CHAPTER

1 Periodic Classification Of Elements And Periodicity

Animation 1.1 : Periodic Table
Source and Credit: eLearn.Punjab

IN THIS CHAPTER YOU WILL LEARN

1. To describe the periodic table in terms of groups and periods.
2. To describe and explain periodicity in physical and chemical properties.
3. To describe the position of hydrogen in the periodic table.

1.1 INTRODUCTION

To achieve a thorough understanding of a complex subject like chemistry, it would be highly desirable to fit all the facts into a simple logical pattern. The periodic table of elements has served the purpose to systematize the properties of the elements for well over 100 years.The development of periodic table is one of the most significant achievements in the history of chemical sciences.

The Periodic Table provides a basic framework to study the periodic behaviour of physical and chemical properties of elements as well as their compounds. In previous classes, you have learnt about the periodic classification of elements. This chapter describes in more detail the periodic table and the periodicity of elements.

1.1.1 Historical Background

The early history of ideas leading up to the Periodic classification of elements is fascinating but will not be treated in detail.Those who made memorable contributions in this field are Al-Razi,Dobereiner,Newland and Mendeleev. Al-Razi's classifications was based on the physical and chemical properties of substances . Dobereiner, a German chemist in 1829, arranged then known elements in group called Triads, as each contained three elements with similar properties. Newland who was an English chemist , in 1864, classified 62 elements, known at that time , in increasing order of thier atomic masses. He noticed that every eighth element had some properties in common with the first one. The principle on which this classification is based was called the Law of Octaves.

In 1871, a Russian Chemist, Dmitri Mendeleev, gave a more useful and comprehensive scheme for the classification of elements. He presented the first regular periodic table in which elements of similar chemical properties were arranged in eight vertical columns called Groups.The horizontal rows of the table were called Periods.

Mendeleev also started by arranging the elements in ascending order of their atomic masses and found that elements having similar chemical properties appeared at regular intervals. This significant observation was called Periodic Law. Mendeleev left some gaps in his table for elements, which had not yet been discovered, and by considering their positions in the periodic table, he predicted properties of these elements. For example, germanium was not known at that time, but Mendeleev was confident that this element must exist so he predicted its properties. A few years later, germanium was indeed discovered and a remarkable agreement was found with Mendeleev's predictions.

1.1.2 Improvements In Mendeleev 's Periodic Table

In order to make the periodic table more useful and accurate, a few improvements were made in Mendeleev s periodic table. After the discovery of atomic number by Moseley in 1911, it was noticed that elements could be classified more satisfactorily by using their atomic numbers, rather than their atomic masses.

Hence, the periodic table was improved by arranging the elements in ascending order of their atomic numbers instead of their atomic masses. This improvement rectified a number of confusions present in the old periodic table.The modern Periodic Law states that: "if the elements are arranged in ascending order of their atomic numbers, their chemical properties repeat in a periodic manner"

Another improvement was the addition of an extra group (group VIIIA) at the extreme right of the periodic table. This group contains noble gases, which had not been discovered in Mendeleev's time.

Another confusion in Mendeleev's table was that elements like Be, Mg, Ca, Sr, Ba and Zn, Cd, Hg were placed in a single vertical group, while according to their properties they belonged to two different categories. The same was true for so many other elements placed in the same vertical group. In modern periodic table, the confusion was removed by dividing the elements in two types of vertical groups, A and B. In modern periodic table, Be, Mg, Ca, Sr and Ba are placed in group IIA and Zn, Cd, Hg in group IIB.

1.2 THE MODERN PERIODIC TABLE

In modern periodic table (see periodic table) all the elements are arranged inascending order of their atomic numbers.
Followings are the essential features of the periodic table.

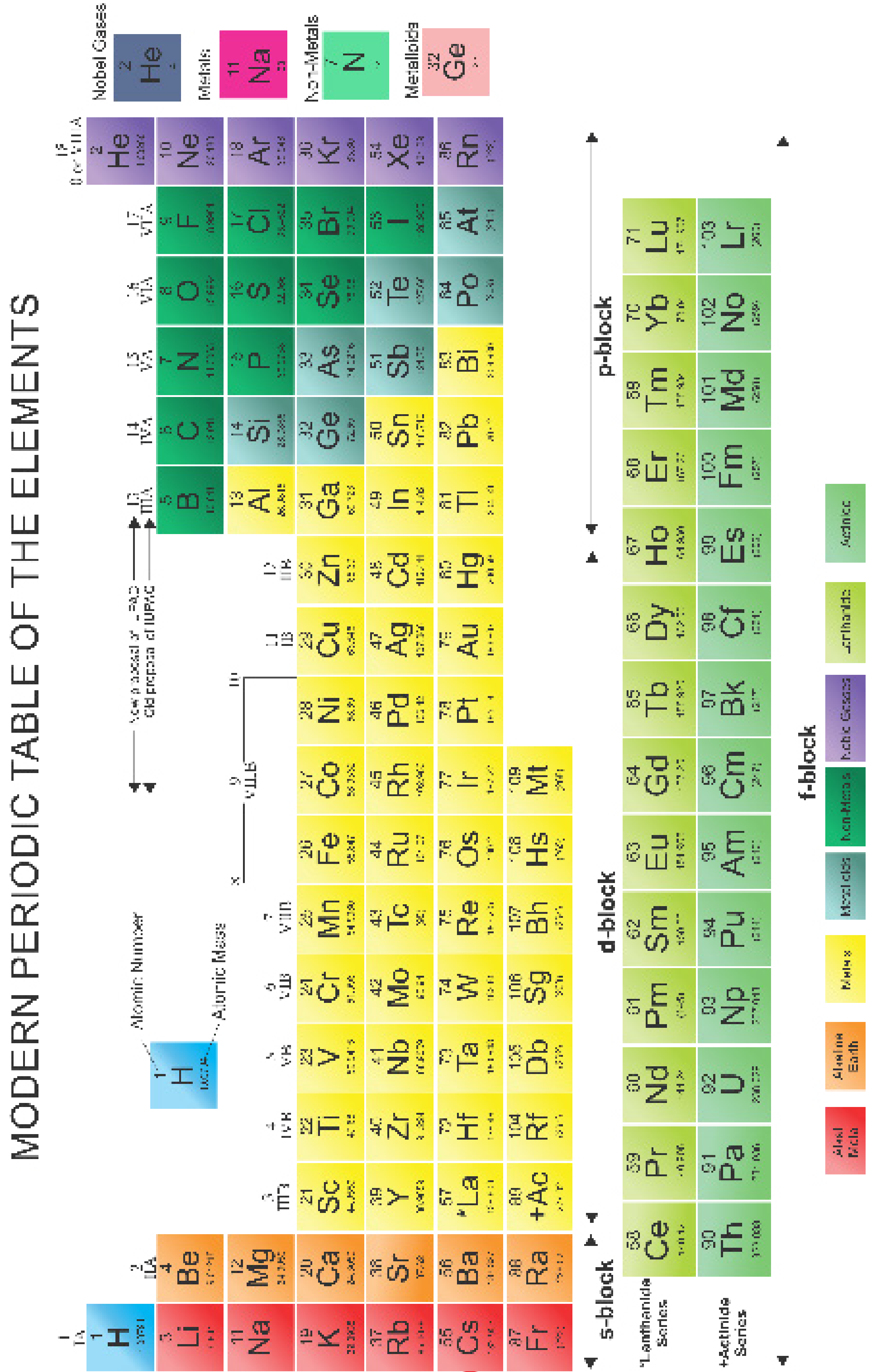
1. Group and Periods

Elements with similar properties are placed in vertical columns called Groups. There are eight groups ,which are usually numbered by Roman numerals I to VIII.Each group is divided into two subgroups, designated as A and B subgroups. The subgroups, containing the representative or normal elements are labelled as A subgroups, whereas B subgroup contain less typical elements, called transition elements and are arranged in the centre of the periodic table. The horizontal rows of the periodic table are called Periods.The essential features of periods are as follows:

a) There are 7 periods in the periodic table numbered by Arabic numerals 1 to 7.
b) The period 1 contains only two elements, hydrogen and helium.

c) The periods 2 and 3 contain eight elements each and are called short periods. All the elements in these periods are representative elements and belong to A subgroup . In these periods, every eighth element resembles in properties with the first element. As lithium and beryllium in the 2nd period resemble in most of their properties with sodium and magnesium of the 3rd period, respectively. Similarly, boron and aluminium both show oxidation state of +3, fluorine in 2nd period has close resemblances with chlorine of 3rd period.

Table 1.1 MODERN PERIODIC TABLE OF THE ELEMENTS



d) The periods 4 and 5 are called long periods. Each long period consists of eighteen elements. Out of these, eight are representative elements belonging to A subgroup similar to second and third periods. Whereas the other ten elements, placed in the centre of the table belong to B subgroups and are known as transition elements. In these periods, the repetition of properties among the elements occurs after 18 elements. As after $_{19}$K (having atomic number 19) the next element with similar properties is $_{37}$Rb.

e) The period 6 is also a long period, which contains thirty-two elements. In this period there are eight representative elements, ten transition elements and a new set of fourteen elements called Lanthanides as they start after $_{57}$La. Lanthanides have remarkably similar properties and are usually shown separately at the bottom of the periodic table.

f) The period 7 is incomplete so far. It contains only two normal elements $_{87}$Fr and $_{88}$Ra, ten transition elements and fourteen inner transition elements. The inner transition elements of this period are called Actinides, as they follow $_{89}$Ac.The actinides are also shown at the bottom of the periodic table under the Lanthanides. Due to their scarcity, the inner transition elements are also called rare earth elements.

2. Some More Families in the Periodic Table:

While studying about periods you have noticed that certain rows of elements with similar properties have assigned common names such as transition elements, Lanthanides, Actinides or Rate Earth elements.Similarly, due to their peculiar characteristics, some typical elements belonging to sub-groups A, have also been assigned family names. For example,elements of the group IA are called Alkali Metals, because of their property to form strong alkalies with water.

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

Similarly,due to their presence in Earth's crust and alkaline character,the elements of group IIA are known as Alkaline Earth Metals. Another important family in the periodic table is Halogen family. The name "Halogens" is given to the elements of group VIIA, due to their salt forming properties. As the gases of group VIIIA 'are least reactive they are called "Noble Gases",These family names are useful for a quick recognition of an element in the periodic table.

3. Blocks in the Periodic Table

Elements in the periodic table can also be classified into four blocks. This classification is based upon the valence orbital of the element involved in chemical bonding. According to this classification, elements of IA and IIA subgroups are called s-block elements because their valence electrons are available in s orbital.The elements of IIIA to VIIIA subgroups (except He) are known as p-block elements as their valence electrons are present in p orbital. Similarly in transition elements, electrons in d-orbital are responsible for their valency hence they are called d-block elements. For Lanthanides and Actinides valence electrons are present in f- orbital hence these elements are called f-block elements. This classification is quite useful in understanding the chemistry of elements and predicting their properties especially the concept of valency or oxidation state.

4. Metals, Non-metals and Metalloids

Another basis for classifying the elements in the periodic table is their metallic character. Generally, the elements on the left hand side, in the centre and at the bottom of the periodic table are metals, while the non-metals are in the upper right corner of the table. Some elements, especially lower members of groups, III A, IVA and VA(as shown in Table 1.1) have properties of both metals as well as non-metals. These elements are called semi-metals or metalloids. In the periodic table elements of groups IVA to VIIIA, at the top right hand corner above the stepped line, are non-metals. The elements just under the "steps' such as Si, As, and Te are the metalloids. All the remaining elements, except hydrogen, are metals.

1.3 PERIODIC TRENDS IN PHYSICAL PROPERTIES

As you have studied so far that in modern periodic table the elements are arranged in ascending order of their atomic numbers and their classification in groups and periods is based on the similarity in their properties. Yet, due to the gradual increase in the number of protons in the nucleus and electrons in outer shells the physical and chemical properties of the elements steadily vary within a group or a period. Here, we study some trends in physical properties.

1. ATOMIC SIZE

a) Atomic Radius:

Atoms are so small that it is impossible to see an atom even with a powerful optical microscope. The size of a single atom therefore cannot be directly measured. However, techniques have been developed which can measure the distance between the centres of two bonded atoms of any element. Half of this distance is considered to be the radius of the atom.

In the periodic table, the atomic radius increases from top to bottom within a group due to increase in atomic number . This is because of the addition of an extra shell of electrons in each period. In a period, however, as the atomic number increases from left to right, the atomic radius decreases . This gradual decrease in the radius is due to increase in the positive charge in the nucleus . As the positive nuclear charge increases, the negatively charged electrons in the shells are pulled closer to the nucleus.

Thus, the size of the outermost shell becomes gradually smaller. This effect is quite remarkable in the elements of longer periods in which “d” and “f ” subshells are involved. For example, the gradual reduction in the size of Lanthanides is significant and called Lanthanide Contraction.

b) Ionic Radius:

When a neutral atom loses one or more electrons, it becomes a positive ion. The size of the atom is decreased in this process because of the two reasons.

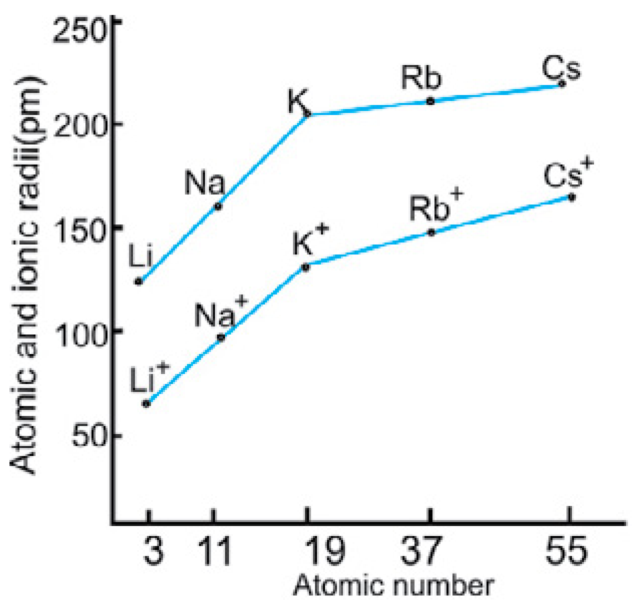


Fig .1.1. Atomic and ionic radii of alkali metals

First the removal of one or more electrons from a neutral atom usually results in the loss of the outermost shell and second, the removal of electrons causes an imbalance in proton-electron ratio. Due to the greater attraction of the nuclear charge, the remaining electrons of the ion are drawn closer to the nucleus.

Thus, a positive ion is always smaller than the neutral atom from which it is derived. The radius of Na is 157pm and the radius of Na^+ is 95pm. On the contrary, a negative ion is always bigger than its parent atom.

The reason is that addition of one or more electrons in the shell of a neutral atom enhances repulsion between the electrons causing expansion of the shell.

