess little or no toxicity to either humans or to environment.
4. **Designing Safer Chemicals:** Chemical products should be designed to deliver their desired function while minimizing their toxicity.
5. **Use safer Solvents and Reaction Conditions:** Use of solvents, separation agents, and other substances should be avoided whenever possible; if not possible, harmless and less toxic raw material should be used.
6. **Increase Energy Efficiency:** Run chemical reactions at room temperature and pressure whenever possible or use of renewable energy sources (such as solar energy) should be used.

7. **Use Renewable Feedstock:** Use starting material (also known as feedstock) that are renewable (plants-based) rather than depletable. The source of renewable feedstock is often agriculture products or the waste or by-products of other processes.
8. **Avoid Chemical Derivatives:** Avoid using blocking or protecting functional groups or any temporary modification by forming unnecessary derivatives, if possible; as such steps require additional reagents and may generate additional waste. This is because more derivatives involve:
   - additional reagents
   - generate more waste products
   - needs more time.
   - higher cost of production.

   Hence, it requires to reduce derivatives.
9. **Use Catalysts:** Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. Reactions at low temperature and pressure are possible due to use of new/improved catalysts.
10. **Design Chemicals and Products to Degrade after use:** Chemical products have to be designed in such a way that, at the end of their life span, disintegrate into nontoxic degradation products more readily.
11. **Analyze the products in real-time to prevent Pollution:** Advanced analytical methods for quality control analysis have to be developed, which permit the real-time, in-line process monitoring well before hazardous substances are generated.
12. **Minimize the potential for accidents:** Design chemicals and their physical forms (solid, liquid, and gas) to minimize the potential for chemical accidents including explosions, fires, and release to the environment.

Key Points

- Environmental chemistry is the branch of chemistry which deals with the presence of harmful and hazardous chemical and bio-chemicals in nature.
- Pollutant is any substance which contaminate our environment.
- Atmosphere is a big blanket of gases, surrounding the Earth's surface.
- The term acid rain is referred to all precipitation (rain, snow or dew) having pH less than 5.6.
- Smog is the combination of smoke and fog.
- Water is an important natural resource on this planet.
- An important aspect of water quality is the amount of dissolved oxygen in it.
- The term green chemistry is defined as the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances.
- There are two major types of smog: 'industrial smog' and 'photochemical smog'.
- Increased concentration of CO_2 increases the Earth's temperature, by greenhouse effect. This in turn results in climate changes and global warming.

Exercise

I. Choose the correct one from the given options.

1. Which one of the following is not a secondary pollutant?
   a. O_3 b. H_2CO_3 c. H_2SO_4. d. CO_2
2. The coldest region of atmosphere is
   a. troposphere. b. thermosphere.
   c. stratosphere. d. mesosphere.
3. Ozone layer in upper atmosphere is being destroyed by
   a. chlorofluorocarbons. b. SO_2..
   c. smog. d. photochemical oxidant.
4. Drained sewage has BOD.
   a. more than that of water. b. less than that of water.
   c. equal to that of water. d. none of above.
5. Photochemical smog is primarily caused by
   a. CO. b. CO_2. c. O_3. d. NO_2
6. Result of ozone hole is
   a. acid rain. b. global warming.
   c. increased amount of CO_2. d. greater exposure of Earth to U.V.
7. Which one of the following substances is not present in acid rain?
   a. H_2SO_4 b. HNO_3
   c. H_2SO_3 d. CH_3COOH
8. Photochemical oxidant PAN is formed by
   a. the action of oxide of nitrogen on hydrocarbons in presence of sunlight.
   b. action of carbon dioxide on hydrocarbon in presence of sunlight.
   c. action of hydrogen sulphide on hydrocarbon in presence of sunlight.
   d. action of SO_2 and hydrocarbons.
9. Which two main gases are produced when you burn a piece of wood?
   a. Oxygen and nitrogen b. Carbon dioxide and oxygen
   c. Carbon dioxide and steam d. Carbon dioxide and nitrogen
10. The temperature range of troposphere is
    a. 15 to –56. b. 56 to –2.
    c. –2 to –92. d. –92 to 1200.

11. In which of the following layer of atmosphere there is more thickness of the ozone layer?
    a. Troposphere
    b. Stratosphere
    c. Mesosphere
    d. Thermosphere
12. Which of the following is more dangerous for the ozone layer?
    a. CFCs
    b. CO_2
    c. CO
    d. Oxides of nitrogen
13. Which of the following factors help to measure the quality of water?
    a. DO
    b. BOD
    c. COD
    d. All of the above
14. In the purification of water the flocculating agent used is
    a. alum.
    b. nickel sulphate.
    c. copper sulphate.
    d. barium sulphate.
15. The basic principle of green chemistry is/are
    a. to prevent waste creation.
    b. to maximize the atom economy.
    c. to create less hazardous synthetic chemicals.
    d. all of the above.

Q2. Write short answers of the following questions.

i. Why is acid rain considered as a threat to historical monuments?
ii. Define the following:
    a. Contaminants
    b. Pollutant
    c. Acid rain
    d. Biological oxygen demand (BOD)
    e. Smog
iii. What is importance of dissolved oxygen in water?
iv. How we can reduce pollution due to SO_2?
v. Write any four principles of Green Chemistry.
vi. Name four major greenhouse gases.
vii. Out of CFCs and CO_2 which one has higher potential to cause global warming and why?
viii. Why does the rain water normally have pH of about 5.6 and when does it change into acid rain?
ix. Which gases are converted to harmless gases by 3-way catalytic converter?

Q3. Write detail answers of the following questions.

1. (i) Green Chemistry is a new route to the protection of environment'. Comment on it.
   (ii) What is greenhouse effect? How is it causing global warming?
2. (i) What is meant by atmosphere? Explain the various layers of atmosphere.
   (ii) Define air pollution and discuss its effects.
3. (i) What is role of ozone layer in upper atmosphere?
   (ii) What will happen if ozone is no more present in upper atmosphere?
4. What is water pollution? What are the main sources of water pollution?
5. Write note on the following.
   (a) Acid rain
   (b) Smog
   (c) Water treatment
   (d) Chemistry of stratosphere

Project

To build a water filtration apparatus

Take a soft drink plastic bottle, cut it in the middle leaving the lower part a little longer than the upper one. The upper part will be used as funnel and the lower part as receiving part. Put some cotton at the mouth of the bottle as a plug and some sand above the cotton plug. (the sand must be washed and dried beforehand so as to remove any dust or water-soluble substances). Put this funnel in the receiving part and add some muddy water slowly in it. You will see the filtered water as clean and transparent as the fresh water.

Unit

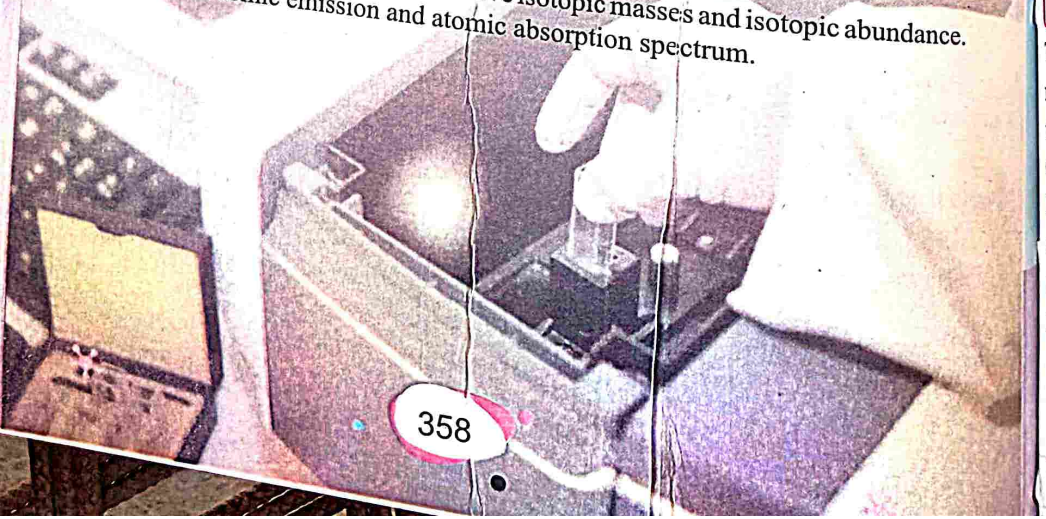
24

Analytical Chemistry

Teaching	Assessment	Weightage %
13	3	11

After studying this unit, students will be able to:

Compare the classical method of analysis with modern methods.
Discuss the procedure of combustion analysis.
Define spectroscopy and discuss its applications in analytical chemistry.
State the regions of electromagnetic spectrum used in IR and U.V-Visible spectroscopy.
Explain the origin of IR absorption of simple molecules.
Determine structures of phenol, toluene, acetone and ethanol from their IR spectrum.
Predict whether a given molecule will absorb in the U.V-Visible region.
Predict the colour of a transition metal complex from its U.V-Vis spectrum.
Outline in simple terms the principles of a proton NMR spectroscopy.
Explain how chemical environment of a proton affects the magnetic field it experiences and hence the absorption of energy at resonance frequency.
Describe standard scales used in proton NMR.
Explain instrumentation and working of Mass Spectrometry (MS).
Outline the use of MS in determination of relative isotopic masses and isotopic abundance.
Define and explain atomic emission and atomic absorption spectrum.



Introduction

Analytical chemistry is a branch of chemistry, which deals with the study of chemical composition of materials; both qualitatively and quantitatively. Qualitative analysis characterizes the identity of a substance, while quantitative analysis examines its mass or concentration. Techniques used in qualitative analysis include chemical tests, spectroscopy, flame tests etc. Quantitative analysis employs gravimetric analysis, volumetric analysis and separation techniques, such as filtration, distillation, precipitation, extraction, centrifugation etc. There is overlap of techniques used between the two branches, especially such samples may require purification in order to characterize them. Spectroscopic techniques are also used for quantitative analysis.

24.1 Classical Methods of Analysis: Combustion analysis and determination of Molecular Formula

Before attempting to deduce the structure of an unknown organic compound by spectroscopic techniques **(Section 24.2)**, we can simplify the problem somewhat by examining the molecular formula of the substance.