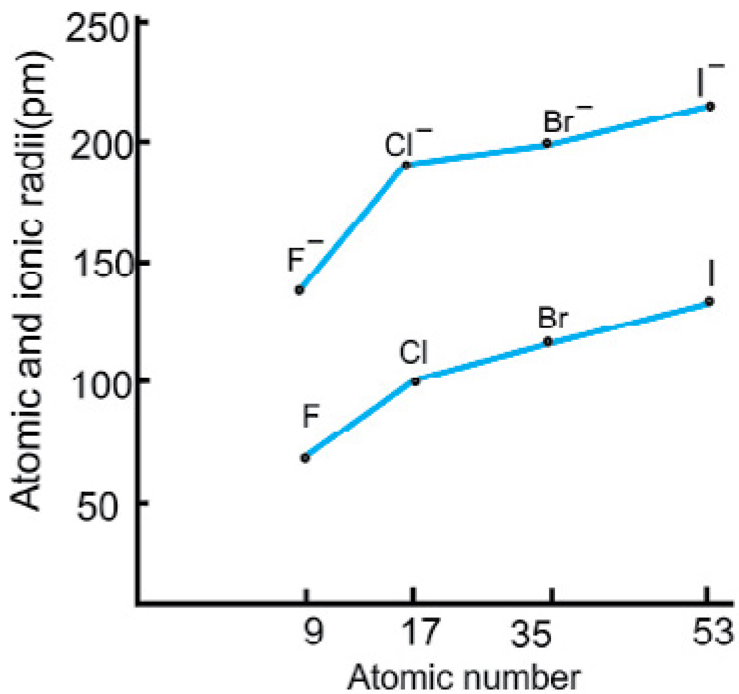


Fig .1.2. Atomic and ionic radii of alkali metals.

Thus, the radius of fluorine atom is 72pm and that of the fluoride ion (F) is 136pm.

In a group of the periodic table, similar charged ions increase in size from top to bottom. Whereas within a period, isoelectronic positive ions show a decrease in ionic radius from left to right, because of the increasing nuclear charge.

The same trend is observed for the isoelectronic negative ions of a period; ionic size decreases from left to right. The variations in atomic and ionic radii of alkali metals and halogens are shown in Fig 1.1 and Fig.1.2.

2. Ionization Energy

The ionization energy of an element is the minimum quantity of energy which is required to remove an electron from the outermost shell of its isolated gaseous atom in its ground state. The ionization energy of sodium is 496kJ mol^{-1}.

$$Na_{(g)} \longrightarrow Na^{+}_{(g)} + e^{-} \qquad i = 496\ kJ\ mol^{-1}$$

Elements with greater number of electrons have more than one values of ionization energy. So for magnesium, the first ionization energy value is the energy required to remove the first electron:

$$Mg_{(g)} \longrightarrow Mg^{+}_{(g)} + e^{-} \qquad i_1 = 738\ kJ\ mol^{-1}$$

Similarly, the second ionization energy value is the energy required to remove the second electron.

$$Mg^{+}_{(g)} \longrightarrow Mg^{++} + e^{-} \qquad i_2 = 1451 kJ\ mol^{-1}$$

a) Variation Within a Group:

The factors upon which the ionization energy of an atom mainly depends are magnitude of nuclear charge, size of the atom, and the "shielding effect". The shielding effect is actually the repulsion due to electrons in between the nucleus and the outermost shell.

This effect increases, as the size of the atom increases due to addition of an extra shell successively in each period hence more number of electrons shields the nucleus.

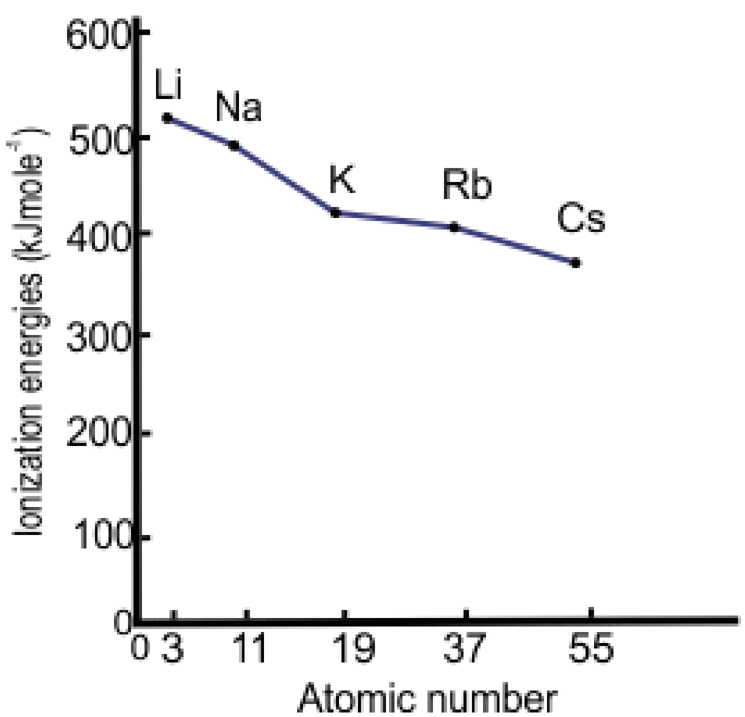


Fig. 1.3 Ionization energies of alkali metals

Going down in a group, the nuclear charge increases but as the size of the atom and the number of electrons causing the shielding effect also increases therefore ionization energy decreases from top to bottom. That is why in alkali metals, for example, it is easier to remove an electron from caesium atom than from lithium atom. The change in ionization energies of IA elements is shown in Fig. 1.3.

b) Variation Across a Period:

Generally, smaller the atom with greater nuclear charge, more strongly the electrons are bound to the nucleus and hence higher the ionization energy of the atom. By moving from left to right in a period, the outer shell remains the same, while the nuclear charge increases effectively that makes the removal of an electron difficult and hence the value of ionization energy increases.

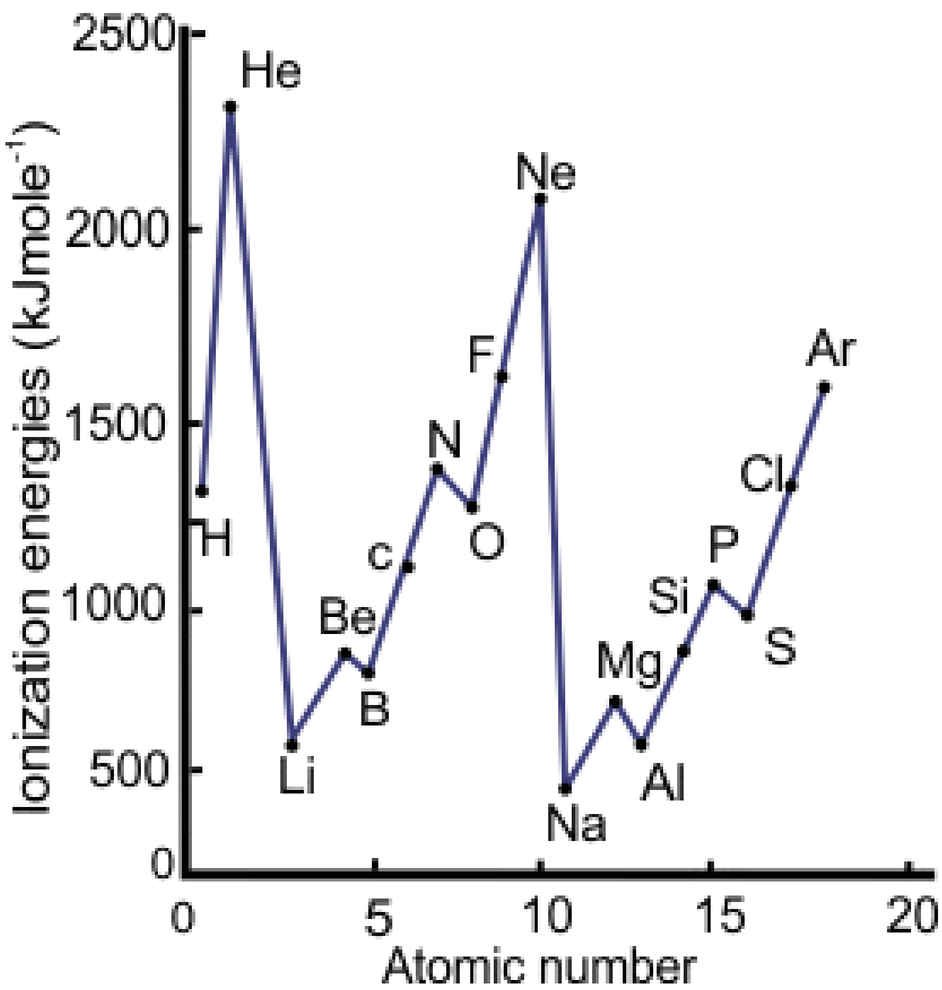


Fig. 1.4 Ionization energies of elements of short periods.

Although, the number of electrons also increases in this case but the shielding is not very effective within the same shell. The trend of ionization energies of short periods is shown in Fig.1.4 The figure also reveals that inert gases have the highest values of ionization energy because due to complete outermost shell in them, the removal of electron is extremely difficult.

3. Electron Affinity (E.A)

The electron affinity is the energy released or absorbed, when an electron is added to a gaseous atom to form a negative ion.

$$F_{(g)} + e^- \longrightarrow F^-_{(g)} \qquad E.A = -337 \text{ kJ mol}^{-1}$$

Energy is usually released when electronegative elements absorb the first electron and E.A. in such cases is expressed in negative figures, as in the case of halogens. When a second electron is added to a uninegative ion, the incoming electron is repelled by the already present negative charge and energy is absorbed in this process.

$$O_{(g)} + e^- \longrightarrow O^-_{(g)} \qquad E.A_1 = -141 \text{ kJ mol}^{-1}$$

$$O^-_{(g)} + e^- \longrightarrow O^{2-}_{(g)} \qquad E.A_2 = +780 \text{ kJ mol}^{-1}$$

The absorbed energy is expressed as the electron affinity in positive figures. Electron affinity depends upon size of the atom, nuclear charge and vacancies in the outermost shell. Relatively smaller atoms with one or two vacancies in the outermost shell show large values of electron affinity.

Electron affinity generally increases with increasing atomic number within a period and decreases from lighter to heavier elements in a given group of the periodic table. Knowledge of electron affinities can be combined with the knowledge of ionization energies to predict which atoms can easily lose electrons and which can accept electrons more readily.

4. Metallic and Non-Metallic Character

It has already been discussed in this chapter that elements of periodic table can be divided into metals, non-metals and metalloids. Chemically all the elements which have a tendency to form positive ions by losing electrons are considered metals. All metals are good conductor of heat and electricity. A characteristic property of metals is that they form basic oxides which give bases when dissolved in water.

$$Na_2O\,(s) + H_2O\,(l) \longrightarrow NaOH\,(aq)$$

As it becomes easier to remove the electron of an atom bigger in size, therefore metallic character increases from top to bottom in a given group of elements. On the contrary, it decreases from left to right across a period. The elements of group VIIA (the halogens) are least metallic in nature.The elements which gain electrons and form negative ions are called non-metals. All the gases are non-metals. The non-metals are normally poor conductor of heat and electricity. Non-metals form acidic oxides which yield acids on dissolving in water.

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

Non-metallic character of an element, decreases as the atomic size increases. Therefore in a group of non-metals like halogens, the non-metallic character decreases from top to bottom. The member at the top, fluorine, is the most non-metallic element of the periodic table. This trend can also be verified in the elements of groups VA and VIA. Nitrogen and oxygen are pure non-metals and usually exist in gaseous state while bismuth and polonium, the members at the bottom of these groups, are fairly metallic in nature.

5. Melting And Boiling Points

Melting and boiling points of elements tell us something about how strong the atoms or molecules in them are bound together.

(a) Variation in a Period

Across the short periods, the melting and boiling points of elements increase with the number of valence electrons upto group IVA and then decrease upto the noble gases. The melting points of group IA elements are low because each atom in them provides only one electron to form a bond with other atom. Melting points of group IIA elements are considerably higher than those of group IA elements because each atom in them provides two binding electrons.

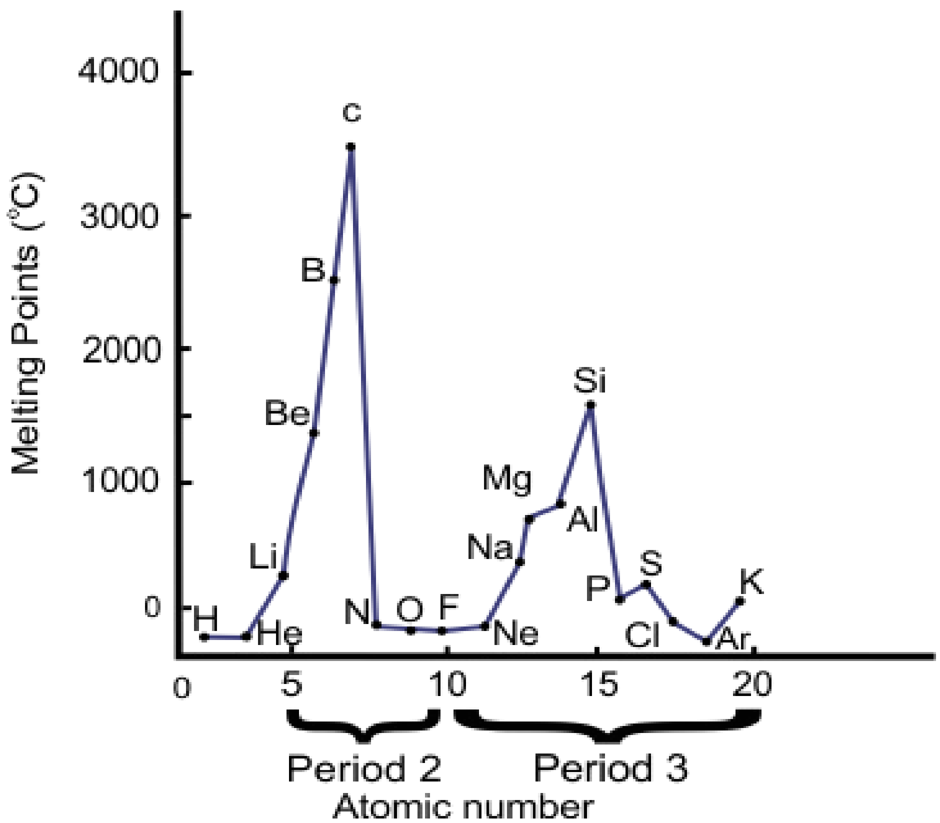


Fig. 1.5 Variation of melting points with atomic number

Since carbon has the maximum number of binding electrons, thus it has a very high melting point in diamond in which each carbon is bound to four other carbon atoms. In general, the elements which exist as giant covalent structures have very high melting points, Fig. 1.5.

An important change occurs when we move from group IVA to groups VA, VIA, VIIA as the lighter elements of these group exist as small, covalent molecules, rather than as three dimensional lattices. For instance, nitrogen,oxygen and fluorine exist as individual molecules which have very weak intermolecular forces between them. Consequently, their melting and boiling points are extremely low.

(b) Variation in a Group

The melting and boiling points of IA and IIA group elements decrease from top to bottom due to the increase in their atomic sizes. The binding forces present between large sized atoms are relatively weaker as compared to those between smaller atoms, Fig. 1.6.

For elements of group VIIA, which exist in the form of molecules, the melting and boiling points increase down the group, Fig. 1.7. This is because large molecules exert stronger force of attraction due to their higher polarizabilities.

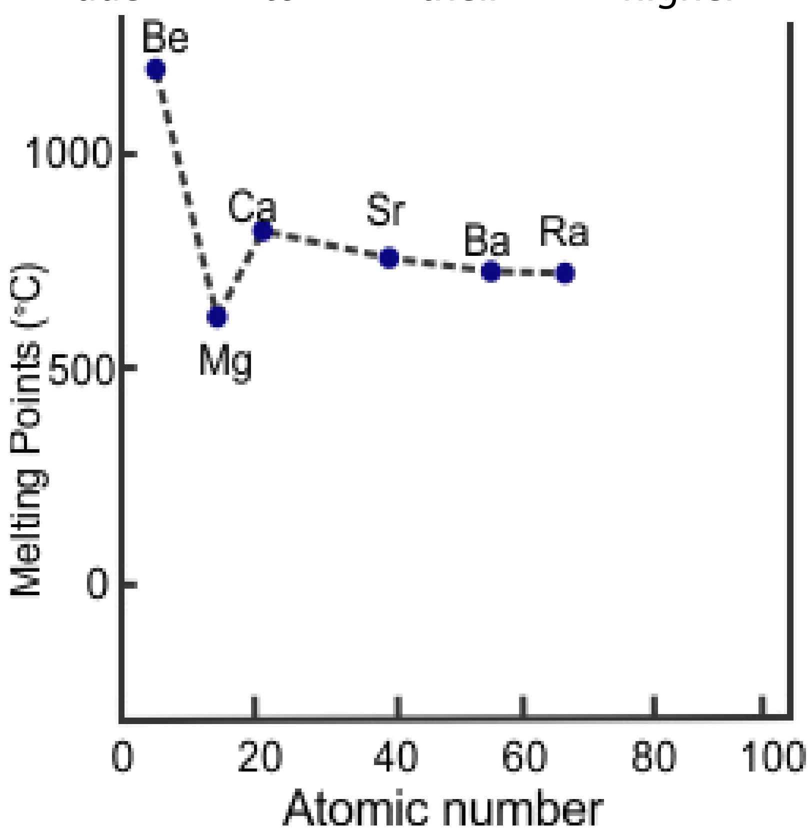


Fig.1.6 Melting points of Group IIA elements.

6. Oxidation State

The oxidation state of an atom in a compound is defined as the charge (with the sign), which it would carry in the compound. In ionic compounds, it is usually the number of electrons gained or lost by the atom. As in the case of sodium chloride, the oxidation states of sodium and chlorine are + 1 and -1, respectively. In covalent compounds, it is decided on the basis of the difference in their relative electronegativities. For example, $SnCl_4$ is a covalent compound. The oxidation state of tin is + 4 and that of chlorine is -1. The oxidation state of an element is zero in its free state. The oxidation state of a typical element is directly or indirectly related to the group number to which the element belongs in the periodic table. The elements of group IA to IVA have the same oxidation states as their group numbers are. Just as B, Al and Ga belong to group IIIA, hence, they always show oxidation state of +3. So, for the elements

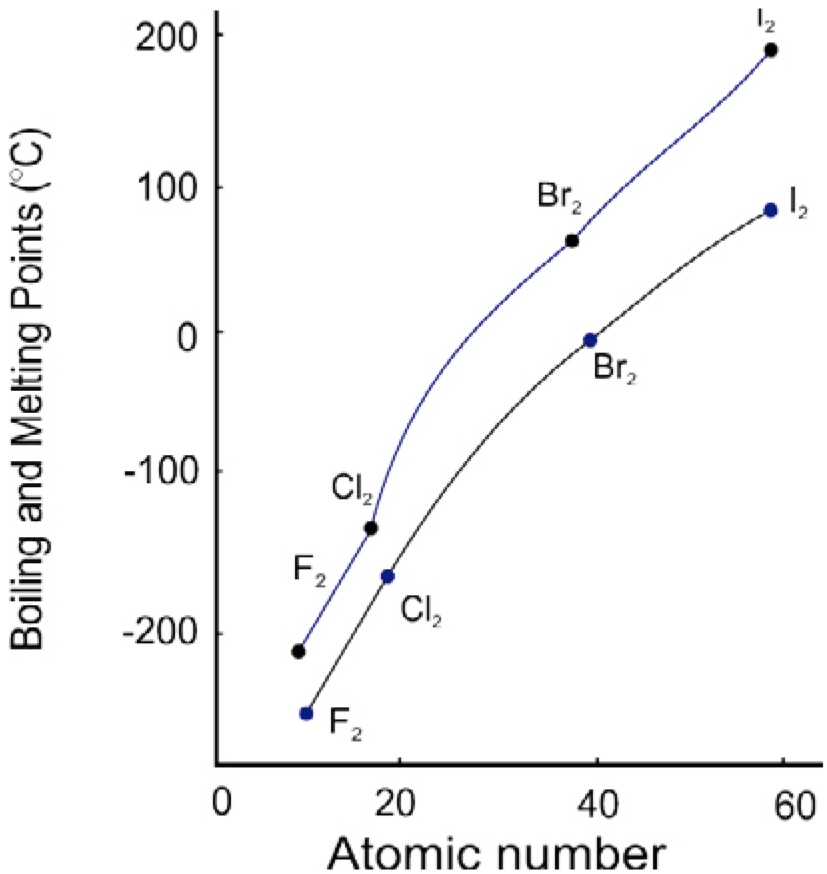


Fig.1.7 . Bloiling (.--------) and melting points(;———) of halogens.

of these groups, the oxidation state is same as the number of electrons present in the valence shells of the elements. However, for the elements of group VA, the oxidation states are either the number of electrons present in the valence shell (which is same as their group number) or the number of vacancies available in these shells.

For example, N, P, As and Sb frequently show +3 as well as +5 oxidation states. Elements of group VIA show almost similar behaviour. In H_2SO_4, sulphur shows the oxidation state of +6, which is the number of electrons in its outermost shell whereas its oxidation state is -2 in H_2S, which is the number of vacancies in the shell.
In group VIIA elements oxidation state is mostly - 1, which is again the number of vacancies in their outermost shells. Group VIIIA elements, which are also called zero group elements, usually show zero oxidation state because there is no vacancy in their outermost shells.

Transition elements, which are shown in B subgroups of the periodic table, also show the oxidation states equal to their group number as it can be seen for Cu(I), Zn(II), V(V), Cr(VI) and Mn (VII). But due to greater number of valence electrons available in partly filled d-orbitals these elements usually, show more than one oxidation states in their compounds.

7 Electrical Conductance

One of the most familiar properties of metals is their ability to conduct electricity. This property is mainly due to the presence of relatively loose electrons in the outermost shell of the element and ease of their movement in the solid lattice. The electrical conductance of metals in groups IA and IIA, generally increases from top to bottom. However, the trend is not free from the individual variation in different atoms. Metals of group IB, which are known as coinage metals, have extraordinary high values of electrical conductance. Non-metals, on the other hand, especially of groups VIA and VIIA, show such low electrical conductance that they can be considered as nonconductors.

In the series of transition metals, the values of electrical conductance vary so abruptly that no general trend can be assigned to them. Carbon, in the form of diamond is non-conductor because all of its valence electrons are tetrahedrally bound and unable to move freely, while in the form of graphite, carbon is fairly good conductor because one of its four valence electrons is relatively free to move. The lower elements of group IVA, tin and lead, are fairly good conductors and their values of electrical conductivity are comparable with those of their counterparts in group IA.

8 Hydration Energy

The hydration energy is the heat absorbed or evolved when one mole of gaseous ions dissolve in water to give an infinitely dilute solution. For example, when one mole of gaseous hydrogen ions are dissolved in water resulting an infinitely dilute solution, a large amount of heat is liberated:

$$H^+(g) + H_2O(\ell) \longrightarrow H_3O^+(aq) \qquad \Delta H_h = -1075 \text{ kJ mol}^{-1}$$

Hydration energies of a few negative and positive ions are shown in the Table 1.2. It is evident from the table that hydration energies highly depend upon charge to size ratio of the ions. For a given set of ions, for example of group IA, charge to size ratio decreases from top to bottom in a group, the hydration energy also decreases in the same fashion. On the contrary, the hydration energy increases significantly by moving from left to right in a period as the charge to size ratio increases, as found in the metal ions of third period.

Table 1.2 Hydration Energies of Ions

Ion	H_h kJ mol^{-1}
Li^+	-499
Na^+	-390
K^+	-305
Mg^{2+}	-1891
Ca^{2+}	-1562
Al^{3+}	-4613
F^-	-457
Cl^-	-384
Br^-	-351
I^-	-307

1.4 PERIODIC RELATIONSHIP IN COMPOUNDS

a) Halides:

Halides are the binary compounds which halogens form with other elements. The physical properties of halides are largely determined by the nature of bonding present in them. On this basis, halides can be classified into twogeneral classes: ionic and covalent.In between the two, there is another class of halides in which the halogen atom acts as a bridge between the two atoms of the other element, such halides are termed as “Polymeric” halides.Strongly electropositive elements, having greater electronegativity difference with halogen atom, form ionic halides.The halides of group IA are considered purely ionic compounds, which are high melting point solids. Such halides have three-dimensional lattices consisting of discrete ions.

Table 1.3 Melting Points of Chlorides of Period Three Elements and Their Bonding Character

Name of compounds	Property	
	Melting point (°C)	Type of bonding
NaCl	808	Ionic
$MgCl_2$	715	Partly ionic
$AlCl_3$	192	Partly ionic
$SiCl_4$	-68	Partly covalent
PCl_3	-93	Partly covalent
S_2Cl_2	-80	Partly covalent

Among the pure ionic compounds, the fluorides have the highest lattice energies due to the small size of fluoride ion. Thus for ionic halides, the fluorides have the highest melting and boiling points which decrease in the order: fluoride > chloride > bromide > iodide. Less electropositive elements, such as Be, Ga and Al form polymeric halides having partly ionic bonding with layer or chain lattices.

The lattice of $SiCl_4$ consists of discrete molecules, which are highly polar. The bonds in PCl_3, and S_2Cl_2 are less polar than those of $SiCl_4$. On moving across the periodic table from left to right, the electronegativity difference reduces and the trend shifts towards covalent halides. The gradual change in bond type and melting points of the chlorides on moving across period 3 of the periodic table is shown in Table. 1.3.

As the intermolecular forces in covalent halide molecules are weak van der Waal's forces so they are often gases, liquids or low melting point solids. Physical properties of covalent halides are influenced by the size and polarizability of the halogen atom.Iodides, as being the largest and more polarizable ions, possess the strongest van der Waal's forces and therefore have higher melting and boiling points than those of other covalent halides.

The variation in bonding character is also present in descending from top to bottom in the halogen group. In general, for a metal the order of decreasing ionic character of the halides is: fluoride > chloride > bromide > iodide. For example, AlF_3 is purely ionic compound having melting point 1290°C and fairly a good conductor, whereas AlI_3 is predominantly covalent with melting point 198°C and electrically a non-conductor. In case of an element forming more than one halides, the metal halide in its lower oxidation state tends to be ionic, while that in the higher oxidation state is covalent. For example, $PbCl_2$ is mainly ionic and $PbCl_4$ is fairly covalent. This can again be explained by the high polarizing power of Pb^{4+} as compared to that of Pb^{2+}.

b) Hydrides

The binary compounds of hydrogen with other elements are called hydrides. According to the nature of bonding, hydrides may be broadly classified into three classes: ionic, covalent and intermediate. The elements of group IA and the heavier members of group IIA form ionic hydrides, which contain H^- (Hydride) ion.These hydrides are crystalline solid compounds, with high melting and boiling points and which conduct electricity in molten state.

The tendency towards covalent character increases by moving from left to right in the Periodic Table. Hydrides of beryllium and magnesium represent the class of intermediate hydrides. Their properties are in between the ionic and covalent hydrides. They have polymeric structures and covalent nature, Table 1.4.

Table 1.4. Hydrides of the Elements of IA to VIIA and IIB Subgroups.

IA	IIA	IIB	IIIA	IVA	VA	VIA	VIIA
LiH	BeH_2		BH_3	CH_4	NH_3	H_2O	HF
NaH	MgH_2		AlH_3	SiH_4	PH_3	H_2S	HCl
KH	CaH_2	ZnH_2	GaH_3	GeH_4	AsH_3	H_2Se	HBr
RbH	SrH_2	CdH_2	InH_3	SnH_4	SbH_3	H_2Te	HI
CsH	BaH_2			PbH_4	BiH_3		
IONIC		INTERMEDIATE		COVALENT			

The covalent hydrides are usually gases or volatile liquids. They are non-conductors and dissolve in organic solvents. Their bond energies depend on the size and the electronegativity of the element. Stability of covalent hydrides increases from left to right in a period and decreases from top to bottom in a group.Fluorine forms the most stable hydride and the least stable are those of thallium, lead and bismuth. These hydrides are formed by elements with electronegativity values greater than 1.8 (Pauling Scale). Since the electronegativity of hydrogen is 2.1, most of these hydrides have polar covalent bonds in which hydrogen is carrying a slight positive charge.

On moving from left to right across a period the electronegativity of the other element increases and the hydrogen-element bond becomes more polar. Due to high polarity the hydrides like H_2O and HF are capable of forming hydrogen bonds between their molecules. The boiling points of covalent hydrides generally increase on descending a group as shown in Table 1.5, except the hydrides like H_2O, HF and NH_3 which, due to hydrogen bonding, have higher boiling points than might be expected.

Table. 1.5. Melting and Boiling points of Hydrides of Groups IV A and VI A

Hydrides	Property	
(Group IVA)	Melting point (°C)	Boiling point' (°C)
CH_4	-184	-164
SiH_4	-185	-112
GeH_4	-165	-90
SnH_4	-150	-52
(Group VIA)		
H_2O	0.00	100
H_2S	-82.9	-59.6
H_2Se	-65.7	-41.3
H_2Te	-48	-1.8

c) Oxides

Oxygen forms compounds, called oxides, with almost every other element in the periodic table. Since, many of these have quite unusual properties, there is an extensive and varied chemistry of the compounds of oxygen. Oxides can be classified in more than one ways: based upon the type of bonding they have as well as their acidic or basic character.We shall discuss here the classification based on their acidic or basic behaviour. In this chapter, you have already studied that metal oxides are basic in character as they yield bases in water and non-metallic oxides are acidic because they form acids in water.Basic oxides and acidic oxides react with one another to give salts, for example:

$$Na_2O_{(s)} + SO_{3\,(g)} \longrightarrow Na_2SO_{4\,(s)}$$

There is a third type of oxides, which show both acidic and basic properties, these oxides are called amphoteric oxides. The classification of elements which form oxides of acidic or basic properties is shown in Table 1.6.