The classical procedure for determining the molecular formula of a substance involves; qualitative elemental analysis, quantitative elemental analysis and then molecular mass determination. A qualitative elemental analysis is used to find out what types of atoms are present: C, H, O etc. **(Section 15.7)**. A quantitative elemental analysis such as combustion analysis, determines the relative percentages of each distinct type of atom in the molecule. Both of these techniques are used to establish the empirical formula for the compound. While knowing the molecular mass, a molecular formula can also be calculated.

24.1.1 Combustion Analysis

The elemental composition of organic compounds may be determined by a gravimetric method known as combustion analysis. Combustion analysis is carried out for finding the percentage composition and empirical formula of an organic compounds containing carbon and hydrogen (C_xH_y) or carbon, hydrogen, and oxygen ($C_xH_yO_z$).

In combustion analysis, a known weight of an organic compound is mixed with cupric oxide (CuO) and taken in a platinum boat, which is placed in a furnace heated to about 850°C, in a stream of pure oxygen gas. Organic compound on burning produces carbon dioxide and water vapours which are swept out of the

Tidbit

If other elements such as N, S, Cl etc. are present in the compound, then conventional combustion analysis cannot be used, for elemental analysis.

furnace and trapped in a pair of absorbers. Water is absorbed in a sample of magnesium perchlorate ($Mg(ClO_4)_2$ of known mass, and carbon dioxide is absorbed by aqueous solution of sodium or potassium hydroxide. The increase in masses of both absorbers is the masses of water and carbon dioxide produced respectively, during combustion.

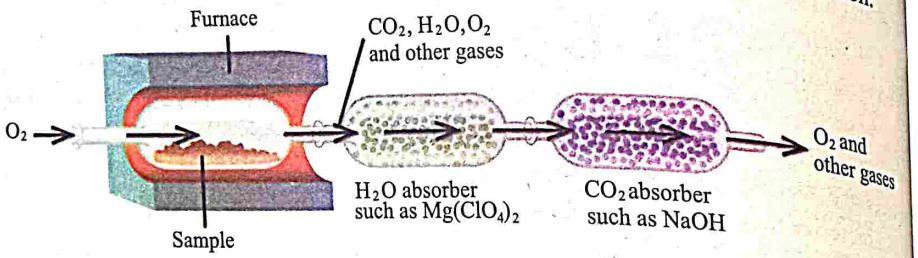


Figure 24.1 Procedure of combustion analysis.

Percentage of C and H in organic compound are calculated by the following formulae.

$$\%C = \frac{\text{mass of } CO_2 \text{ produced}}{\text{mass of organic compound}} \times \frac{12.011}{44.010} \times 100$$

$$\%H = \frac{\text{mass of } H_2O \text{ produced}}{\text{mass of organic compound}} \times \frac{2.0158}{18.0153} \times 100$$

Percentage of oxygen is calculated as;

$$\%O = 100 - (\%C + \%H)$$

Calculation of Empirical Formula

Empirical formula is the formula that gives the simplest whole number ratio of the atoms of elements present in the compound. In order to find the empirical formula of a compound, the following steps should be followed.

- Number of moles of carbon, hydrogen and oxygen is calculated by the following formulae.

$$\text{moles of C} = \frac{\%C}{12.011}$$

$$\text{moles of H} = \frac{\%H}{1.0079}$$

$$\text{moles of O} = \frac{O\%}{15.9994}$$

- The simplest ratio between the numbers of moles is found out by dividing the number of moles of each element by the smallest number of moles.

- If the ratio is not in whole numbers then number of moles of each element is multiplied by a suitable small number to get the whole number ratio.
- Finally the symbol of each element is written and their number of moles are written as subscripts. This gives the empirical formula of a compound.

Calculation of Molecular Formula

Molecular formula shows the actual number of atoms of each kind of element in a compound. Molecular formula is either same to empirical formula or integral multiple of the empirical formula.

$$\text{molecular formula} = n \times \text{empirical formula}$$

where

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

The molecular mass can be obtained from mass spectrometric experiment **(Section 24.2.2.4)** or with the help of colligative properties of solution.

Example 24.1: Trioxane (1,3,5-trioxane) is a cyclic trimer of formaldehyde, a precursor for the production of polyoxymethylene plastics. 17.471 g of trioxane upon complete combustion produces 10.477 g of water and 25.612 g of carbon dioxide. The molecular mass of trioxane determined by mass spectrometry, is 90.079 a.m.u. Calculate the empirical and molecular formulae of trioxane.

Solution:

$$\%C = \frac{\text{mass of } CO_2 \text{ produced}}{\text{mass of organic compound}} \times \frac{12.011}{44.010} \times 100$$

$$\%C = \frac{25.612g}{17.471g} \times \frac{12.011}{44.010} \times 100 = 40.008\%$$

$$\%H = \frac{\text{mass of } H_2O \text{ produced}}{\text{mass of organic compound}} \times \frac{2.0158}{18.0153} \times 100$$

$$\%H = \frac{10.477g}{17.471g} \times \frac{2.0158}{18.0153} \times 100 = 6.71\%$$

$$\%O = 100 - (40.008 + 6.71) = 53.282\%$$

Now find the moles of each element;

$$\text{moles of C} = \frac{40.008}{12.011} = 3.33$$

$$\text{moles of H} = \frac{6.71}{1.0079} = 6.66$$

$$\text{moles of O} = \frac{53.282}{15.9994} = 3.33$$

Now calculate the mole ratio;

C	:	H	:	O
$\frac{3.33}{3.33}$	:	$\frac{6.66}{3.33}$	:	$\frac{3.33}{3.33}$
1	:	2	:	1

Thus empirical formula of trioxane is 'CH_2O' Now find the value of n;

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{90.079\text{amu}}{30.026\text{amu}} = 3$$

Thus, $\text{molecular formula} = n \times \text{empirical formula}$

$$\text{molecular formula of trioxane} = 3 \times (CH_2O) = C_3H_6O_3$$

Practice problem 12.1

- Vanillin, a flavoring agent, is made up of carbon, hydrogen, and oxygen atoms. When a sample of vanillin weighing 2.50 g burns in oxygen, 5.79 g of carbon dioxide and 1.188 g of water are obtained. The molecular mass of vanillin determined from mass spectrometry is 152.15 amu. Calculate the empirical and molecular formulae of vanillin.
- Glucose has C = 39.99%, H = 6.72% and O = 53.2%. Molecular mass of glucose is 180 amu: Calculate its empirical and molecular formulae.

24.2 Modern Methods of Analysis

Structural identification is of prime importance in organic chemistry, as it provides complete information about that substance. The molecular formula of organic compound determined from combustion analysis may not give complete information about structure, as a number of structures (isomers) may be possible for the given formula. When a compound is isolated from a natural source or synthesized, its structure must be completely determined prior to applications.

In many cases, a compound can be identified by chemical means. We find the molecular formula by analyzing the elemental composition and determining the molecular weight. If the compound has been characterized before, we can compare its physical properties

(melting point, boiling point, etc.) with the published values. For example; C_2H_6O is the molecular formula of both ethyl alcohol and dimethyl ether. But ethyl alcohol (C_2H_5OH) at room temperature is liquid and its boiling point is 78°C, while dimethyl ether ($CH_3 - O - CH_3$) is gas at room temperature having a boiling point of –24°C. Chemical tests can suggest the functional groups and narrow the range of possible structures before the physical properties are used to make an identification. For example ethanol reacts with sodium metal liberating hydrogen, while dimethyl ether does not react with it.

Chemical analysis is insufficient for new compounds that have never been synthesized and characterized. They are also impractical with compounds that are difficult to obtain, because a relatively large sample is required to complete the elemental analysis and all the functional group tests. We need analytical techniques that work with tiny samples and that do not destroy the sample. Spectroscopic techniques are modern methods of analysis which often meet these requirements.

24.2.1 Spectroscopy

Spectroscopy is the measurement of the amount of light absorbed (or emitted) by a compound as a function of the wavelength (or frequency) of light. In general, a spectrometer irradiates the sample with light, measures the amount of light transmitted as a function of wavelength (or frequency) and plots the results on a graph, called a spectrum.

Organic compounds absorb energy on interaction with electromagnetic radiations. The electromagnetic radiation (emr) extends from high-energy gamma rays to low-energy radio waves. X–rays and gamma rays (very high energy) are so energetic that they excite electrons, above all the energy levels, causing ionization. Energies in the ultraviolet–visible range excite electrons to higher energy levels within molecules. Infrared energies excite molecular vibrations, and microwave energies excite rotations. Radio-wave frequencies (very low energy) excite the nuclear spin transitions observed in NMR spectroscopy. Unlike chemical tests (classical methods of analysis), most of the spectroscopic and chromatographic techniques are nondestructive, required small amount of sample, less time consuming and provide more accurate and rapid results. These methods are simple and do not involve much chemistry as compared to the classical methods. The regions of electromagnetic spectrum of electromagnetic radiations is given in **Figure 24.2.**

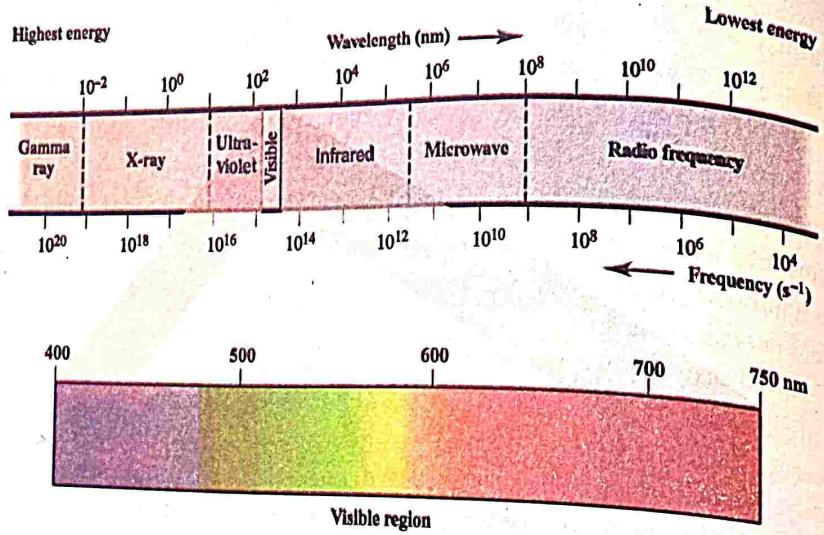


Figure 24.2 The electromagnetic spectrum.