Table 1.6 Classification of Oxides Based on their Acid and Base Character

IA	IIA	IIB	IIIA	IVA	VA	VIA	VIIA
Li	Be		B	C	N	O	F
Na	Mg		Al	Si	P	S	Cl
K	Ca	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Cd	In	Sn	Sb	Te	I
Cs	Ba	Hg	Tl	Pb	Bi	Po	At
BASIC				AMPHOTERIC		ACIDIC	

The oxides of alkali and alkaline earth metals except beryllium are basic and contain O^{2-} ions. The O^{2-} ion has high affinity for proton and cannot exist alone in an aqueous solution. Therefore, it immediately takes proton from water and forms OH^- ion. Oxides of nonmetallic elements i.e. of C, N, P and S are acidic in nature. They generally dissolve in water to produce acidic solutions. Oxides of relatively less electropositive elements, such as BeO, Al_2O_3, Bi_2O_3 and ZnO are amphoteric and behave as acids towards strong bases and as bases towards strong acids.

$$ZnO(s) + H_2SO_4\,(aq) \longrightarrow ZnSO_4\,(aq) + H_2O\,(l)$$

$$ZnO\,(s) + 2NaOH\,(aq) + H_2O\,(l) \longrightarrow Na_2[Zn(OH)_4]\,(aq)$$

In a given period, the oxides progress from strongly basic through weakly basic,amphoteric, and weakly acidic to strongly acidic, e.g. Na_2O, MgO, Al_2O_3, P_4O_{10} , SO_3 , Cl_2O_7.The basicity of main group metal oxides increases on descending a group of the periodic table, (e.g. $BeO<MgO<CaO<SrO<BaO$), though the reverse trend is observed in the transition metal oxides. The oxidation state of the metal also affects the acid/base character of its oxide. The acidity increases with increasing oxidation state (e.g. the acidity of $MnO < Mn_2O_3 < MnO_2 < Mn_2O_7$).

1.5 THE POSITION OF HYDROGEN

Although, it is not a metal but in most of the modern versions of periodic table, hydrogen is placed at the top of the group IA. This is because of the fact that some of the properties of hydrogen resemble with those of alkali metals. Like alkali metals hydrogen atom has one electron in Is sub-shell, which it can lose to form H^+ .

Both hydrogen and alkali metals have a strong tendency to combine with electronegative elements such as halogens. Similar to alkali metals hydrogen also forms ionic compounds, which dissociate in water. However, hydrogen is also markedly different from alkali metals. For example, hydrogen is a non-metal in true sense. It does not lose electron as easily as most of the alkali metals do. Unlike alkali metals molecular hydrogen exists in open atmosphere.

Hydrogen resembles halogens in certain respects and can be placed at the top of VIIA group in the periodic table. Hydrogen is a gas like most of the halogens and is stable in diatomic form such as F_2, Cl_2 and Br_2. As required by halogens, hydrogen also needs one electron to complete its outermost shell. By accepting one electron hydrogen forms H^- (Hydride ion) similar to F^- , Cl^- and Br^-. Both hydrogen and halogens form stable ionic compounds with alkali metals. However, hydrogen differs from halogens as well. By losing its only electron, hydrogen forms H^+ but halogens do not form positive ions. Combining with oxygen, hydrogen forms very stable oxides while halogens lack this property.

Some of the characteristic properties of hydrogen also resemble with those of group IVA elements such as C and Si, etc. For example, valence shell of hydrogen is half filled like those of group IVA elements. Both, hydrogen and group IV elements combine with other elements through covalent bonding. Like carbon, hydrogen also possesses remarkable reducing properties.

$$CuO\,(s) + H_2O\,(l) \longrightarrow Cu\,(s) + H_2O\,(l)$$

$$SnO_2\,(s) + C\,(s) \longrightarrow Sn\,(s) + CO_2\,(g)$$

Hydrogen also shows marked differences with carbon and rest of the group members. For example, carbon and silicon form long chain compounds, when their atoms combine with each other, while hydrogen do not form such compounds. Similarly, carbon can simultaneously form bonds with more than one elements, whereas hydrogen due to having only one electron can combine with only one element at a time.

Some of the properties of hydrogen are similar to those of the elements of certain groups, as discussed above, but this is a fact that hydrogen is a unique element whose properties do not match exactly with any of the groups in the periodic table. However, due to partial resemblance in properties with alkali metals and monovalent nature, hydrogen is usually placed at the top of elements in group IA.

Key Points

1. Although a number of chemists attempted to classify the elements but Dmitri Mendeleev gave the most useful and comprehensive classification.
2. In Mendeleev's periodic table the elements were arranged according to the ascending order of their atomic masses.
3. The modern periodic law states "if the elements are arranged in ascending order of their atomic numbers, their chemical properties repeat in a periodic manner."
4. In modern periodic table elements with similar properties are placed in eight vertical columns called groups. Each group is divided into two subgroups A and B. Normal or typical elements are placed in subgroups A and transition elements are placed in subgroups B.
5. The seven horizontal rows of the periodic table are called "periods".
6. Metals of subgroups IA and IIA are called Alkali metals and Alkaline-earth metals, respectively. Members of subgroup VIIA are called halogens.
7. Due to their less reactivity the elements shown in subgroup VIII A are called noble gases.
8. Elements of periodic table can also be classified into s-block, p-block, d-block and f-block elements depending upon the valence orbital which is in the process of completion.
9. Elements of periodic table can also be divided into metals, non-metals and metalloids depending upon their properties.
10. Atomic radii increase from top to bottom in a group and decrease along a period.
11. Positive ions are always smaller than their parent atoms while the negative ions are usually larger than the atoms from which they are formed.
12. Ionization energies increase along a period and decrease down the group.
13. Electron affinities generally increase with increasing atomic number within a period and decrease from lighter to heavier elements in a given group.
14. Metallic character of elements increases down the group and decreases along a period.
15. The oxidation state of a typical element is directly or indirectly related to the group number to which the element belongs in the periodic table.
16. The electrical conductance of an element depends upon the number of free or moveable electrons.
17. There are three types of halides: ionic, polymeric and covalent. Halides of group IA are ionic in nature, have three dimensional lattices with high melting and boiling points.
18. There are three types of hydrides formed by the elements of periodic table: ionic, intermediate and covalent.
19. Highly polar hydrides show hydrogen bonding in them.
20. Oxides may be divided on the basis of their acidic, basic or amphoteric character.

21. Metallic oxides are basic in character, non-metallic oxides are acidic in character and oxides of less electropositive elements like Zn and Pb are amphoteric.
22. Hydrogen is unique element of the periodic table. Due to similarities in properties it can be placed at the top of group IA or IVA or VIIA.

EXERCISE

Q1. Fill in the blanks

(i) Mendeleev in his periodic table, arranged the elements according to their atomic_____________.
(ii) Vertical columns in modern periodic table are called__________and horizontal rows are called________.
(iii) Members of group VIIA are called ________ and alkali metals is the family name of_________ group members.
(iv) Metals form____________ oxides and non-metals form__________ oxides.
(v) Hydrogen can be placed above the groups________ of the periodic table.
(vi) Shielding effect is actually the________________ due to electrons in between the nucleus and the outermost shell.
(vii) Noble gases have the_____________values of ionization energy due to their complete outermost shells.
(viii) When a second electron is added to a uni-negative ion, the incoming electron is ___________ by the already present negative charge.
(ix) Due to having partly filled d-orbitals ______________metals usually show variable valency.
(x) Melting and boiling points of halogens__________down the group.

Q2. Indicate True or False

(i) In Mendeleev's periodic table elements Be, Mg, Zn and Cd are placed in the same group.
(ii) The second and third periods contain eighteen elements each.
(iii) Alkaline earth metals are present in Group IIA.
(iv) Metals are present in the top right corner of the periodic table.
(v) Metalloids are present in the lower half of Groups IVA, VA and VIA
(vi) Hydrogen forms uninegative ion like halogens.
(vii) Oxidation state of an element is related to the number of period it belongs.
(viii) Diamond is a good conductor of electricity.
(ix) Melting points of halogens decrease down the group.
(x) Zinc oxide is an example of amphoteric oxide.

Q 4. What are the improvements made in the Mendeleev's periodic table ?
Q 5. How the classification of elements in different blocks helps in understanding their chemistry?
Q 6. How do you justify the position of hydrogen at the top of various groups?
Q 7. Why the ionic radii of negative ions are larger than the size of their parent atoms?
Q 8. Why ionization energy decreases down the group and increases along a period?

Q 9. Why the second value of electron affinity of an element is usually shown with a positive sign?
Q10. Why metallic character increases from top to bottom in a group of metals?
Q11. Explain the variation in melting points along the short periods.
Q12. Why the oxidation state of noble gases is usually zero?
Q13. Why diamond is a non-conductor and graphite is fairly a good conductor?
Q14. Give brief reason for the following.

a) d and f-Block elements are called transition elements.
b) Lanthanide contraction controls the atomic sizes of elements of 6th and 7th periods.
c) The melting and boiling points of the elements increase from left to the right upto the middle of s- and p-block elements and decrease onward.
d) The oxidation states vary in a period but remain almost constant in a group.
e) The hydration energies of the ions are in the following order: $Al^{3+} > Mg^{2+} > Na^{+}$
f) Ionic character of halides decreases from left to the right in a period.
g) Alkali metals give ionic hydrides.
h) Although both sodium and phosphorus are present in the same period of the periodic table yet their oxides are different in nature, Na_2O is basic while P_2O_5 is acidic in character.

CHAPTER

2

s-BLOCK ELEMENTS

Animation 2.1 : s block elements
Source and Credit: eLearn.Punjab

IN THIS CHAPTER YOU WILL LEARN

1. To write the electronic configuration of s-block elements in sequence.
2. The occurrence of group IA and IIA elements and the peculiar behaviours of lithium and beryllium.
3. The difference in the physical properties of group IA and IIA elements as well as the differences in the chemical behaviour of their compounds.
4. The commercial preparation of sodium.
5. How sodium hydroxide is commercially prepared.
6. The role of gypsum and lime in agriculture and industry.

2.1 INTRODUCTION

The s-block elements are the metals in Group IA and Group IIA of the periodic table.They are called the s-block elements because s-orbitals are being filled, in their outer most shells.The elements of group IA except hydrogen are called “Alkali metals” while those of IIA are named “Alkaline-earth metals”.

The name alkali came from Arabic, which means ‘The Ashes’. The Arabs used this term for these metals because they found that the ashes of plants were composed chiefly of sodium and potassium. Alkali metals include the elements, lithium, sodium, potassium, rubidium, caesium and francium. These are very reactive metals, produce strong alkaline solutions with water.The alkaline-earth metals are beryllium, magnesium, calcium, strontium, barium and radium.They are called alkaline-earth because they produce alkalies in water and are widely distributed in earth’s crust.

The alkali and alkaline-earth metals include the most reactive electropositive elements and a study of their electronic configurations will help in understanding their properties.

Animation 2.2 : Haloform_reaction
Source and Credit: wiki

2.1.1 Electronic Configurations of s-Block Elements.

Alkali Meta1

Alkali metals have only one electron in 's' orbital of their valence shell. All alkali metals lose their one electron of the valence shell to form monopositive ions M^+ because their ionization energy values are very low. They form ionic compounds and show +1 oxidation state. The electronic configurations and some physical constants of alkali metals are given in Table2.1

Table 2.1 Electronic Configurations and Physical Constants of Alkali Metals

Properties	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Electronic configurations	$1s^2 2s^1$	$[Ne]3s^1$	$[Ar]4s^1$	$[Kr]5s^1$	$[Xe]6s^1$
Ionization energy (kJ/ mol)	520	496	419	403	376
Electron affinity (kJ/mol)	60	53	48	47	48
Electronagetivity	1.0	0.9	0.8	0.8	0.7
Atomic radius	123	158	203	216	235
Ionic radius of 1+ion (pm)	60	95	133	148	169
Melting points (°C)	187.0	97.5	63.6	39.0	28.5
Boiling points (°C)	1325	889	774	688	690
Density gm/cm^3 at (20°C)	0.53	0.97	0.86	1.53	1.9
Heat of hydration (kJ/mol)	505	475	384	345	310

Alkaline-Earth Metals

Alkaline earth metals have two electrons in 's' orbital of their valence shell. All alkaline earth metals lose their two electrons to form dipositive ions M^{2+}, because their ionization energy values are low. They form ionic compounds and show + 2 oxidation state.

The electronic configurations and some physical constants of alkaline earth metals are given in Table 2.2.

Table 2.2 Electronic Configurations and Physical Constants of Alkaline-Earth Metals

Properties	Be	Mg	Ca	Sr	Ba
Atomic number	4	12	20	38	56
Electronic configurations	$1s^2 2s^2$	$[Ne]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$
Ionization energy (kJ/ mol)	899	738	590	549	503
Electron affinity (kJ/mol)	240	230	156	168	52
Electronagetivity	1.5	1.2	1.0	1.0	0.9
Atomic radius	89	136	174	191	198
Ionic radius of 2+ion (pm)	31	65	99	113	135
Melting points (°C)	1289	649	839	769	725
Boiling points (°C)	2970	1107	1484	1384	1640
Density gm/cm^3 at (20°C)	1.85	1.74	1.55	2.6	3.5
Heat of hydration (kJ/mol)	2337	1897	1619	1455	1250

In going down a group the number of shells increase by one at each step and equal to the number of the period to which the element belongs.

Animation 2.3 : s-block elements
Source and credit: Crescen

2.1.2 Occurrence of Alkali Metals

Due to high reactivity, the alkali metals occur in nature in the combined state. None of the alkali metals is found free in nature. Sodium and potassium are abundant alkali metals and each constitute about 2.4 percent of earth's crust. Most of the earth's crust is composed of insoluble alumino-silicates of alkali metals.

Table 2.3 Common Minerals of The Most Important Alkali Metals

Name of Mineral	Chemical Formula
Lithium	
Spodumene	$LiAl(SiO_3)_2$
Sodium	
Rock Salt (Halite)	$NaCl$
Chile saltpetre	$NaNO_3$
Natron	$Na_2CO_3.H_2O$
Trona	$Na_2CO_3.2NaHCO_3.2H_2O$
Borax	$Na_2B_4O_7.10H_2O$
Potassium	
Carnallite	$KCl.MgCl_2.6H_2O$
Sylvite	KCl
Alunite(Alum Stone)!	$K_2SO_4, Al_2(SO_4)_3.4Al(OH)_3$

Animation 2.4 : Metals
Source and credit: wordpress

Lithium deposits, usually in the form of complex minerals, are widely scattered over the earth. An important commercial source of lithium is the mineral spodumene, $LiAl(SiO_3)_2$.