24.2.2 Spectroscopic Methods

This book covers the Ultraviolet-Visible (UV–Vis) Spectroscopy, Infrared (IR) Spectroscopy, Nuclear Magnetic Resonance (NMR) Spectroscopy and Mass Spectrometry (MS) that serve as powerful tools for structure and molecular mass determination. This unit also includes Atomic Emission and Atomic Absorption Spectroscopy, which are used for qualitative and quantitative analysis of elements.

Tidbit

A spectrometer is a device used to detect spectrum of a substance in a range; for example, a range of mass-to-charge values as in mass spectrometry or a range of wavelengths as in absorption spectrometry like infrared spectroscopy etc. A spectrophotometer is a spectrometer that only measures the intensity of electromagnetic radiations absorbed (and transmitted) by a material.

24.2.2.1 Ultraviolet-Visible (UV-Vis) Spectroscopy

Absorption of electromagnetic radiation by a molecule in ultraviolet (10–400 nm) and visible (400–750 nm) region leads to electronic transitions. It is therefore, discussed together as Ultraviolet-Visible spectroscopy. This technique is also called electronic spectroscopy. Normal U.V-Visible spectrometers uses near ultraviolet region of ultraviolet radiation which has wavelength range of 200 nm to 400 nm.

Absorption in Ultraviolet/Visible Radiation and Its Measurement

Absorption of UV-Visible radiations by a molecule is associated with excitation of electron from ground to excited states. The common electronic transition that are associated with the absorption of UV-Vis radiation by organic molecules, are of four types i.e. $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, as shown in **Figure 24.3.**

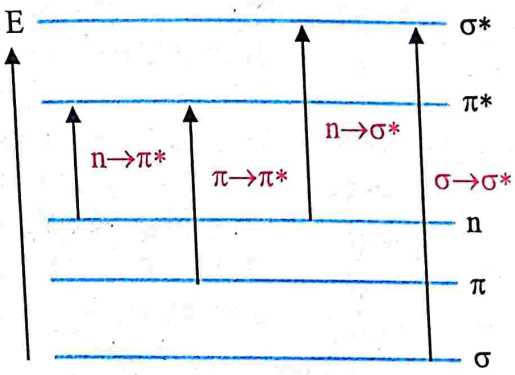


Figure 24.3 Common types of electronic transition in organic molecules.

i. The $\sigma \rightarrow \sigma^*$ transitions occur in a saturated hydrocarbons such as alkanes and cycloalkanes which contain only sigma bonds. $\sigma \rightarrow \sigma^*$ transition requires greater energy, thus C–C bond absorbs at 135 nm and C–H bond absorbs at about 125 nm.

ii. The $n \rightarrow \sigma^*$ transitions occur in a saturated molecules containing heteroatoms, such as oxygen, sulphur, nitrogen or halogens. This transition requires slightly less energy than required for $\sigma \rightarrow \sigma^*$ transition. For example methyl alcohol shows $n \rightarrow \sigma^*$ absorption at 183 nm.

iii. The $\pi \rightarrow \pi^*$ transitions occur in molecule, containing double or triple bonds or aromatic rings. For example ethylene absorbs at 171nm for $\pi \rightarrow \pi^*$ transition. However, a conjugated system of unsaturated bonds absorbs at much longer wavelength, e.g. buta-1,3-diene and isoprene (2-methylbuta-1,3-diene) shows maximum absorption at 217 nm and 222 nm respectively **(Figure 24.4)**.

iv. The $n \rightarrow \pi^*$ transitions occur in molecules that contain double or triple bonds involving hetero atoms such as aldehydes, ketones, nitriles etc. The $n \rightarrow \pi^*$ absorption band for acetone appears at 279 nm.

The d–d transitions **(Section 14.2.4)** of transition metal complexes occurs usually in visible region. The colour of transition metal complexes are usually coloured due to d–d transition. When a substance absorb a particular wavelength in visible region, the colour that our eyes perceives is not the colour corresponding to the wavelength of the light absorbed but its complementary colour that is transmitted. We can also predict the possible colour of a transition metal complex from its UV–Visible spectrum showing its absorption wavelength, using **Table 24.1.**

Tidbit

Lycopene, a pigment in ripped tomatoes, has a conjugated system of 11 double bonds and absorbs visible light. Its longest wavelength absorption is at 505 nm.

Table 24.1 Complementary Colours and their Approximate Wavelength Ranges

Colour of light absorbed	Wavelength (nm)	Colour of Complex (complementary colour)
Violet	400 – 435	Yellow
Blue	435 – 480	Orange
Blue-green	480 – 500	Orange-red
Green	500 – 560	Red
Yellow	560 – 595	violet
Orange	595 – 620	Blue
Orange-red	620 – 650	Blue-green
Red	650 – 750	Green

The U.V-Visible Spectrum

The U.V-Vis Spectrum is a plot of absorbance (A) against wavelength (λ). The wavelength at which absorption is maximum is referred to λ_{max} and intensity of absorption at this wavelength is referred to as ε_{max}.

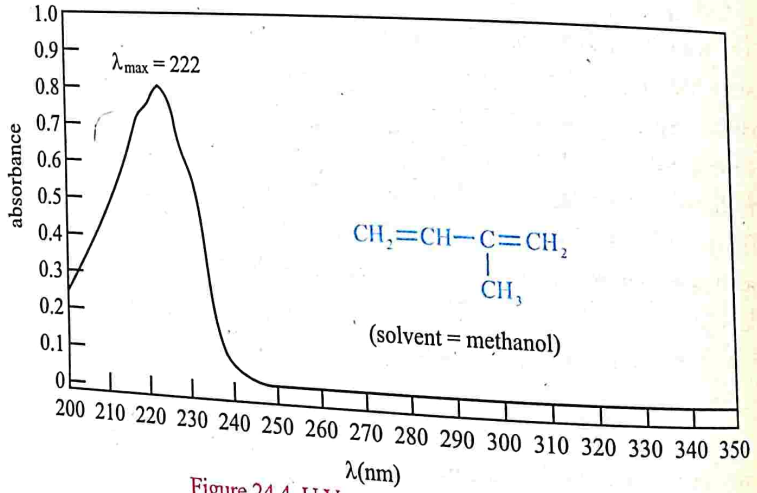


Figure 24.4 U.V. spectrum of isoprene.

Applications of U.V-Visible Spectroscopy

Any structural feature in a molecule that is responsible for the absorption of electromagnetic radiations in U.V-Visible region is called chromophore. Since different chromophores absorbs different wavelengths, it is sometimes possible to identify the unknown compound by comparing its λ_{max} with that of a known compound. The U.V-Visible spectroscopy can also give information about presence of conjugated systems and groups like carbonyl groups etc. UV-Visible spectroscopy is more meaningful when combined with Infrared **(Section 24.2.2.2)**, Nuclear Magnetic Resonance **(Section 24.2.2.3)** and Mass spectroscopy **(Section 24.2.2.5)** for complete identification of a compound.

UV-Visible spectroscopy is also used for quantitative analysis, using Beer-Lambert's Law.

$$A = \varepsilon.c.l$$

Where A is the absorbance, c is the molar concentration of solution and l is the path length of the sample solution in centimetres. ε is called molar absorptivity (formerly molar extinction coefficient) a constant characteristic of the solute at a given wavelength. The concentration (c) of a sample solution can be calculated from this law, by measuring the absorbance (A) of solution at wavelength of maximum absorption (λ_{max}) provided that molar absorptivity (ε_{max}) and pathlenght (l) are known. Another method to find the concentration of unknown solutions is to record the absorbances of solutions of known concentrations at wavelength of maximum absorption, using U.V-Visible spectrometer. A graph is then constructed by plotting the concentrations on x- axis and absorbance on y-axis. This graph is called working curve or calibration curve. The concentration of unknown solution can be determined easily, from its absorbance using working curve.

24.2.2.2 Infrared (IR) Spectroscopy

The infrared region of the spectrum corresponds to wavelengths of about 0.8 μm to 100 μm, just above the visible region. Common infrared spectrometers operate in the middle of this region, at wavelengths between 2.5μm to 16μm, corresponds to wavenumber to 4000-625 cm^{-1}. Infrared photons do not have enough energy to cause electronic transitions, but they can cause groups of atoms to vibrate with respect to the bonds that connect them. Like electronic transitions, these vibrational transitions correspond to distinct energies, and molecules absorb infrared radiations only at certain wavelengths and frequencies.

Molecular Vibrations

Absorption of a photon of infrared radiation excites a molecule from its lowest, or *ground*, vibrational state to a higher one. For a vibration to be IR active, the dipole moment of molecule must be changed. The bond vibration may be stretching or bending. In stretching vibrations, the bond length is increased or decreased at regular intervals. There are two types of stretching vibrations, symmetrical stretching and asymmetrical stretching. In bending vibrations, a change in bond angle occurs between bonds with a common atom. The bending vibrations are also called as deformation

vibrations. Deformation vibrations are of two types i.e. in-plane bending and out of plane bending vibrations. Scissoring and rocking are examples of in-plane bending while twisting and wagging are examples of out of plane bending. Different types of vibrations of methylene ($-CH_2-$) groups are shown in **Figure 24.5.**

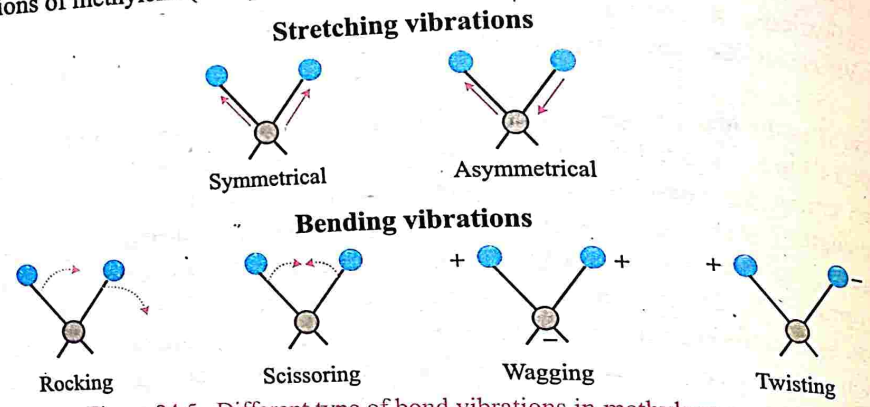


Figure 24.5 Different type of bond vibrations in methylene group.