Small amounts of rubidium and caesium are found in potassium salts deposits. Francium has not been found in nature. It has been prepared artificially in the laboratory and is very unstable, so that a very little is known about this metal.

2.1.3 Occurrence of Alkalme-Earth Metals

Being very reactive, alkaline earth metals also do not occur in free state. The compounds of these metals occur widely in nature.

Magnesium and calcium are very abundant in earth's crust. The outer portion of the earth was originally in the form of silicates and alumino-silicates of alkaline-earth metals. Magnesium and calcium, with sodium and potassium are present in the rocks as cations.Magnesium halides are found in sea water. Magnesium is an essential constitutent of chlorophyll. Calcium phosphate, $Ca_3(PO_4)_2$ and calcium fluoride, CaF_2 are also found as minerals.Calcium is an essential constituent of many living organisms. It occurs as skeletal material in bones, teeth, sea-shells and egg shells.Radium is a rare element. It is of great interest because of its radioactive nature.

Table 2.4 Common Minerals of the Alkaline-Earth Metals

Name of Mineral	Chemical Formula
Beryllium	
Beryl	$Be_3Al_2(SiO_3)_6$
Chrysoberyl	Al_2BeO_4
Magnesium	
Magnesite	$MgCO_3$
Dolomite	$MgCO_3 . CaCO_3$
Carnallite	$KCl.MgCl_2.6H_2O$
Epsom salt	$MgSO_4.7H_2O$
Soap stone (talc)	$H_2Mg_3(SiO_3)_4$
Asbestos	$CaMg_3(SiO_3)_4$
Calcium	
Calcite (Lime Stone)	$CaCO_3$
Gypsum	$CaSO_4.2H_2O$
Fluorite	CaF_2
Phosphorite	$Ca_3(PO_4)_2$
Strontium	
Strontionite	$SrCO_3$
Barium	
Barite	$BaSO_4$

2.1.4 Peculiar Behaviour of Lithium

In many of its properties, lithium is quite different from the other alkali metals.This behaviour is not unusual, because the first member of each main group of the periodic table shows marked deviation from the regular trends of the group as a whole.

The deviation shown by lithium can be explained on the basis of its small radius and high charge density. The nuclear charge of Li^+ ion is screened only by a shell of two electrons. The so-called 'anomalous' properties of lithium are due to the fact that lithium is unexpectedly far less electropositive than sodium. Some of the more important differences of lithium from other alkali metals are listed below:

1. Lithium is much harder and lighter than the other alkali metals.
2. The lithium salts of anions with high charge density are generally less soluble in water than those of the other alkali metals, e.g. LiOH, LiF, Li_3PO_4, Li_2CO_3.
3. Lithium forms stable complex compounds, althongh complex formation generally is not a property of alkali metals. One of the stable complexes formed by lithium is $[Li(NH_3)_4]^+$
4. Lithium reacts very slowly with water, while other alkali metals react violently.
5. Lithium salts of large polarizable anions are less stable than those of other alkali metals. Unlike other alkali metals lithium does not form bicarbonate, tri-iodide or hydrogen sulphide at room temperature.
6. When burnt in air lithium forms only normal oxide, whereas the others form peroxides or superoxides.
7. Lithium hydride is more stable than the hydrides of other alkali metals.
8. Lithium compounds are more covalent, that is why its halides are more soluble in organic solvents and the alkyls and aryls of lithium are more stable than those of other alkali metals.
9. Lithium is the least reactive metal of all the alkali metals.

Animation 2.5 : ALKALI METALS
Source and Credit: Docbrown

10. When acetylene is passed over strongly heated lithium, it does not produce lithium acetylide, but other alkali metals form the corresponding metallic acetylides.

$$2Na_{(s)} + C_2H_{2(g)} \longrightarrow \underset{\text{Sodium acetylide}}{Na^+C^- \equiv C^-Na^+} + H_{2(g)}$$

11.Lithium has low electropositive character, thus its carbonate and nitrate are not so stable and therefore decompose giving lithium oxide. Carbonates of other alkali metals do not decompose.Decomposition of lithium nitrate gives different products than the nitrates of other alkali metals.

$$Li_2CO_3(s) \longrightarrow Li_2O(s) + CO_2(g)$$

$$4LiNO_3(s) \longrightarrow 2Li_2O(s) + 4NO_2(g) + O_2(g)$$

$$2NaNO_3(s) \longrightarrow 2NaNO_2(s) + O_2(g)$$

12. Lithium hydroxide when strongly heated , forms lithium oxide but the other alkali metal hydroxides do not show this behaviour.

$$2LiOH \xrightarrow{\text{Red hot}} Li_2O(s) + H_2O(l)$$

13. Lithium reacts with nitrogen to form nitride, while the other members of the group do not give this reaction.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

14. Lithium chloride has an exothermic heat of solution, whereas chlorides of sodium and potassium have endothermic heats of solution.

15. Lithium carbide is the only alkali metal carbide formed readily by the direct reaction.

2.1.5 Peculiar Behaviour of Beryllium

Beryllium is the lightest member of the series and differs from the other group IIA elements in many ways.This is due to its small atomic size and comparatively high electronegativity value. The main points of difference are:

1. Beryllium metal is almost as hard as iron and hard enough to scratch glass. The other alkaline earth metals are much softer than beryllium but still harder than the alkali metals.
2. The melting and boiling points of beryllium are higher than other alkaline earth metals. (Table 2.2)
3. As reducing agents, the group IIA metals are all powerful enough to reduce water, at least in principle. However, with water, beryllium forms insoluble oxide coating that protects it from further attack.

4. Beryllium in particular is quite resistant towards complete oxidation, even by acids, because of its BeO coating.
5. Beryllium is the only member of its group which reacts with alkalies to give hydrogen. The other members do not react with alkalies.

$$Be_{(s)} + 2NaOH_{(aq)} \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_{2\,(aq)}} + H_{2\,(g)}$$

2.2 GENERAL BEHAVIOUR OF ALKALI METALS

The reducing property of an element depends on the magnitude of its ionization energy. Reducing agent is a substance which can lose electrons. Since alkali metals have got low ionization energies, so they are strong reducing agents. They are highly electropositive. They react readily with halogens giving alkali metal halides.

2.2.1 Trends in Chemical Properties of Alkali Metals

1. Low ionization energies make the alkali metals, the most reactive family of metals.
2. Very high second ionization energies indicate that oxidation number higher than 1, are ruled out for the alkali metals.
3. The cations of alkali metals have low charge and large radii than the radius of any cation from the same period, so the lattice energies of their salts are relatively low. Consequently, most of the simple salts of the alkali metals are water-soluble. Most of the salts are dissociated completely in aqueous solution and the hydroxides are among the strongest bases available.

4. They react with oxygen and the surface is tarnished due to the oxides formed. Only lithium burns in air to form the normal oxide, Li_2O (white solid).

$$4\,Li(s) + O_2(g) \longrightarrow 2\,Li_2O(s)$$

Lithium oxide

The exposed metals are oxidized almost immediately by oxygen in air, and in the presence of moisture. The oxides formed react with CO_2 in the atmosphere to form carbonates.

$$Li_2O(s) + CO_2(g) \longrightarrow Li_2CO_3(s)$$

Lithium oxide Lithium carbonate

Sodium will undergo a similar reaction, but only if the supply of oxygen is limited. In the presence of excess of oxygen, sodium forms the pale yellow peroxide.

$$2Na(s) + O_2(g) \longrightarrow \underset{\text{Sodium peroxide}}{Na_2O_2(s)}$$

Potassium, rubidium and caesium react with oxygen to form superoxides (orange yellow). Caesium explodes spontaneously when it is in contact with air or oxygen.

$$K(s) + O_2(g) \longrightarrow \underset{\text{Potassium superoxide}}{KO_2(s)}$$

5. Very rapid reactions occur when alkali metals react with water. A small piece of sodium (potassium or lithium) floated on water reacts vigorously to liberate hydrogen and produce metal hydroxide. The reaction is highly exothermic. The energy produced by the reaction may even ignite the hydrogen.

$$2Na(s) + 2H_2O(\ell) \longrightarrow 2NaOH(aq) + H_2(g)$$

The reaction becomes increasingly vigorous from lithium to caesium. Potassium, rubidium and caesium are so highly reactive that they react with ice even at -100°C.

6. Alkali metals form ionic hydrides with hydrogen.

$$2M(s) + H_2(g) \longrightarrow 2M^+H^-(s)$$

Rubidium and caesium react violently with hydrogen at room temperature. The other three metals require elevated temperature in order to form the hydride. Lithium and sodium hydrides are useful sources of hydrogen when treated with water.

$$LiH(s) + H_2O(\ell) \longrightarrow LiOH(aq) + H_2(g)$$

Due to the presence of hydride ion (H^-), the ionic hydrides are used as powerful reducing agents.

7. Lithium is the only Group IA metal that combines with nitrogen and carbon to form nitride and carbide, respectively.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

Lithium nitride

$$4Li(s) + C(s) \longrightarrow Li_4C(s)$$

Lithium carbide

Alkali metals react easily with halogens to give halides. Lithium and sodium, for example, react slowly with chlorine at room temperature. Molten sodium burns with a brilliant yellow flame in a chlorine atmosphere to form sodium chloride.

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

Potassium, rubidium and caesium react vigorously with all the halogens, forming metal halides. All alkali metals form their sulphides when treated with molten sulphur. The general reaction is:

$$2M(s) + S(s) \longrightarrow M_2S(s)$$

2.2.2 Trends in Chemical Properties of Alkaline-Earth Metals

1. The alkaline-earth metals burn in oxygen to form oxides or in the case of barium, the peroxide. Beryllium is the least reactive metal in the group. It is resistant to complete oxidation and stable in air at ordinary temperature but oxidizes rapidly at about 800"C. Therefore beryllium is not tarnished by atmospheric attack but the metal soon loses the silvery appearance.

$$2Be(s) + O_2(g) \xrightarrow{800^\circ C} 2BeO(s)$$

When exposed to air magnesium quickly becomes coated with the layer of MgO.
This layer protects the surface from further corrosion at ordinary temperature.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

When magnesium is burnt in air a small amount of nitride is also formed along with magnesium oxide: When barium is heated in air or oxygen at 500 - 600°C, its peroxide is formed.

$$Ba(s) + O_2(g) \xrightarrow{500-600^\circ C} \underset{\text{Barium peroxide}}{BaO_2(s)}$$

2. Hydrides are produced by treating the molten alkaline earth metals with hydrogen, usually under high pressures. Magnesium reacts with hydrogen at high pressure and in the presence of a catalyst (MgI_2) forming magnesium hydride.

$$Mg(s) + H_2(g) \xrightarrow[(MgI_2)]{Pressure} MgH_2(g)$$

similarly $$Ca(s) + H_2(g) \longrightarrow CaH_2(g)$$

3. All Group II-A elements react with nitrogen on heating giving nitrides. For example, magnesium reacts with nitrogen to give magnesium nitride.

$$3Mg(s) + N_2(g) \longrightarrow \underset{\text{Magnesium nitride}}{Mg_3N_2(g)}$$

The nitrides hydrolyse vigorously when treated with water, giving ammonia and the respective hydroxides.

$$Mg_3N_2(s) + 6H_2O(\ell) \longrightarrow 2NH_3(g) + 3Mg(OH)_2(s)$$

4. With sulphur, magnesium gives magnesium sulphide, MgS. The other Group II-A metals also react similarly.

$$Mg + S \longrightarrow \underset{\text{Magnesium sulphide}}{MgS}$$

5. All group II-A elements react directly with halogens giving halides of the type MX_2 e.g.

$$Ca(s) + Cl_2(g) \longrightarrow CaCl_2(g)$$

6. Magnesium is more reactive than beryllium, even though it is not attacked by cold water. Magnesium reacts slowly with boiling water and quite rapidly with steam to liberate hydrogen.

$$\underset{\text{Steam}}{Mg(s) + H_2O(g)} \xrightarrow{100^\circ C} MgO(s) + H_2(g)$$

Beryllium does not react with water even at red hot temperature but remaining alkaline earth metals produce hydroxides with water.

$$M(s) + 2H_2O(l) \xrightarrow{100^\circ C} M(OH)_2(s) + H_2(s)$$

2.2.3 General Trends in Properties of Compounds of Alkali and Alkaline Earth metals

i) Oxides

Alkali metal oxides dissolve in water to give strong alkaline solutions. For example:

$$Li_2O(s) + H_2O(l) \longrightarrow 2LiOH\,(aq)$$

$$2Na_2O_2(s) + 2H_2O(l) \longrightarrow 4NaOH\,(aq) + O_2(g)$$

The reaction of an alkali metal oxide with water is an acid-base reaction and not an oxidation reduction reaction since no element undergoes a change in its oxidation number. The reaction simply involves the decomposition of water molecule by an oxide ion.

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2OH^-(aq)$$

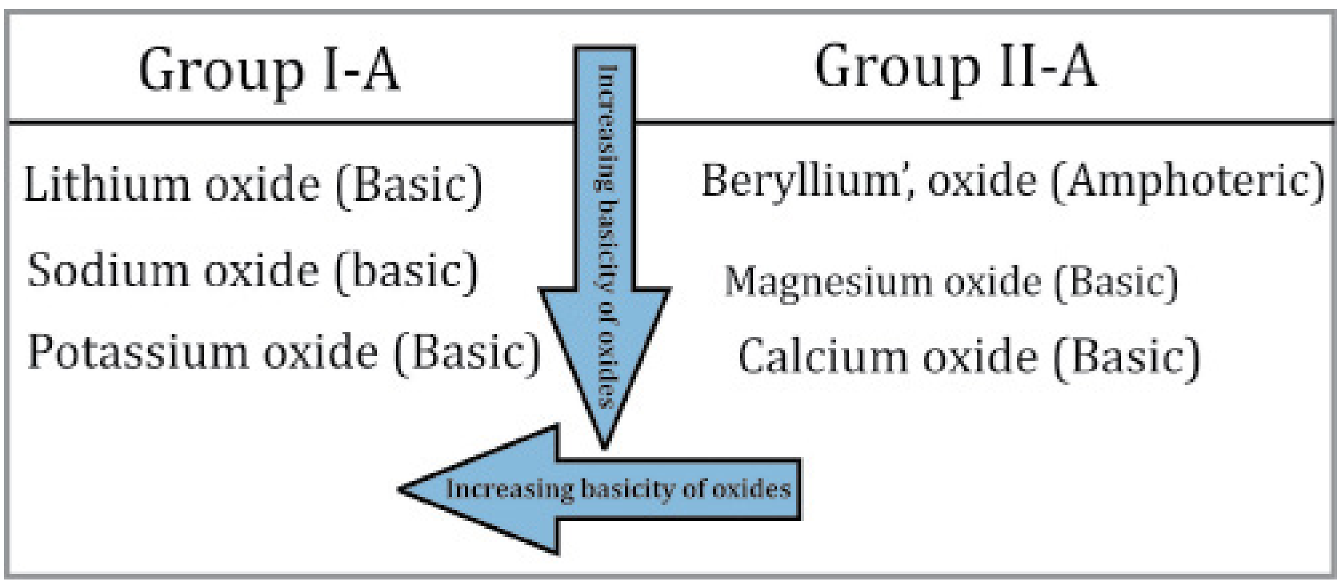
The basic character of alkali metal oxides increases down the group. Potassium superoxide ($K0_2$) has a very interesting use in breathing equipments for mountaineers and in space craft. It has the ability to absorb carbon dioxide while giving out oxygen at the same time.

$$4KO_2(s) + 2CO_2(g) \longrightarrow 2K_2CO_3(s) + 3O_2(g)$$

The solubility of alkaline earth metal oxides in water increases down the group. BeO and MgO are insoluble but CaO, SrO and BaO are soluble and react with water to form the corresponding hydroxides.

The basic character of the oxides of alkaline earth metals increases down the group. The tendency for group IIA oxides to form alkaline solution is relatively less than that of alkali metals .

Animation 2.6 : Reaction with acids
Source and Credit: Learn



BeO is amphoteric in nature since it reacts with both acids and bases.

$$BeO(s) + H_2SO_4(aq) \longrightarrow BeSO_4(s) + H_2O(\ell)$$

$$BeO(s) + 2NaOH(aq) \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2(aq)} + H_2O(\ell)$$

ii) Hydroxides

The alkali metal hydroxides are all crystalline solids, very soluble in water except LiOH, which is slightly soluble.They are generally hygrsocopic and are very strong bases, execpt LiOH. The solubility of alkaline earth metal hydroxides in water increases down the group. $Be(OH)_2$ is quite insoluble. $Mg(OH)_2$ is sparingly soluble while Ba $(OH)_2$ is more soluble.This increase in solubility is due to low lattice energy of hydroxides which is, in turn, due to higher ionic size.

Alkali metal hydroxides are stable to heat except LiOH, while alkaline earth metal hydroxides like $Mg(OH)_2$ and $Ca(OH)_2$ decompose on heating.

$$2LiOH(s) \longrightarrow Li_2O(s) + H_2O(\ell)$$

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

A saturated solution of $Ca(OH)_2$ in water is called lime water and is used as a test for CO_2. A suspension of $Mg(OH)_2$ in water is called milk of magnesia and it is used for treatment of acidity in stomach.

iii) Carbonates

The carbonates of alkali metals are all soluble in water and are stable towards heat except Li_2CO_3 which is not only insoluble but also decompose on heating to lithium oxide. The decomposition is made easy because the electrostatic attraction in converting from carbonate to oxide is considerable. In case of large cation like K^+ in K_2CO_3, the gain in electrostatic attraction is relatively much less and the decomposition is difficult. Sodium carbonate is very important industrial chemical. At temperature below 35.2°C, Na_2CO_3 crystallizes out from water as $Na_2CO_3.10H_2O$, which is called washing soda. Above this temperature it crystallizes as $Na_2CO_3.\ H_2O$. On standing in air, $Na_2CO_3.10H_2O$ slowly loses water and converted to a white powder $Na_2CO_3.H_20$. The solution of Na_2CO_3 in water is basic due to hydrolysis of carbonate ion.

$$Na_2CO_3(s) + 2H_2O(\ell) \longrightarrow 2NaOH(aq) + H_2CO_3(aq)$$

Unlike the alkali metal carbonates, the alkaline earth metal carbonates are only very slightly soluble in water, with the solublity decreasing down the group. They also decompose on heating and the ease of decomposition decreases down the group.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

The ease of decomposition can be related to the size of the metal ion, the smaller the ion, the more is the lattice energy of the resulting oxide and hence higher the stability of the product.

iv) Nitrates

Nitrates of both alkali and alkaline-earth metals are soluble in water. Nitrates of Li, Mg , Ca and Ba decompose on heating to give O_2, $NO_2$and the metallic oxide whereas nitrates of Na and K decompose to give different products.

$$4LiNO_3(s) \longrightarrow 2Li_2O(s) + 4NO_2(s) + O_2(g)$$

$$2Mg(NO_3)_2(s) \longrightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$$

$$2Ca(NO_3)_2(s) \longrightarrow 2CaO(s) + 4NO_2(g) + O_2(g)$$

$$2NaNO_3(s) \longrightarrow 2NaNO_2(s) + O_2(g)$$

v) Sulphates

All the alkali metals give sulphates and they are all soluble in water. The solubilities of sulphates of alkaline earth metals, gradually decrease down the group. $BeSO_4$ and $MgSO_4$ are fairly soluble in water. $CaSO_4$ is slightly soluble, while $SrSO_4$ and $BaSO_4$ are almost insoluble.

Calcium sulphate occurs in nature as gypsum $CaSO_4.2H_2O$. When it is heated above 100°C, it loses three quarters of its water of crystallization, giving a white powder called' Plaster of Paris.

$$\underset{\text{Gypsum}}{2CaSO_4 . 2H_2O} \longrightarrow \underset{\text{Plaster of Paris}}{(CaSO_4)_2 . H_2O} + 3H_2O$$

2.3 COMMERCIAL PREPARATION OF SODIUM BY DOWNS CELL

Most of sodium metal is produced by the electrolysis of fused sodium chloride. Since the melting point of sodium chloride is 801°C, some calcium chloride is added to lower its melting point and to permit the furnace to operate at about 600^{0}C.

In the electrolytic cell, the large block of graphite at the centre is the anode, above which there is a dome for the collection of chlorine. The cathode is a circular bar of copper or iron which surrounds the anode but is separated from it by an iron screen, which terminated in a gauze. The arrangement permits the electric current to pass freely but prevents sodium and chlorine from mixing after they have been set free at the electrodes, Fig. 2.1

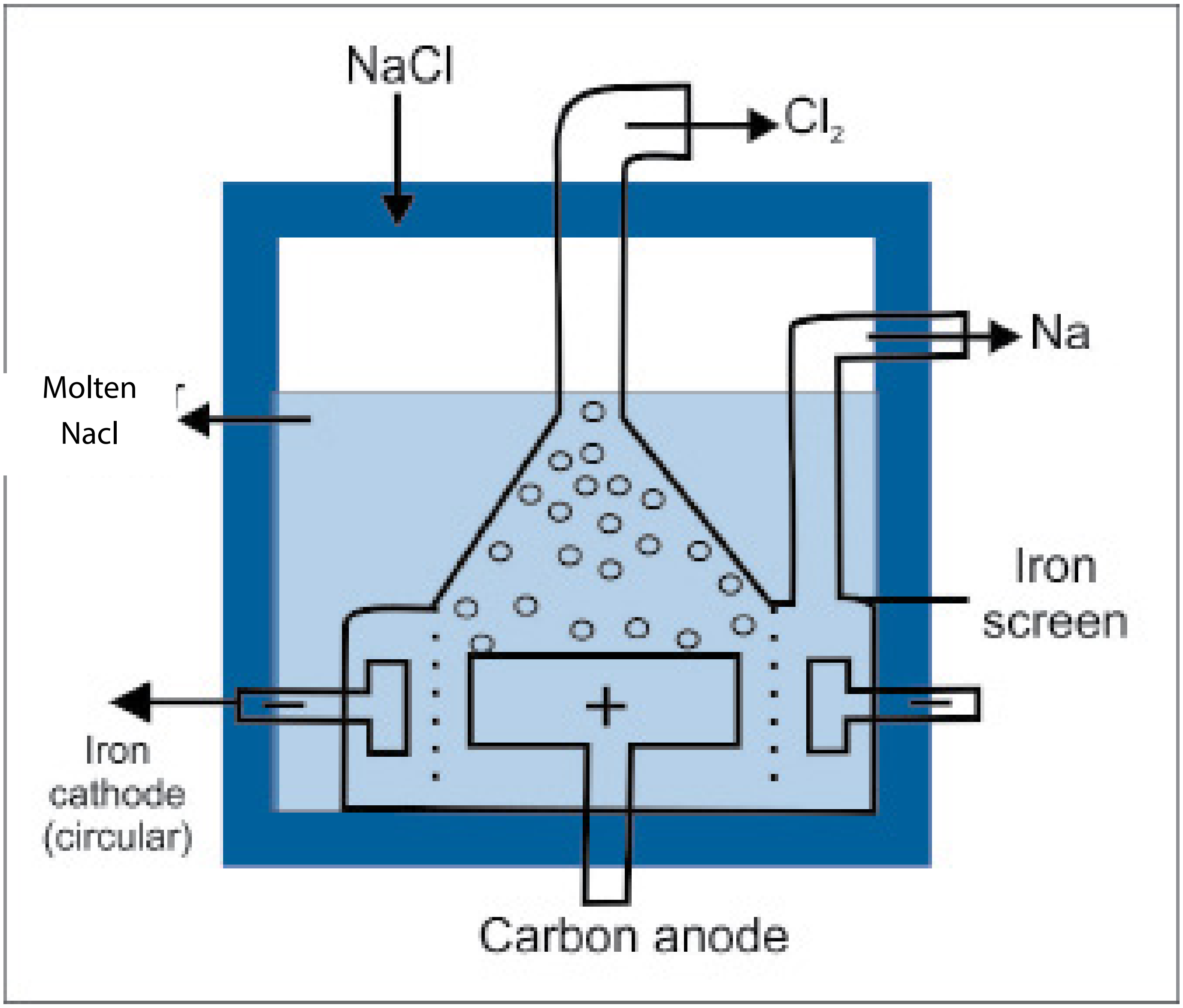


Fig.2.1 Down's Cell

Animation 2.7 DOWN'S CELL
Source and Credit: eLearn.Punjab

Sodium metal rises in a special compartment from which it is taken out at intervals.
The cell produces dry chlorine and 99.9 percent pure sodium. The process is carried out at 600°C and it has the following advantages.

(a) The metallic fog is not produced.
(b) Liquid sodium can easily be collected at 600°C.
(c) Material of the cell is not attacked by the products formed during the electrolysis.
During the process the following reactions take place:

$$NaCl \longrightarrow Na^+ + Cl^-$$

At cathode $$Na^+ + e^- \longrightarrow Na$$

At anode $$Cl^- \longrightarrow 1/2Cl_2 + 1e^-$$

2.4 COMMERCIAL PREPARATION OF SODIUM HYDROXIDE BY THE DIAPHRAGM CELL

Sodium hydroxide is manufactured on a large scale by the electrolysis of aqueous solution of common salt in a diaphragm cell Fig. 2.2 (a)

The cell is made of steel tank. An oblong perforated steel vessel lined inside with asbestos diaphragm serves as a cathode. It is provided with a constant level device to keep the vessel filled to the specified level with brine. A graphite anode is held within the U shaped diaphragm and it projects into the salt solution. The steam is blown during the process which keeps the electrolyte warm and helps to keep the perforations clear.

The chlorine released at the anode, rises into the dome at the top while hydrogen released at the cathode, escapes through a pipe. The sodium hydroxide solution slowly percholates into a catch basin.

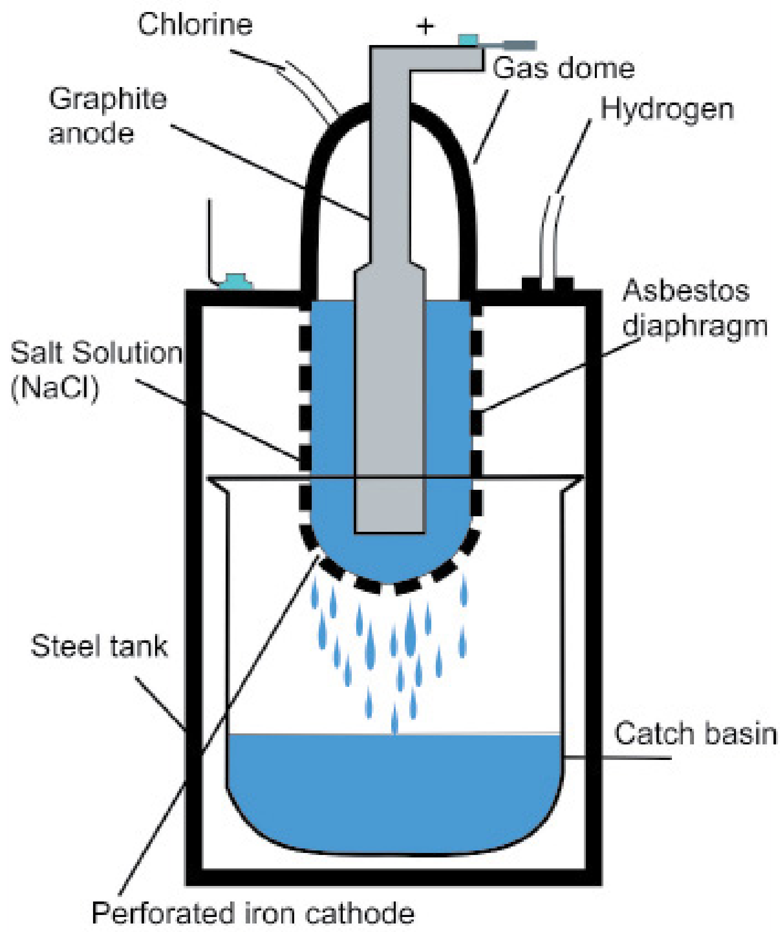


Fig.2.2(a) Nelson Cell for the Production of NaOH

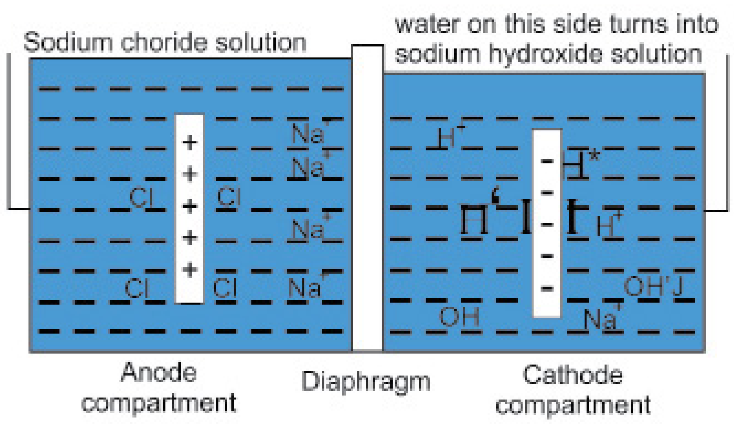


Fig.2.2(b)

The Fig. 2.6 (b) shows a simplified version of the cell in order to understand the purpose of diaphragm. When the electrolysis takes place, chlorine is given off at the anode according to the following reaction.