The Infrared Spectrum

The plot of wavenumber, cm^{-1} (or sometimes wavelength in micron, μm) versus percent transmittance (%T) is called Infrared spectrum. This is recorded as percent transmittance because the spectrometer records the ratio of the intensities of the two beams.

$$\text{percent transmittance (\%T)} = \frac{I_s}{I_r} \times 100$$

Where I_s is the intensity of the sample beam, and I_r is the intensity of the reference beam. In many parts of the spectrum, the transmittance is nearly 100%, meaning that the sample is nearly transparent (no absorbance) to radiation of that wavenumber.

In using infrared spectroscopy for structure determination, peaks in the range 4000-1500 cm^{-1} are usually emphasized because this is the region in which the vibrations characteristic of particular functional groups are found and therefore called functional groups region. The region 1500–625 cm^{-1} is known as the fingerprint region. It is highly unlikely that the IR spectra of two different compounds (except enantiomers) will show the same frequencies for all of their various complex vibrations. Hence, this region of the infrared spectrum provides a "fingerprint" of a molecule. The IR spectra of ethanol and toluene are shown in **Figure 24.6 and 24.7.**

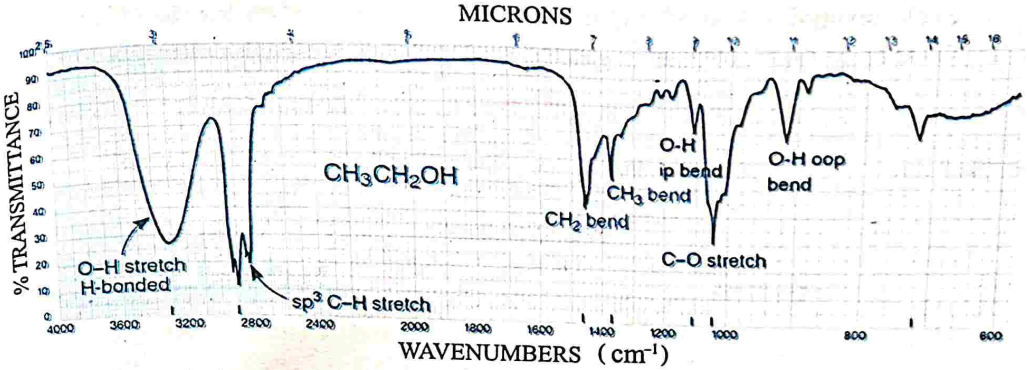


Figure 24.6 IR spectrum of ethanol.

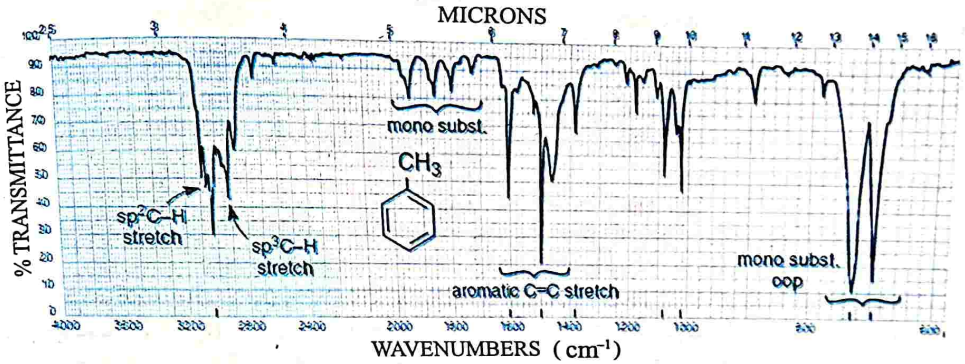


Figure 24.7 IR spectrum of toluene.

Applications of Infrared Spectroscopy

i. Infrared spectroscopy gives information about presence of different organic functional groups in a molecule.

ii. The identity of a compound can also be established by comparing the finger print region of infrared spectrum with that of a known compound.

iii. The presence of some extra absorption bands, where the compounds does not absorb, shows the presence of impurities. For example the presence of cyclohexanone impurity in cyclohexanol can be readily detected by the intense carbonyl band at 1715 cm^{-1} in spectrum of cyclohexanol.

iv. The progress of most of the reactions can also be monitored using infrared spectroscopy, by taking the spectra of small samples of reaction mixture continuously at suitable intervals of time. For example, in oxidation of

cyclohexanol to that of cyclohexanone is accompanied by the disappearance of O–H band near 3600 cm^{-1}, and the appearance of C=O band at 1715 cm^{-1}.

Table 24.2 Infrared Absorption Frequencies of Some Common Structural Units

Structural unit	Frequency, cm^{-1}	Structural unit	Frequency, cm^{-1}
Stretching vibrations			
Single bonds		**Double bonds**	
–O–H (alcohols)	3200–3600	C=C	1620–1680
–O–H (carboxylic acids)	2500–3600		
		C=O	
N–H	3350–3500		
		Aldehydes and ketones	1710–1750
sp C–H	3310–3320	Carboxylic acids	1700–1725
sp^2 C–H	3000–3100	Acid anhydrides	1800–1850 and 1740–1790
sp^3 C–H	2850–2950	Acyl halides	1770–1815
sp^2 C–O	1200	Esters	1730–1750
sp^3 C–O	1025–1200	Amides	1680–1700

24.2.2.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) is the most powerful tool available for organic structure determination. Like infrared spectroscopy, NMR can be used with a very small amount of sample, and it does not harm the sample. The NMR spectrum provides a great deal of information about the structure of the compound, and many structures can be determined using only the NMR spectrum. More commonly, however, NMR spectroscopy is used in conjunction with other forms of spectroscopy and chemical analysis to determine the structures of complicated organic molecules.

Nuclear spin and spin flipping

Like electrons, atomic nucleus proton also has the property of spin. Thus, the atomic nuclei behave like tiny magnets, as the spinning charged bodies produce magnetic field. In fact, any atomic nucleus that possesses either odd atomic number, odd mass number, or both has a quantized nuclear spin and a magnetic moment, and can be detected in NMR spectroscopy. Nuclei which have even atomic number and even mass number have zero spin and zero magnetic moment, and are therefore NMR inactive.

NMR is used to study a wide variety of nuclei, including ^{1}H, ^{13}C, ^{15}N, ^{19}F, and ^{31}P. Organic chemists find proton (^{1}H) and carbon-13 (^{13}C) NMR to be most useful because

hydrogen and carbon are major components of organic compounds. In this book, we will discuss only the proton NMR (^{1}H NMR) spectroscopy.

In the absence of an external magnetic field, proton magnetic moments have degenerate (of same energy) random orientations. When an external magnetic field is applied, each proton in a sample assumes either low energy alpha-spin (α-spin) state, in which the proton magnetic field is aligned with the applied field, or high energy beta-spin (β-spin) state, which has magnetic field aligned against the applied field. Because the α-spin state is lower in energy, there are more α-spin states than β-spins. In a strong magnetic field, the energy difference between the two spin states is larger than it is in a weaker field. In fact, the energy difference is proportional to the strength of the magnetic field.

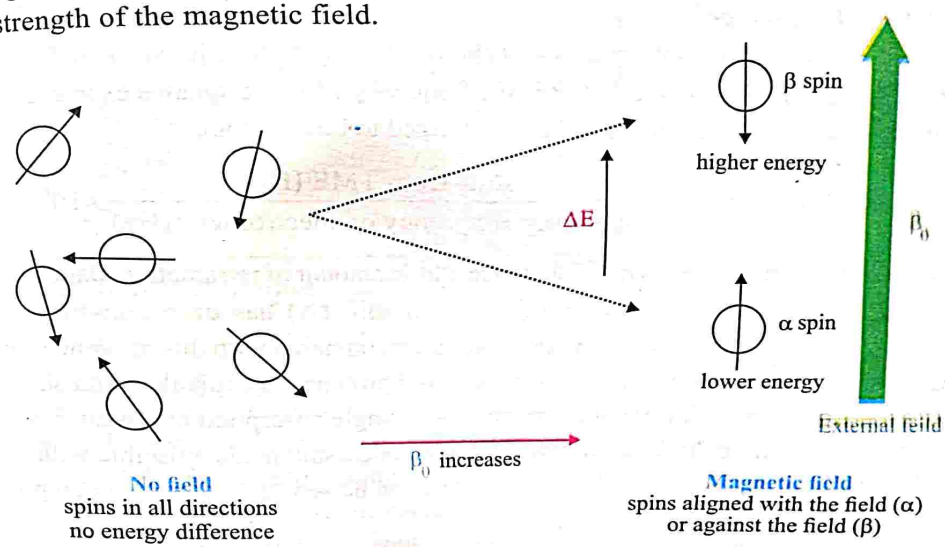


Figure 24.8 Nuclear spin states in absence and presence of magnetic field.

The nuclear magnetic resonance phenomenon occurs when nuclei aligned with an applied field are induced to absorb energy and change their spin orientation with respect to the applied field. The energy of absorption is a quantized process and the energy absorbed must equal the energy difference between the two spin states involved. A nucleus, when irradiated with radio-frequency photons having energy equal to the energy difference between the two spin states, a proton in the α-spin state can absorb a photon and flip to the β-spin state. The phenomenon is called flipping.

$$\Delta E = E_\beta - E_\alpha = h\nu$$

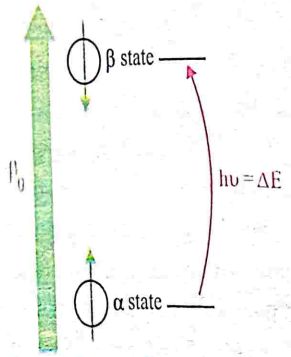


Figure 24.9 Nuclear spin flipping.