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$$

At the cathode hydrogen is discharged by the reduction of water.

$$2H_2O + 2e^- \longrightarrow 2OH^-(aq) + H_2(g) \quad \text{(Cathode)}$$

The overall result of the above reactions is that the brine loses its chloride ions and the solution turns increasingly alkaline in cathode compartment.

We can face two major problems during the working of the cell.

1. Chlorine produced can react with hydroxide ions in cold giving hypochlorite ions.

$$Cl_2(g) + 2OH^-(aq) \longrightarrow OCl^-(aq) + Cl^-(aq) + H_2O$$

2. Hydroxide ions may be attracted towards anode, where they can be discharged releasing oxygen gas. This oxygen gas may contaminate the chlorine and renders it impure.

The first problem is solved by using asbestos diaphragm. This keeps the two solutions separate while allowing sodium ions to move towards the cathode. This movement of ions keep the current following through the external current.

The second problem is solved keeping the level of brine in anode compartment slightly higher, this keeps the direction of flow of liquid toward the cathode and thus preventing the possibility of hydroxides ions to reach the anode.

The solution that flows out of the cathode compatment contains 11% NaOH and 16% NaCl. Evaporation of this solution crystallizes the less soluble NaCl which is filtered off, the liquid left contains about 50% NaOH and only 1% NaCl as an impurity. For commercial purposes this small impurity is not important.

2.5 ROLE OF GYPSUM IN AGRICULTURE AND INDUSTRY

(a) Role of Gypsum in Agriculture

Gypsum, a hydrated calcium sulphate, is a mineral that occurs in large deposits throughout the world.Gypsum is applied to the soil as a source of calcium and sulphur. The calcium supplied by gypsum in fertilizers is of importance in crop production in area where soils are subject to extensive leaching.

Sulphur has been recognised as an essential constituent of plants. For centuries, sulphur compounds had been applied to soils because of their observed beneficial effect on plant growth. Aside from serving as a constituent of protein and various other compounds in plants, sulphur has an influence on chlorophyll development in plant leaves. Although not a constituent of chlorophyll, plants deficient in sulphur exhibits a pale green colour. The root system of several plants have been observed to be greatly enlarged by the application of sulphur. It has been reported that good crops are produced by the application of sulphur containing materials such as gypsum.

(b) Role of Gypsum in Industries

When gypsum is heated under carefully controlled conditions, it loses three quarters of water of crystallization. The resulting product is called Plaster of Paris. Gypsum must not be heated too strongly as the anhydrous salt is then formed which absorbs water slowly. Such plaster is called 'Dead burnt'.

Plaster of Paris when mixed with half of its weight of water, it forms a plastic type viscous mass and then sets to a hard porous mass. This process is completed within 10 to 15 minutes. During the process expansion about 1% in volume also occurs, which fills the moulds completely and thus a sharp impression is achieved Plaster of Paris is used for making plaster walls, casts of statuary,coins, etc.

It is used in surgery, Plaster of Paris bandages are used for holding in place fractured bones after they have been set.

Special plasters contain plaster of Paris and other ingredients which vary with the demands of the use to which they are to be put. Two varieties of plasters are made.

(1) Cement Plaster.

It is plaster of Paris to which usually glue or other oils have been added as retarders to prolong the time of setting.

(2) Hard Finish Plasters

These are made by the calcination of the anhydrous sulphate with alum or borax.These plasters are set very slowly but give a hard finish. When mixed with wood pulp and allowed to set in the form of boards, it forms a material, much used in the construction of buildings as wall boards and partitions. Gypsum is also used as a filler in paper industries.

Portland cement is made by strongly heating a finely powdered mixture of clay and limestone. The final product, known as clinker, is cooled and then ground into a very fine powder. During the grinding there is added about 2% of gypsum which prevents the cement from hardening too rapidly.The addition of gypsum increases the setting time of cement.

2.6 ROLE OF LIME IN AGRICULTURE AND INDUSTRY

Lime, (CaO) is a soft, white compound which is obtained by the thermal decomposition of $CaCO_3$.

(a) Role of Lime in Agriculture

Large quantities of calcium oxide are used in agriculture for neutralizing acidic soils.

It has been found that application of lime to acidic soils increases the amount of readily soluble phosphorus. Calcium oxide is also used in large amounts for making lime-sulphur sprays which have a strong fungicidal action. The hydroxide of calcium is obtained when the oxide of the calcium is allowed to react with water. The process is called slaking of lime and it is an exothermic reaction.

$$CaO + H_2O \longrightarrow \underset{\text{Slaked lime}}{Ca(OH)_2}$$

Functions of Calcium in Plant-Growth

The presence of calcium is essential for the normal development of plants. The quantity of calcium required by different plants varies considerably. An adequate supply of calcium appears to stimulate the development of root hairs and, in fact, the entire root system. Calcium is also necessary for normal leave development and tends to accumulate in leaves as well as in bark. An adequate supply of calcium is also essential for the optimum activity of microorganisms that produce nitrates. The effect of calcium on the supply of available phosphorus in the soil is of special significance. Soils containing sufficient calcium are slightly alkaline in nature. When a deficiency of calcium exists various substances such as aluminium and manganese may accumulate in plants in harmful concentrations.

(b) Role of Lime in Industries

1. Large quantities of lime are used in the extraction and refining of metals.
2. Lime is also used in paper, cement and leather industries
3. The ability of lime to react with sand at high temperature forming calcium silicate
($CaSiO_3$) serves as an important basis for glass manufacture.
4. Lime is used in ceramic industry for producing different types of sanitary materials.

5. Ordinary mortar, also called lime mortar, is prepared by mixing freshly prepared slaked lime (one volume) with sand (three or four volumes) and water to form a thick paste. This material when placed between the stones and bricks hardens or sets, thus binding the blocks firmly together. The equations for the chemical reactions which take place when mortar hardens are:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$Ca(OH)_2 + SiO_2 \longrightarrow CaSiO_3 + H_2O$$

6. Lime is also used in refining of sugar and other food products.
7. Lime is used in the manufacturing of bleaching powder, which is used for the bleaching of the fabric and paper pulp.
8. A suspension of the calcium hydroxide is called milk of lime and is used as a white-wash.
9. When lime is heated with coke at about 2800°C in an electric furnace, calcium carbide is produced, which on hydrolysis yields acetylene (C_2H_2).

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2} + CO$$

10. Lime is often employed as a dehydrating agent, for example, in the preparation of absolute alcohol and the drying of ammonia gas. A mixture of sodium hydroxide and calcium hydroxide (soda lime) is often employed to remove both water and carbon dioxide from certain gases.

Animation 2.8 : Gals(The most radio active alkali metal 2)
Source and Credit: Targeticse

Key Points

1. The elements of group IA except hydrogen are called 'alkali metals' while those of group IIA are named as alkaline earth metals.
2. Alkali metals have only one electron in s-orbital of their valence shell. They lose one electron of the valence shell forming monovalent positive ions.
3. Alkaline earth metals have two electrons in s-orbital of their valence shell. They lose two electrons forming dipositive ions M^{2+}.
4. Spodumene, Chile saltpetre, trona, borax, carnallite, sylvite, alunite, halite, natron, are the common minerals of alkali metals.
5. Beryl, magnesite, dolomite, epsom salt, asbestos, calcite, gypsum, strontionite and barite are the important minerals of alkaline earth metals.
6. Lithium behaves different from the other alkali metals.
7. Lithium forms only normal oxide, whereas the others form higher oxides like peroxides and superoxides.
8. Beryllium is the only member of group II, which reacts with alkalies to give hydrogen. The other member do not react with alkalies.
9. Nitrates of lithium, magnesium and barium on heating give oxygen, nitrogen peroxide and the corresponding metallic oxides.
10. When gypsum is heated above 100°C, it loses three quarters of its water of crystallization, giving white powder of $CaSO_4.1/2H_2O$ which is called Plaster of Paris.
11. Sodium is prepared by the electrolysis of molten sodium chloride in Down's cell.
12. Calcium is necessary for development of leaves and it tends to accumulate in leaves and bark. An adequate quantity of calcium is essential for the optimum activity of microorganisms that produce nitrates.
13. Lime is used in paper and glass industries. It is also used for refining sugar and other food products.

EXERCISE

Q1. Fill in the blanks:

(i) Alkali metals are reactive than alkaline-earth metals.

(ii) Alkali metals decompose water vigorously producing________ and hydrogen.

(iii) When heated in a current of dry hydrogen, alkaline earth metals form white crystalline of the type MH_2.

(iv) The beryllium hydroxide, like the hydroxide of aluminium is amphoteric, while the hydroxides of the other members of the group IIA are________ .

(v) The elements of the group IA are termed as alkali metals, because their________are alkaline.

(vi) Spodumene is an ore of_______ metal.

(vii) Alkali metal nitrates on heating give the corresponding_______ and oxygen.

(viii) $Na_2CO_3.H_2O$ is the chemical formula of a mineral of sodium which is known as______ .

(ix) Metallic bicarbonates are decomposed on heating into their carbonates, along with________ and________ .

(x) Metal nitrates other than the alkali metals on heating decompose into the corresponding metal__________along with the evolution of nitrogen peroxide and oxygen.

Q2. Indicate True or False.

(i) Group IA elements are called alkali metals because their chlorides are alkaline in nature

(ii) Alkali metals are very good conductor of electricity.

(iii) The hydroxides of alkali metals and alkaline-earth metals are soluble in water.

(iv) Plaster of Paris is a hemihydrate.

(v) Alkali metals have low melting and boiling points as compared to those of alkaline earth metals.

(vi) Lithium carbonate is decomposed to its oxide, but the carbonates of the other alkali metals are stable towards heat.

(vii) All alkali metal sulphates are insoluble in water.

(viii) Lithium combines with nitrogen to form lithium nitride but other alkali metals do not react with nitrogen.

(ix) Trona is a mineral of lithium.

(x) Alkaline earth metals are stronger reducing agents than alkali metals.

Q 4. (a) Give the names, electronic configurations and occurrence of s-block elements.

(b) Discuss the peculiar behaviour of lithium with respect to the other members of alkali metals.

Q 5. Discuss the trends in chemical properties of compounds like oxides, hydroxides, carbonates, nitrates and sulphates of IA and IIA group elements.

Q 6. Compare the chemical behaviour of lithium with magnesium.

Q 7. (a) Mention the properties of beryllium in which it does not resemble with its own family.

(b) Why the aqueous solution of Na_2CO_3 is alkaline in nature?

Q 8. (a) Describe with diagram the manufacture of sodium by Down's cell.

(b) Point out the three advantages of this process.

Q9. (a) Compare the physical and chemical properties of alkali metals with those of alkaline earth metals.

(b) What happens when:

(i) Lithium carbonate is heated.

(ii) Lithium hydroxide is heated to red hot.

(iii) Beryllium is treated with sodium hydroxide.

(iv) Lithium hydride is treated with water.

Q10.Give formulas of the following minerals.

(a) Dolomite (b) Asbestos (c) Halite (d) Natron

(e) Beryl (f) Sylvite (g) Phosphorite (h) Chile saltpetre

Q.11. Answer the following questions briefly.

(a) Why alkali and alkaline earth metals are among the reactive elements of the periodic table?

(b) Why line water turns milky with CO_2 but becomes clear with excess CO_2?

(c)How gypsum is converted into plaster of paris?

(a) Why 2% gypsum is added in the cement?

(e)Why lime is added to an acidic soil?

(f) How lime and sand are used to make glass?

(g) How lime mortar is prepared?

CHAPTER

3

GROUP IIIA AND GROUP IVA ELEMENTS

Animation 3.1 : Periodic Table
Source and Credit: eLearn.Punjab

IN THIS CHAPTER YOU WILL LEARN

1. The names, electronic configurations and occurrence of IIIA and IVA group elements.
2. The peculiar properties of boron and carbon in their respective groups.
3. The preparation and properties of borax and orthoboric acid.
4. The reactions of aluminium.
5. Structures and properties of oxides of carbon and silicon, silicates, silicones and their uses.
6. The uses of silicon and germanium in semi-conductor industries and lead in paints.

3.1 GROUP IIIA ELEMENTS

The Group IIIA of the Periodic Table comprises the elements boron, aluminium, gallium, indium and thallium.Electronic configurations and some physical properties of group IIIA elements are shown in Table 3.1.

Table 3.1 Electronic Configurations and Physical Properties of Group IIIA Elements

Properties	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Electronic configurations	$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]\ 3d^{10}4s^2 4p^1$	$[Kr]4d^{10}5s^2 5p^1$	$[Xe]4f^{14}\ 5d^{10}6s^2 6p^1$
Ionization energy (kJ/ mol)	801	577	579	558	589
Electron affinity (kJ/mol)	-27	-45	-29	-29	-30
Electronagetivity	2.0	1.5	1.6	1.7	1.8
Atomic radius (pm)	80	125	126	144	148
Ionic radius of 1+ion (pm)	20	52	60	81	95
Melting points (°C)	2300	660	30	157	304
Boiling points (°C)	2550	2467	2403	2080	1457
Density (g/cm^3)	2.33	2.7	5.93	7.3	11.85

The small size and high nuclear charge make boron non-metallic while all the other elements of this group are metals. The abrupt increase in metallic character from B to Al is associated with the increased size of aluminium atom. The increase in the atomic size is not regular in this group. This is due to the presence of d electrons in heavier members which have poor shielding effect than s and p electrons.

3.1.1 Occurrence (Boron and Aluminium)

Boron is not an abundant element. It occurs in traces in most soils and has been found to be essential in very small amounts for the proper growth of many plants.
Boron is always found in nature combined with oxygen, usually as oxyborate ions. Boron occurs principally as salts of various polyboric acids.

Table 3.2 Common Minerals of Boron

Name of Minerals of Boron	Chemical Formula
Borax or Tincal	$Na_2B_4O_7.10H_2O$
Colemanite	$Ca_2B_6O_{11}.5H_2O$
Orthoboric Acid	H_3BO_3

Aluminium is the third most abundant element in the earth's crust (after oxygen and silicon)

Table 3.3 Common Minerals of Aluminium

Name of Minerals of Aluminium	Chemical Formula
Feldspar	$KAlSi_3O_8$ or $K_2O.Al_2O_3.6SiO_2$
Mica (Muscovite)	$KH_2Al_3(SiO_4)_3$
Kaolin (Clay)	$H_2Al_2(SiO_4)_2.H_2O$ or $Al_2O_3.2SiO_2.2H_2O$
Corundum	Al_2O_3
Emerald	AlF_2SiO_4
Gibbsite	($Al_2O_3.3H_2O$ or $AlO(OH)_3$)
Bauxite	$Al_2O_3.2H_2O$
Cryolite	Na_3AlF_6
Diaspore	($Al_2O_3.H_2O$ or $AlO(OH)$

It occurs primarily as alumino-silicate minerals found in the rocks of the outer portion of the earth.