The ^{1}H NMR Spectrum

The graph of absorption on the y-axis and chemical shift (δ, delta in ppm) on the x-axis is NMR spectrum. The chemical shift is the frequency of the resonance expressed with reference to a standard compound which is defined to be at 0 ppm.

$$\text{chemical shift } (\delta) = \frac{\text{shift from TMS (Hz)}}{\text{operating frequency of spectrometer(Hz)}} \times 10^6$$

For taking the NMR spectrum of a substance a little amount of tetramethylsilane (TMS) is added to it. For TMS the value of chemical shift (δ) has been chosen as zero arbitrarily. Chemical shifts of other compounds are compared with this reference value. TMS has been chosen as a standard because all of protons are equivalent and shielded due to electropositive nature of silicon, and show single absorption at lowest δ value. Moreover it is chemically inert to most of the organic compounds, miscible with most of the organic solvents, and highly volatile, and can be separated from the compound after its spectrum has been recorded.

Magnetic Shielding by Electrons

Protons in a molecule are surrounded by electrons and exist in slightly different electronic (magnetic) environments from one another. The electron densities vary from one proton to another. Thus, the net field felt by a proton in a molecule will always be less than the applied field and the proton is said to be shielded. All of the protons of a molecule are shielded from the applied field by the electrons, but some are less shielded than others, because they may have less surrounding electron cloud and termed as deshielded protons. Deshielded protons are generally in vicinity of electronegative atoms in a molecule. More shielded protons absorb low radio-frequency radiations and their signals appear to the right side of spectrum, upfield region; while deshielded protons absorb high radio-frequency radiations and their signals therefore, appears at left side of spectrum, downfield region. Protons in identical chemical environments with the same shielding have the same chemical shift and are called equivalent protons. In general, the number of NMR signals corresponds to the number of protons present in different electronic environment in the molecule. Methyl alcohol has two type of protons, therefore its ^{1}H NMR spectrum has only two signals; an upfield signal for three equivalent and shielded, methyl protons and a downfield signal for the deshielded proton of hydroxyl. **(Figure 24.10)**

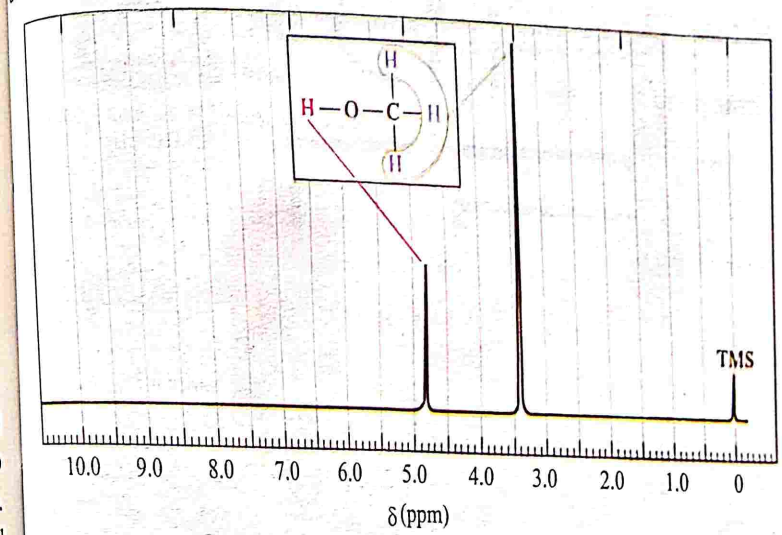


Figure 24.10 ^{1}H NMR spectrum of methyl alcohol.

24.2.2.4 Atomic Emission and Absorption Spectroscopy

The study of the electromagnetic spectrum of elements is called Atomic Spectroscopy. Electrons exist in energy levels within an atom. These levels have well defined energies and electrons moving between them must absorb or emit radiations having energy equal to the difference between them. Every element has a unique emission or absorption spectrum. Thus, the emission or absorption atomic spectra are used as finger print to identify the elements. Atomic spectroscopy is thought to be the oldest instrumental method for the identification of elements. Atomic emission and absorption spectrophotometry is used for qualitative and quantitative analysis of different metals.

Flame Photometry

One of the widely used emission spectroscopic technique is flame photometry (more accurately called Flame Atomic Emission Spectrophotometry). An aqueous analyte

is introduced into flame. Water evaporates and solid salt is left behind. The salt breaks into constituent atoms. The atoms go to vapour state. The gaseous atoms get excited in the flame. The excited atoms loose energy of characteristic wavelength, which is dispersed by a grating or prism and detected in the spectrophotometer. The intensity of light emitted by the atoms is directly proportional to the concentration of analyte.

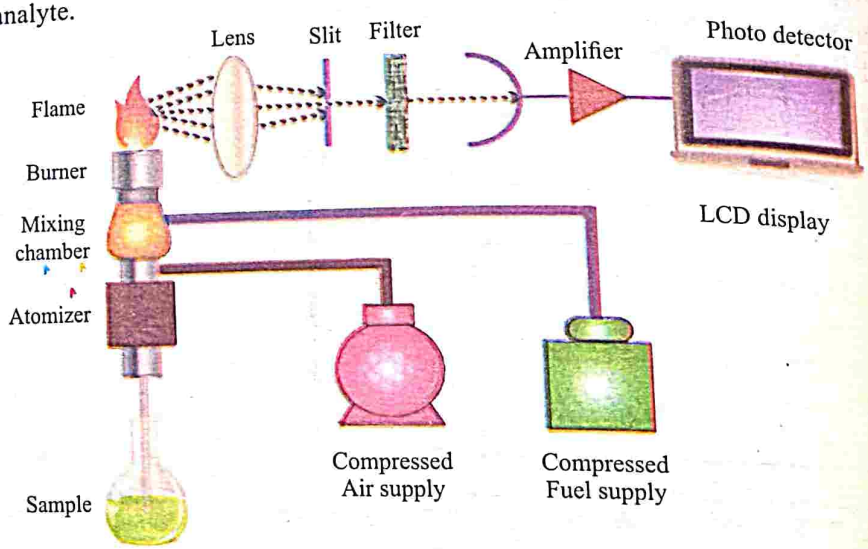


Figure 24.11 Schematic diagram of Flame Photometer.

Flame photometer has both qualitative and quantitative applications. The radiations emitted by the flame photometer are characteristic to particular metal. Flame photometer with monochromators emits radiations of characteristic wavelengths which help to detect the presence of a particular metal in the sample. The concentration of unknown solution can be calculated from working curve of standard solutions. This technique is usually used to find the concentration of various alkali and alkaline earth metals in soil samples which are critical for soil cultivation. Flame photometry is also used to determine the concentrations of Na^+ and K^+ ions in biological samples and also estimation of various metals in soft drinks and juices.

Atomic Absorption Spectrophotometry

Atomic absorption spectrophotometry is used for the analysis of elements. The sample solution is evaporated in a flame, and the sample is converted to atomic vapour. Some of the atoms in the flame get excited but majority of them are in ground state. When a light of particular wave length from the hollow cathode lamp is passed through these

atoms, they absorb the light for excitation from ground state to high energy state. The absorbance of light by atoms is directly proportional to the concentration of atomic vapours in the flame. For the analysis of different elements different types of lamps are used which produce light of different wave lengths. Each element shows absorption of particular wave length. Before introducing the sample of unknown concentration, solution of known concentrations of that element are aspirated into the flame one by one. Their absorbances are recorded and a working curve is constructed, between concentration and absorbance. Then sample of unknown concentration is aspirated into the flame and its concentration is determined from their absorbance using working curve.

Atomic absorption spectroscopy is used for the estimation of over sixty metals in polluted water, body fluids, soft drinks etc.

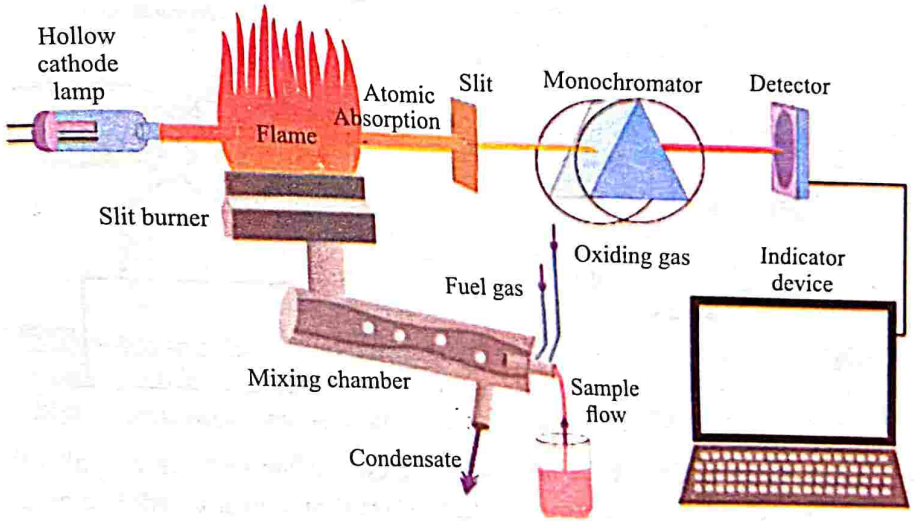


Figure 24.12 Schematic diagram Atomic Absorption Spectrophotometer.

24.2.2.5 Mass Spectrometry

Atomic and molecular masses are determined by mass spectrometry. Mass spectrometry is a highly sensitive instrumental technique. A mass spectrometer ionizes gaseous atoms and molecules in a high vacuum, sorts the ions according to their masses, and records the abundance of ions of each mass.

Mass Spectrometer and Mass Spectrum

The gaseous sample is bombarded with high energy electrons from electron-gun and the resulting positively charged ions (which are radical cations) are directed into an analyzer tube surrounded by a magnet. This magnet deflects the ions from their original

trajectory, causing them to adopt a circular path, the radius of which depends on their mass-to-charge ratio *(m/z)*. Ions of small *m/z* values are deflected more than those of larger *m/z*. By varying the magnetic field strength, ions of a particular *m/z* can be selectively focused through a narrow slit onto a detector, where they are counted. A mass spectrum is the graph plotted by the mass spectrometer, with the *m/z* values on x-axis and the relative number of ions of each mass on the y-axis. Higher the peak of a species higher will be its abundance.

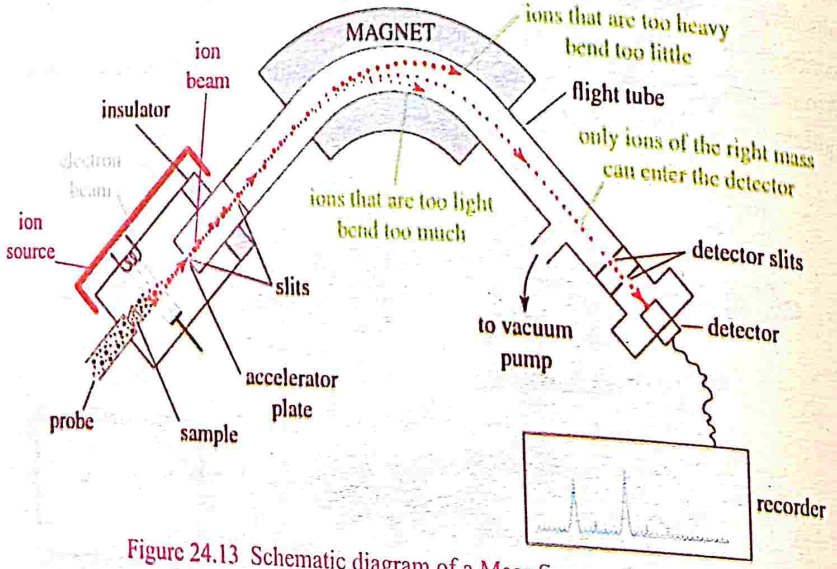


Figure 24.13 Schematic diagram of a Mass Spectrometer.

Mass spectrum helps in finding the number of isotopes of an element and also their relative abundances. The mass spectrum of neon shows three peaks with *m/z* equal to 20, 21, and 22 which correspond to ^{20}Ne, ^{21}Ne and ^{22}Ne respectively. Neon–20 is the most abundant and Neon–21 is the least abundant isotope as clear from the heights of their peaks.

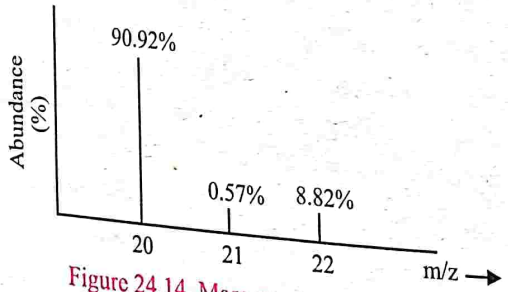


Figure 24.14 Mass spectrum of Neon.

When a molecule is introduced into mass spectrometer, the molecular ion (M^+) is produced due to loss of an electron. The molecular ion has the highest *m/z* value that represents the molecular mass of molecule. In addition to the molecular ion, more ions are produced due to fragmentation of the molecule. Fragmentation occurs due to rupture of chemical bonds. A mass spectrum of chlorine molecule is given in **Figure 24.15** shows that there are two isotopes of chlorine ^{35}Cl (*m/z* = 35) and ^{37}Cl (*m/z* = 37) and three types of chlorine molecules, $^{35}Cl–^{35}Cl$ (*m/z* = 70), $^{35}Cl–^{37}Cl$ (*m/z* = 72) and $^{37}Cl–^{37}Cl$ (*m/z* = 74).

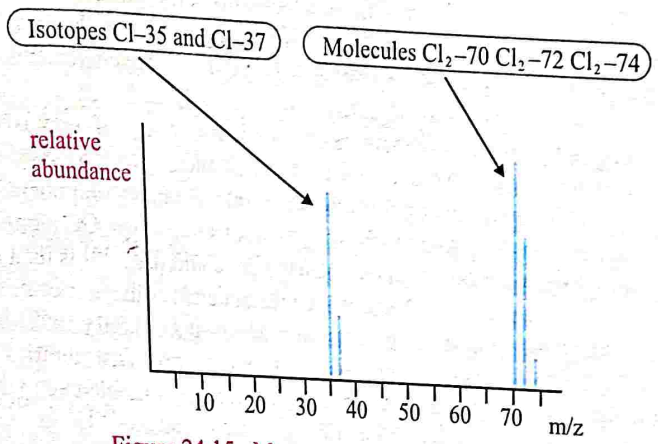


Figure 24.15 Mass spectrum of chlorine (Cl_2).

The fragmentation pattern of a molecule gives an idea of the structure of the molecule. Thus mass spectrometry is very helpful in the identification of molecular structures as well. Mass spectrum of methyl alcohol is given in **Figure 24.16.**

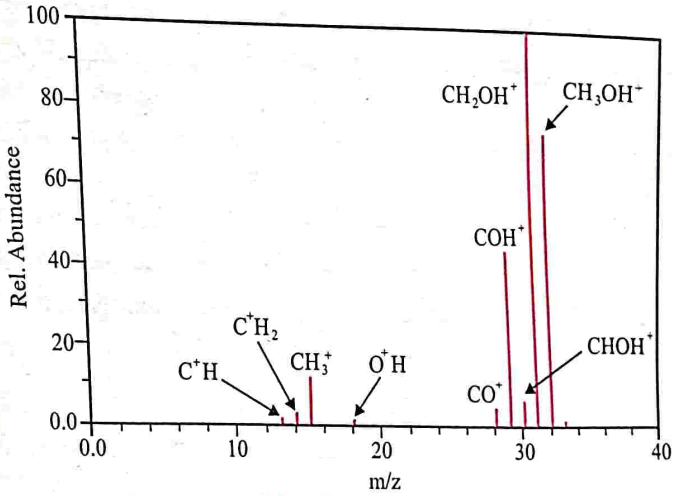


Figure 24.16 Mass Spectrum of methyl alcohol.

Society, Technology And Science

Forensic science applies science principles, techniques, and methods to the investigation of crime. Forensic analytical chemistry is defined as analytical chemistry as it pertains to law. Forensic chemists perform specialized analysis to identify materials and learn the nature of such evidences.

A wide array of laboratory techniques and instrumentation is used in forensic studies. This includes ultraviolet, infrared, and visible spectrophotometry, gas chromatography and mass spectrometry; high pressure liquid chromatography and atomic absorption spectrophotometry. The techniques and instrumentation chosen depend on the type of sample or substance to be examined.

Gas chromatography is most widely used in identification of explosive, accelerator, propellants and drugs or chemicals involved in chemical weapons production. The gas chromatograph (GC) separates volatile substances into separate components by passing the volatile materials through a long absorbent column. In some cases, GC alone is not adequate method for identification such as containments in food and drugs. It is then combined with another method to separate the compound even further and results in greater sensitivity. The GC is often connected to a mass spectrometer. Mass spectrometry (MS) breaks samples apart and separates the ionized fragments by mass and charge. Vast libraries of comparison fragments make computer-aided identification of materials possible even when the sample is very small. Most forensic laboratories have access to a combined gas chromatograph/mass spectrometer (GC/MS). High pressure liquid chromatography (HPLC) separates many types of drugs and may also be combined with MS.

Key Points

- A set of experiments used to know about the quality of a substance is called qualitative analysis.
- Methods used to find the quantities of substances are quantitative analysis.
- Burning of substances in the presence of oxygen is called combustion.
- Most organic compounds on burning produces CO_2 and H_2O.
- Empirical formula shows the simplest ratio of atoms present in a molecule of compound.
- Molecular formula gives the exact number of atoms present in a molecule of a compound.
- Two or more compounds may have the same molecular formula and are called isomers.
- Structural formula gives the arrangement of atoms in molecule of a compound.
- Spectroscopy helps us to identify atoms/functional groups in a substance by the interaction of electromagnetic radiation with the substance.
- In IR spectroscopy organic compounds are exposed to weak radiations in the range of 4000–625 cm^{-1}.
- A 100% transmittance means no absorption.
- In UV/Visible spectroscopy, the radiations having wavelengths in the range of 200—800 nm are used.
- These radiations are more energetic and can change the distribution of loosely bound electrons.
- Like electrons, atomic nuclei protons also spin about an axis.
- Spinning charged bodies produce magnetic field.
- All nuclei having spin quantum number greater than zero are NMR active.

Exercise

Q 1. Choose the correct one from the given options.

1. Which one of the following is quantitative chemical analysis?
   a. Salt analysis
   b. Titration
   c. Flame test
   d. Bromine-water test

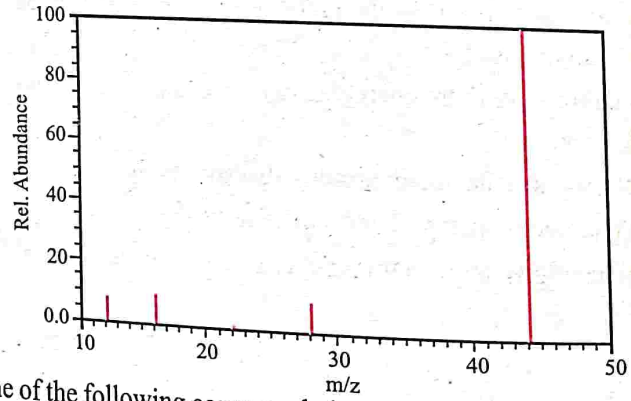
2. C_2H_6O is the molecular formula of
   (i) ethanol (ii) methanol (iii) dimethyl ether (iv) diethyl ether
   a. (i) and (ii)
   b. (ii) and (iii)
   c. (i) and (iii)
   d. (ii) and (v)

3. Which one of the following techniques is mainly used for determination of functional group in a compound?
   a. IR Spectroscopy
   b. NMR
   c.
   d. Mass spectroscopy

4. Two different compounds will always give different absorption peak in ____ region of IR.
   a. 1500–625 cm^{-1}
   b. 4000–1500 cm^{-1}
   c. 3000–2500 cm^{-1}
   d. 3500–1500 cm^{-1}

5. Which one of the following methods, relatively gives more information about the structure of an organic compound?
   a. Mass Spectroscopy
   b. NMR Spectroscopy
   c. IR Spectroscopy
   d. UV-Visible Spectroscopy

6. A mass spectrum is shown below.



Which one of the following compound gives complete mass spectrum illustrated?
   a. CO_2
   b. N_2
   c. C_3H_8
   d. Mixture of CH_4 and N_2

7. The wavelength range of UV region is from
   a. 400–800 nm.
   b. 800–1200 nm.
   c. 1200–1600 nm.
   d. 10–400 nm.

8. Which one of the following hydrocarbon produces a proton NMR spectrum with more than one peak?
   a. Methane
   b. Ethane
   c. Butane
   d. Cyclobutane

9. How many signals/peaks would you expect in the proton NMR spectrum of 1,1-dicholorethane?
   a. 2
   b. 4
   c. 6
   d. 8

10. How many types of protons are there in butanoic acid?
   a. 8
   b. 2
   c. 6
   d. 4

11. In combustion analysis water is absorbed by
   a. $Mg(ClO_4)_2$
   b. NaOH
   c. CuO
   d. $CuSO_4$

12. Modern methods of analysis are superior to classical one because
   a. they give more accurate results.
   b. small amounts of chemicals are used.
   c. less time consuming.
   d. all of the above.

13. Which one is an in-plane bending vibration?
   a. Wagging
   b. Scissoring
   c. Twisting
   d. None of these

14. Pi to pi star transition occurs in
   a. ethane.
   b. ethene.
   c. ethyl alcohol.
   d. methyl chloride.

15. Which one is NMR inactive nucleus?
   a. ^{31}C
   b. ^{1}H
   c. ^{15}N
   d. ^{16}O

Q2. Write short answers of the following questions.

i. What is meant by stretching and bending vibrations?
ii. If a compound shows 100% transmittance, what do we infer from it?
iii. What does λ_{max} mean to you?
iv. Define and explain Bear-Lambert's Law.
v. Why tetramethyl silane is used as a standard in NMR spectroscopy?
vi. Explain the use of ionization chamber in mass spectrometer.
vii. Why magnesium perchlorate is used as H_2O absorber?
viii. Why modern method of analysis is superior over classical method of analysis?

ix. Mass spectrum of on element can give information of number of isotopes, atomic masses and natural abundance of each isotope. Explain with an example.

x. Explain the nuclear spin flipping briefly.

Q3. Solve the numerical questions.

i. A compound containing C, H and O, is found to contain 32% carbon and 4% hydrogen. Its molecular mass is 150 amu. Find its molecular formula.

ii. Calculate the empirical formula of the compound that contains 27.3% carbon and 72.7% oxygen.

iii. Acetic acid contains only C, H and O. A 5 g sample of acetic acid is completely burnt. It gives 7.33 g of carbon dioxide and 3 g of water. What is the mass percentage of each elements in acetic acid? Also calculate the empirical formula of acetic acid.

iv. Isoprene is a liquid compound that can be polymerized to form synthetic rubber. It is composed of 88.17% carbon and 11.83% hydrogen. Its molecular mass is 68.11 amu. What are its empirical and molecular formulae?

v. Polyethylene is a hydrocarbon polymer used to produce food-storage bags and many other flexible plastic items. A combustion analysis of a 1.26 g sample of polyethylene yields 3.94 g of carbon dioxide and 1.61 g of water. What is the empirical formula of polyethylene?

Q4. Write detail answers of the following questions.

1. (a) Define mass spectroscopy. Explain the construction and working of mass spectrometer.
   (b) How a mass spectrum of an element and compound can give information about atomic mass and molecular mass, respectively?
2. (a) Differentiate between atomic emission and absorption spectroscopy.
   (b) Explain the working of flame photometer and atomic absorption spectrometer.
   (c) How atomic emission and absorption spectrophotometry is used for qualitative and quantitative analysis of elements?
3. (a) What is meant by proton NMR spectroscopy?
   (b) Explain how chemical shift varies with shielding?
   (c) From proton NMR spectrum of a molecule, how would you know about presence of different types of protons in molecule?
4. (a) Explain the principle of UV-Visible spectroscopy.
   (b) Explain different types of electron transitions in organic molecules.
5. (a) What is IR spectroscopy?
   (b) Explain different types of molecular vibrations in a molecule.
   (c) Explain the significance of functional group and fingerprint regions in IR spectrum.

Project

- The molecular formula of a compound determined from combustion analysis and mass spectrometry is C_3H_6O. Proton NMR spectrum of compounds has only one signal. Draw the possible structure of compound.
- Draw the structures of four isomeric butyl bromides (C_4H_9Br) and predict the number of signals in proton NMR spectrum of each of the isomer.

ANSWERS OF MCQS

Unit- 13

1. a	2. a	3. c	4. c	5. a	6. d
7. b	8. c	9. b	10. b	11. b	12. c
13. c	14. a	15. a			

Unit- 14

1. d	2. d	3. a	4. d	5. b	6. d
7. c	8. a	9. c	10. d	11. d	12. b
13. a	14. c	15. c			

Unit- 15

1. b	2. a	3. a	4. c	5. d	6. b
7. c	8. a	9. d	10. d	11. d	12. c
13. a	14. c	15. d			

Unit- 16

1. b	2. b	3. b	4. d	5. c	6. d
7. d	8. a	9. d	10. c	11. c	12. c
13. c	14. b	15. b			

Unit- 17

1. a	2. b	3. a	4. a	5. a	6. d
7. b	8. b	9. b	10. c	11. a	12. d
13. b	14. d	15. a			

Unit- 18

1. b	2. c	3. d	4. a	5. c	6. d
7. c	8. b	9. c	10. b	11. b	12. c
13. a	14. d	15. a			

Unit- 19

1. b	2. c	3. d	4. d	5. b	6. b
7. c	8. c	9. a	10. d	11. a	12. b
13. a	14. d	15. b			

Unit- 20

1. c	2. c	3. a.	4. b	5. d	6. a
7. b	8. d	9. a	10. d		

Unit- 21

1. c	2. a	3. a	4. c	5. a	6. a
7. d	8. b	9. b	10. c	11. b	12. d
13. d	14. c	15. c			

Unit- 22

1. a	2. d	3. c	4. c	5. d	6. b
7. c	8. a	9. d	10. d	11. c	12. a
13. b	14. a	15. b			

Unit- 23

1. d	2. d	3. a	4. a	5. d	6. d
7. d	8. a	9. c	10. a	11. b	12. a
13. d	14. a	15. d			

Unit- 24

1. b	2. b	3. a	4. a	5. b	6. a
7. d	8. c	9. a	10. d	11.	12. d
13. b	14. b	15. d			

GLOSSARY

Alcohols:- Alcohols are organic compounds, in which a hydroxyl group(–OH) is attached to carbon atom of an alkyl group.

Alkanes:- These are saturated acyclic hydrocarbons which contain all carbon-carbon single bond.

Alkyl halide:- The organic compounds in which one or more halogen atoms are directly bonded to carbon atom of an alkyl group.

Alkylation of Ammonia :- The reaction in which hydrogen atoms of NH_3 are replaced by alkyl groups.

Amines:- Amines are the organic compounds of nitrogen that may be considered as derived from ammonia (NH_3) by replacing one or more of the hydrogen atoms by organic radicals ($-CH_3$, $-C_6H_5$) or organic functional groups.

Beer Lambert's Law: Bear Lambert's Law is the linear relationship between absorbance (A) and concentration (C) of an absorbing species in the solution i.e. absorbance is directly proportional to the concentration of the solution and path length (l) of the solution through which the light passes. $A = \varepsilon cl$

Bond Enthalpy: The bond enthalpy of a specific bond is the enthalpy change involved in breaking that covalent bond into individual gaseous atoms at 298 K. It is a measure of bond strength or bond dissociation energy.

Carbocation:- A group of atoms having positively charged carbon atom which has six electrons in its valence shell is called carbocation. Among the simplest examples are methanium CH_3^+ and ethanium $C_2H_7^+$ ions.

Carbonyl group: A carbonyl group is a functional group composed of a carbon atom double-bonded to an oxygen atom >C=O.

Catenation: Catenation is the binding of an element to itself through covalent bonds to form chain or ring molecules.

Coal: A naturally occurring solid material, of black or brownish colour normally occur in rock strata called coal beds consisting mostly of high molecular weight hydrocarbons. Produced by decomposition of prehistoric plant material under high temperature and pressure. Used principally as a fossil fuel.

Complex Ion: A complex ion is an ion comprising one or more ligands attached to a central metal cation with a c-ordinate covalent bond. A ligand is a species which can use its lone pair of electrons to form a co-ordinate covalent bond with a transition metal. Examples of ligands are H_2O, NH_3, Cl^-, OH^-, CN^-.

Contact process: The industrial process for the manufacture of sulfuric acid in high concentrations needed for use in industrial processes.

Dextrorotatory isomer:- An optically active compound that rotates the plane of plane-polarized light clockwise, (symbol: *d* or +).eg. (*S*)-Lactic acid is dextrorotatory

diamagnetic:– Diamagnetic is a term which indicates that a substance contains no unpaired electrons and thus is not attracted to a magnetic field.

Diazonium Salt or diazonium compound: – A diazonium compound is an organic compound with structure RN=NX where R is an aryl ring and X is any anion.

Effect of heat on nitrates: Most nitrates tend to decompose on heating to produce metal oxide, nitrogen oxide and oxygen.

Electronic effect: Effects by which the reactivity at one part of a molecule is affected by electron attraction or repulsion originating in another part of a molecule. Often this is called an **inductive effect**.

Electrical Conductivity: The measure of the amount of electrical current, a material can carry or it's ability to carry a current. Electrical conductivity is also known as specific conductance.

Electrophile: (Electron-Loving) An electrophile is a molecule that forms a bond to its reaction partner (the nucleophile) by accepting both bonding electrons from that reaction partner. Electrophilic reagents are Lewis acids.

Elimination reaction: Those reactions which involve the elimination or removal of atoms or group of atoms from two adjacent carbon atoms in the substrate molecule to form a multiple bond.

Electromagnetic spectrum: The range of wave lengths and frequencies over which electromagnetic radiation extends.

Empirical formula: The formula that gives the simplest whole number ratio of the atoms of elements present in compound.

Enantiomers: Such stereoisomers (Optical isomers) which are non-superimposable mirror reflection of each other.

Entering Group: The atom, ion or group of atoms which attacks the substrate molecule and form a new bond with its carbon atom.

Ester: An ester is an organic compound where the hydrogen in the compound's carboxyl group is replaced with a hydrocarbon group. Esters have the general formula of RCOOR.

Esterification: It is the process of combining an organic acid (RCOOH) with an alcohol (ROH) to form an ester (RCOOR) and water.

Ether: A class of compounds in which two alkyl groups or two aryl groups or one alkyl and one aryl group are attached to oxygen atom. The general formula for an ether is R-O-R. The compound dimethyl ether is commonly known as ether.

Fatty Acid: A fatty acid is a carboxylic acid with a long aliphatic chain, which is either saturated or unsaturated. Most naturally occurring fatty acids have an unbranched chain of an even number of carbon atoms, from 4 to 28.

Formyl group: A functional group that consists of a carbonyl group joined by a single bond to a hydrogen atom.

Fullerenes: A fullerene is an allotrope of carbon whose molecule consists of carbon atoms connected by single and double bonds so as to form a closed or partially closed mesh, with fused rings of five to seven atoms. The molecule may be a hollow sphere, ellipsoid, tube or many other shapes and sizes.

Functional group: A functional group is a specific atom or group of atoms or bonds within a compound that is responsible for the characteristic chemical reactions of that compound.

Gasification: It is a process that converts biomass- or fossil fuel-based carbonaceous materials (coal) into coal gas (carbon monoxide, hydrogen and carbon dioxide.) This is achieved by reacting the material at high temperatures (>700 °C), without combustion, with a controlled amount of oxygen and/or steam.

Grignard reagent: It is a chemical compound with the generic formula R–Mg–X, where X is a halogen and R is an organic group, called as alkyl magnesium halide.

Group-II A elements: The Group 2 elements, the alkaline earth metals, include beryllium, magnesium, calcium, barium, strontium and radium.

Group IV A elements: The Group-IV A of the periodic table consist of five elements, also called the carbon group elements. Members of this group include: C, Si, Ge, Sn and Pb.

Hemiacetal: In the simplest form, the hemiacetal is the combination of two functional groups. A hemiacetal is an alcohol and ether attached to the same carbon.

Heterolysis: It is the process of cleaving a covalent bond where one previously bonded species takes both original bonding electrons from the other species. During heterolytic bond cleavage of a neutral molecule, a cation and an anion will be generated.

Homologues series: In organic chemistry, a homologous series is a sequence of compounds with the same functional group and similar chemical properties in which the members of the series can be branched or unbranched, in which two adjacent members differ by $-CH_2$ and can be represented by a general formula.

Homolysis: or homolytic cleavage is the breaking of a covalent bond in such a way that each fragment gets one of the shared electrons. In homolytic cleavage, the two electrons in the bond are divided equally between the products.

Hydroxide: Hydroxide is a compound that contains hydroxide ion (OH^-) or hydroxyl group (–OH) covalently bonded to an atom of an element.

Inductive Effect: It refers to the phenomenon where in a permanent dipole arises in a given molecule due to unequal sharing of the bonding electrons in the molecule.

Iso alkane: Any branched-chain alkane, but especially one having a methyl group attached to the penultimate (second last) carbon atom of the main chain.

Isomerism: Isomerism is the phenomenon in which more than one compounds have the same chemical formula but with the different chemical and physical properties.

Inert pair effect: The tendency of the two electrons in the outermost atomic *s*–orbital to remain unshared in compounds is called inert pair effect.

Infra Red Spectroscopy: Infra Red (IR) spectroscopy is a chemically specific analysis technique that identifies the chemical bonding or molecular structure of materials, based on absorption by the molecule in the infrared region of the electromagnetic spectrum.

Keto group : Ketone functional group is called keto group (>C= O)

Leaving group: The group or species which leaves the substrate or which is being replaced by the incoming entering group.

Levorotatory isomer: An optically active compound that rotates the plane of plane-polarized light anti-clockwise is said to be levorot along (symbol: L or –)

Lucas Test : Lucas test is used to differentiate and categorize primary, secondary and tertiary alcohols using a solution of anhydrous zinc chloride in concentrated hydrochloric acid. This solution is commonly referred to as the Lucas reagent.

Markovnikove's Rule: The rule states that in the addition of asymmetric molecule to an asymmetric alkene or alkyne, the positive part gets attached to the carbon with more hydrogen substituents.

Mass spectrometry: Mass spectrometry is an analytical tool useful for measuring the mass-to-charge ratio *(m/z)* of one or more molecules present in a sample. These measurements can often be used to calculate the exact molecular weight of the sample components as well.

Meta-Director: In electrophilic aromatic substitution, the substituents which direct the second incoming substituent to meta position is meta director.

For example, alkylation of nitro benzene gives m-alkylnitro benzene as major product.

Metamerism: Metamerism is a type of structural isomerism in which compounds have the same molecular formula but different number of carbon atoms (alkyl groups) on either side of functional group (i.e., –O–,–S–, –NH–, –C(=O)–,esters, amides, etc.). For example, diethyl ether and methyl propyl ethers are metamers.

Monochromatic light: Monochromatic light is light (optical radiation) where the optical spectrum contains only a single optical frequency.

Molecular formula: A molecular formula consists of the chemical symbols for the constituent elements followed by numeric subscripts describing the number of atoms of each element present in the molecule.

Neo-alkane: Prefix **neo** is used for those alkanes in which two methyl groups are attached to the next to end carbon atom (second last) of the continuous chain.

Nitriles: Nitriles are the organic compounds which are also called as Cyano Compounds. These class of organic compounds have the functional group called cyano group represented as (−C ≡ N), and it is attached to the carbon atom.

Nucleophilic Substitution: A nucleophilic substitution is a class of chemical reactions in which an electron-rich nucleophile displaces the functional group to the central carbon of an electron-deficient molecule (known as the electrophile).

Nuclear Magnetic Resonance: (NMR) spectroscopy is a technique used to precisely identify the molecular structure of the compound by recording the interaction of radiofrequency (Rf) electromagnetic radiations with the nuclear spin of molecules placed in a strong magnetic field.

Nucleophile: (Nucleus-Loving) A nucleophile is an atom or a molecule that forms a bond with its reaction partner (the electrophile) or the positive centre by donating both electrons for that bond. Nucleophiles are Lewis bases. Examples of nucleophiles are the halide ion (I^-, Cl^-, Br^-), the hydroxide ion (OH^-), the cyanide ion (CN^-), ammonia (NH_3), water etc.

Ortho- para Directors: Atoms or groups that make the benzene molecule more reactive by increasing the ring's electron density are called **activating groups**.

Para magnetism: It refers to a property of certain materials that are weakly attracted by an externally applied magnetic fields. When exposed to an external magnetic field, internal induced magnetic fields form in these materials that are ordered in the same direction as the applied field.

Petroleum: Petroleum also called crude oil is a naturally occurring liquid found beneath the earth's surface it is a liquid mixture of hydrocarbons and other compounds. Petroleum is a fossil fuel, meaning that it has been created by the decomposition of organic matter over millions of years. When fractionally distilled, it yields paraffin, fuel oil, kerosene, gasoline, etc.

Phenol : A corrosive poisonous crystalline acidic compound, C_6H_5OH, present in the tars of coal and wood that in dilute solution (called carbolic) is used as a disinfectant. In this organic compounds the –OH group is attached directly to the aromatic ring.

Polarimeter: A polarimeter is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically active substance. Some chemical substances are optically active, and polarized light will rotate either to the left or right when passed through these substances.

Polymerization: A Process in which relatively small molecules, called monomers, combine chemically to produce a very large chain-like or network molecule of with high molecular weight called a polymer.

Resonance Energy: The resonance energy of a molecule is the difference between the energy of the most stable canonical form and that of the actual molecule.

Resonance: Two or more valence-bond structures differing only in the placement of electrons. Such as different structures are called resonance structures or resonance forms or canonical form because they are not different molecules, just different ways of drawing the same molecule.

Saturated Hydrocarbon: These are the hydrocarbons that contain only single bonds between carbon atoms. Saturated hydrocarbons are given the general name of alkanes.

S_N1 Mechanism: **S_N1** stands for **S**ubstitution, **N**ucleophilic, unimolecular. It is a two-step mechanism. First step is slow (rate determining or rate limiting step) and involves the formation of intermediate carbocation. The second step is fast and involves the attack of nucleophile on planar carbocation and formation of product. S_N1 mechanism is generally followed by tertiary alkyl halides.

Stearic Hindrance: The phenomenon of physical blockage of a particular site within a molecule by the presence or crowding of local atoms or groups of atoms. This can cause reactions to either slow down or stop completely with respect to the atom.

Stereoisomerism: Isomerism in which molecules have the same molecular formula and sequence of bonded atoms (constitution), but differ in the three-dimensional orientations of their atoms in space.

Spectroscopy: It deals with measuring and interpreting spectra that arise from the interaction of electromagnetic radiation with matter.

Substituent group: A substituent is an atom or group of atoms which replaces one or more hydrogen or other atom or group of atoms on the parent molecule.

Substrate : It is a molecule or a compound that undergoes a chemical reaction, whether under the action of a catalyst, an enzyme or an inhibitor. It can also refer to a surface on which other chemical reactions are performed.

Sulphydryl or Marcapto : A mercapto group is a functional group containing a sulfur atom bonded to a hydrogen atom. General formula: –SH.

Synthetic Organic Compound: The compounds which can be synthesized in laboratory by chemical manipulations (chemical reactions) from living or non-living organisms.

Tautomerism: A type of isomerism wherein the isomers interchange into one another very early to exist together in equilbrim.

Electronegativity: Electronegativity is a measure of the tendency of an atom to attract a shared pair of electrons in a covalent bond.

Ultra violet visible spectroscopy: An instrumental scanning method that analyses the absorption of light within UV-Visible region.

Unsaturated Hydrocarbon: Unsaturated hydrocarbons are hydrocarbons that have double or triple covalent bonds between adjacent carbon atoms.

Vital force theory: A theory that an organic molecule cannot be produced from inorganic molecules, but can only be produced from a living organism or some part of a living organism.

Williamson Synthesis: A method of synthesizing ethers by reaction of a sodium alkoxide with a halogen derivative of a hydrocarbon (as an alkyl halide).



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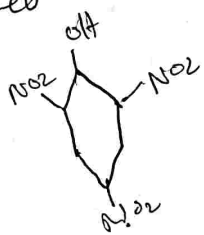
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