The other elements of group IIIA gallium, indium and thallium are relatively rare and are obtained as by-products during the processing of other metals.

3.1.2 Peculiar Behaviour of Boron

Boron is the first member of the Group IIIA, it shows many dissimilarities with the members of its own group.The difference in the properties of boron and those of the other members of the series is mainly due to the large difference in their sizes and ionization energies.

1. Boron is the only elementinGroupIIIAwhichisnon-metallic in behaviour
2. It is the only element with less than four electrons in the outermost shell which is not a metal.
3. Boron always uses all the three of its valence electrons for bonding purposes and its common oxidation states are + 3 and -3.
4. One of the outstanding features of the chemistry of boron is its ability to form molecular addition compounds.
5. Boron does not form ionic compounds with sulphate, nitrate or other anions because boron does not from a stable cation.

3.2 COMPOUNDS OF BORON

3.2.1 Borax (Sodium Tetraborate $Na_2B_4O_7.lOH_2O$)

Borax is the sodium salt of tetraboric acid. It is the most important of all borates.

Occurrence:

Borax occurs as a natural deposit called tincal in the dried up lakes of Tibet and California.

Manufacture:

1. Formally borax was manufactured by treating a hot solution of boric acid with the proper amount of soda ash.

$$\underset{\text{Boric acid}}{4H_3BO_3(s)} + Na_2CO_3(s) \longrightarrow \underset{\text{Borax}}{Na_2B_4O_7(s)} + 6H_2O(l) + CO_2(g)$$

2. Now-a-days borax is almost exclusively obtained from calcium borate. Finely powdered colemanite is boiled with Na_2CO_3 solution, when $CaCO_3$ precipitates out and a mixture of borax and sodium metaborate is formed.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}(s)} + 2Na_2CO_3(s) \longrightarrow 2CaCO_3(s) + Na_2B_4O_7(s) + 2NaBO_2(s)$$

The clear solution from the top is taken off and is then allowed to crystallize, when crystals of borax separate out. To get more borax, CO_2 is blown through the mother-liquor, the sodium metaborate is decomposed into borax, which separates out in the form of fine crystals.

$$\underset{\text{Sodium metaborate}}{4NaBO_2(s)} + CO_2(g) \longrightarrow Na_2CO_3(s) + \underset{\text{Borax}}{Na_2B_4O_7(s)}$$

3. Borax may also be obtained from tincal ($Na_2B_4O_7.10H_2O$) by treating tincal with water and subsequently evaporating the clear solution, when crystals of borax separate out.

Properties:

1. Borax is a white, crystalline solid. It is sparingly soluble in cold water but is more soluble in hot water: 100 grams of water dissolve 3 grams of decahydrate at 10°C and 99.3 grams at 100°C. If a saturated solution be allowed to crystallize above 62°C, octahedral crystals of the pentahydrate, $Na_2B_4O_7.5H_2O$separate out, if the temperature is below 62°C, the decahydrate is formed. Its aqueous solution is alkaline in nature due to hydrolysis.

$$Na_2B_4O_7(s) + 7H_2O(l) \longrightarrow \underset{\text{Strong alkali}}{2NaOH(aq)} + \underset{\text{Weak acid}}{4H_3BO_3(s)}$$

The hydrolysis is prevented in the presence of glycerine.

2. When heated, borax loses water and swells up into a white porous mass due to the expulsion of water: on further heating it melts into a clear transparent glass, which dissolves many metallic oxides forming coloured beads. This reaction forms the basis of borax bead test.

$$Na_2B_4O_7.10H_2O(s) \xrightarrow{\Delta} \underbrace{Na_2B_4O_7(s) + 2NaBO_2(s) + B_2O_3(s)}_{\text{Glassy mass}}$$

3. Its aqueous solution reacts with HCl or H_2SO_4 to form boric acid:

$$\underset{\text{Borax}}{NA_2B_4O_7(s)} + 2HCl(aq) + 5H_2O \longrightarrow 2NaCl(aq) + \underset{\text{Boric acid}}{4H_3BO_3(s)}$$

$$NA_2B_4O_7(s) + H_2SO_4(aq) + 5H_2O(l) \longrightarrow Na_2SO_4(s) + 4H_3BO_3(s)$$

4. When borax is heated with ammonium chloride, boron nitride is produced:

$$Na_2B_4O_7(s) + 2NH_4Cl(aq) \longrightarrow 2NaCl(s) + 2BN(s) + B_2O_3(s) + 4H_2O(l)$$

5. Borax when dissolved in water ionizes as:

$$Na_2B_4O_7(s) \longrightarrow 2Na^+(s) + B_4O_7^{2-}(s)$$

Hydrolysis of $B_4O_7^{-2}$ occurs as follows:

$$B_4O_7^{2-}(s) + 7H_2O(l) \longrightarrow 4H_3BO_3(s) + 2OH^-(l)$$

So, a strong alkali (NaOH) is formed which is highly ionized. On the other hand, boric acid (H_3BO_3) is ionized to a little extent, because it is a weak acid. Hence, solution of borax as a whole is alkaliine in nature.

6. Borax Bead Test

Prepare a loop at the end of a platinum wire. Heat the wire and take a little powdered borax on the hot loop. Heat again, borax first swells up and then melts into colourless, glasslike bead on the loop. Now put a few grains of the substance, under examination, on the beads and re-heat it first in the oxidizing flame and then in the reducing flame.

Chemistry of the Borax-bead Test:

Borax, when fused, is decomposed into sodium metaborate and boric anhydride.

$$Na_2B_4O_7(s) \longrightarrow 2NaBO_2(s) + B_2O_3(s)$$

The metallic oxide formed from the substance, under examination, combines with B_2O_3 giving the coloured metallic borates. With cupric oxide, the beads are coloured blue in the oxidizing flame because cupric borates are blue in colour.

$$CuO(s) + B_2O_3(s) \longrightarrow Cu(BO_2)_2(s)$$

Uses of Borax:

1. It is used to prepare borate glass, which is heat resistant.
2. It is used in softening of water.
3. It is employed in borax bead test, for the detection of metallic cations.
4. It is used in metallurgical operations.
5. It is used as a flux in welding and in metallurgy.
6. It is employed in making washing powders.
7. It is used in leather industry for tanning and dyeing.
8. It is used in cosmetics, soaps, textiles, paints, medicine, match industry and as a preservative.

3.2.2 Boric Acids

There are four important boric acids.Out of these orthoboric acid is the most important and the stable one. The remaining acids are stable in solid state and change into orthoboric acid in solution:
(i) Orthoboric Acid, H_3BO_3
(ii) Metaboric Acid, HBO_2
(iii) Tetraboric Acid, $H_2B_4O_7$
(iv) Pyroboric Acid, $H_6B_4O_9$

$$HBO_2(s) + H_2O(l) \longrightarrow H_3BO_3(s)$$

Metaboric acid → Boric acid

$$H_2B_4O_7(s) + 5H_2O(l) \longrightarrow 4H_3BO_3(s)$$

Tetraboric acid → Boric acid

$$H_6B_4O_9(s) + 3H_2O(l) \longrightarrow 4H_3BO_3(s)$$

Pyroboric acid → Boric acid

Orthoboric Acid or Boric acid (H_3BO_3)

It is a white crystalline chemical substance (triclinic), sparingly soluble in cold water (2.6% at 40 ^{0}C) but dissolves readily in hot water (37% at 107°C). This temperature variation in solubility forms the basis for its separation and purification.

Preparation of Boric acid on Commercial Scale

1. From Colemanite

On commercial scale, boric acid is prepared from a natural calcium borate called colemanite ($Ca_2B_6O_{11}$. $5H_2O$) by suspending it in boiling water while, sulphur dioxide is passed through it. Boric acid crystallizes out from the solution while, the other product $CaSO_3$ remains in the solution.

$$\underset{\text{Colemanite}}{Ca_2B_6O_{11}.5H_2O(s)} + 2SO_2(g) + 4H_2O(l) \longrightarrow 2CaSO_3(aq) + 6H_3BO_3(s)$$

From Borax:

A hot concentrated solution of borax is treated with a calculated quantity of conc. H_2SO_4. On cooling, crystals of boric acid formed separate out.

$$Na_2B_4O_7(s) + H_2SO_4(aq) + 5H_2O(l) \longrightarrow Na_2SO_4(s) + 4H_3BO_3(s)$$

Borax Boric acid

Properties of Boric Acid

1. Boric acid is a white lustrous crystalline solid having a soft soapy touch, very slightly soluble in cold water but fairly soluble in hot.
2. It is volatile in steam.
3. It reacts with ethyl alcohol forming ethyl borate.

$$H_3BO_3(s) + 3C_2H_5OH(l) \longrightarrow (C_2H_5)_3BO_3(l) + 3H_2O(l)$$

4. When heated strongly, it swells to frothy mass losing water molecules.
It is first converted into metaboric acid, thep to tetra boric acid and finally to boric anhydride.

$$H_3BO_3(s) \xrightarrow{100^o\ C} HBO_2(s) + H_2O(l)$$

Metaboric Acid

$$4HBO(s) \xrightarrow{140^o\ C} H_2B_4O_7(s) + H_2O(l)$$

Tetraboric acid

$$H_2B_4O_7(s) \xrightarrow{\text{Red hot}} 2B_2O_3(s) + H_2O(l)$$

Boric anhydride

5. It is a very weak acid and ionizes to a very limited extent mainly as a monobasic acid.

$$H_3BO_3(s) + H_2O(l) \longrightarrow [B(OH)_4]^-(s) + H^+$$

6. Its solution has no effect on methyl orange, although it turns blue litmus red.
7. It is partially neutralised by caustic soda to give borax.

$$4H_3BO_3(aq) + 2NaOH(aq) \longrightarrow Na_2B_4O_7(aq) + 7H_2O(l)$$

8. When boric acid is neutralized by soda ash (Na_2CO_3), borax is obtained.

$$4H_3BO_3(aq) + Na_2CO_3(aq) \longrightarrow \underset{\text{Borax}}{Na_2B_4O_7(s)} + 6H_2O(l) + CO_2(g)$$

9. Boric acid being a weak acid, cannot be titrated with alkalies in the usual manner. In the presence of glycerol, however, it can be titrated against a standard alkali using phenolphthalein as an indicator.

Uses of Boric Acid

1. Boric acid is used in medicines as an antiseptic, e.g. dusting powder, boric ointment and boric solution is used as an eye-wash.
2. It is used in pottery as a glaze because borate glazes are more fusible than silicate glazes and possess a higher coefficient of expansion.
3. It is also used in candle industry for stiffening of wicks.

3.3 REACTIONS OF ALUMINIUM

1. Reaction with Air

When a piece of aluminium sheet is exposed to moist air it acquires a thin, continuous coating of aluminium oxide, which prevents further attack on the metal by atmospheric oxygen and water under normal conditions. Because of this aluminium sheets are said to be corrosion-free. However, if the aluminium powder is heated to 800°C and above, the metal will react with air to form aluminium oxide, Al_2O_3, and aluminium nitride, AlN. The reaction is accompanied by the evolution of heat and intense white light. This property of aluminium is made use of in flash light photography.

$$4Al(s) + 3O_2(g) \longrightarrow 2Al_2O_3(s)$$

$$2Al(s) + N_2(g) \longrightarrow 2AlN(s)$$

Because of its ability to combine with both oxygen and nitrogen, the metal is often used to remove air bubbles from molten metals. Salt solutions corrode aluminium badly so aluminium and aluminium alloys are not suitable for marine use.

2. Reaction with Non-Metals

Heated aluminium combines with the halogens, sulphur, nitrogen, phosphorus and carbon, accompanied by the evolution of heat.

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

Aluminium on heating with hydrogen forms aluminium hydride.

$$2Al(s) + 3H_2(g) \longrightarrow 2AlH_3(s)$$

3. Reaction with Acids and Alkalies

Aluminium is amphoteric. It dissolves in both acids and bases with the liberation of hydrogen gas. Aluminium reacts slowly with dilute acid and more rapidly with concentrated hydrochloric acid to displace hydrogen.

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3\,(aq)} + 3H_{2\,(g)}$$

Aluminium does not react with dilute sulphuric acid. However, it is oxidized by hot concentrated sulphuric acid to liberate sulphur dioxide gas.

$$2Al_{(s)} + 6H_2SO_{4\,(aq)} \longrightarrow Al_2(SO_4)_{3\,(aq)} + 6H_2O_{(\ell)} + 3SO_{2\,(g)}$$

Aluminium does not react with nitric acid at any concentration, probably because of the formation of protective layer of aluminium oxide. The acid is said to render the aluminium passive. Nitric acid is, therefore, frequently transported in aluminium containers.Aluminium dissolves in both sodium and potassium hydroxides to form a soluble aluminate, with the evolution of hydrogen.

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(\ell)} \longrightarrow 2NaAl(OH)_{4\,(aq)} + 3H_{2\,(g)}$$

USES

1. Aluminium is very-light (nearly three times less dense than iron) but posseses high tensile strength. These properties account for its extensive use in the transport industries, in the construction of aircrafts, ships and cars.
2. It is an excellent conductor of both electricity and heat. Thus, it is used as heat exchanger in chemical, oil and other industries. Heavy duty electrical cables are made of aluminium metal.
3. Aluminium is an excellent reflector of radiant energy. For this reason, it is commonly used to insulate buildings. Aluminium foil is also used to jam radar.
4. It is non-magnetic and is thus used in navigational equipment.
5. It is a good reducing agent and can thus be used for this purpose in the chemical and steel industries.
6. It is non-toxic and can be used for making food and brewing equipments and in packaging.
7. Aluminium readily forms alloys with other metals like copper, magnesium, nickel and zinc.
8. At homes, aluminium is found in the form of cooking utensils, window frames and kitchen foil.
9. Aluminium is used for making petrol and milk storage tanks because it reflects heat and prevents them of being over heated in the sun.

3.4 GROUP IVA ELEMENTS

Group IVA of the periodic table comprises elements, carbon, silicon, germanium, tin and lead.

Table 3.4 Electronic Configurations and Physical Properties of Group IVA Elements

Properties	C	Si	Ge	Sn	Pb
Atomic number	6	14	32	50	82
Electronic configurations	$[He]2s^22p^2$	$[Ne]3s^23p^2$	$[Ar]3d^{10}4s^24p^2$	$[Kr]4d^{10}5s^25p^2$	$[Xe]4f^{14}5d^{10}6s^26p^2$
Ionization energy (kj/ mol)	1086	736	760	707	715
Electron affinity (kj/mol)	-122.5	-120	-116	-121	-101
Electronagetivity	2.5	1.8	1.8	1.8	1.8
Atomic radius (pm)	77	117	122	140	154
Ionic radius of 2+ion (pm)	60	71	73	93	121
Melting points (°C)	3570	1410	937	232	328
Boiling points (°C)	sublimes	2355	2830	2270	1750
Density gm/cm^3 at (20°C)	2.33	2.7	5.93	7.3	11.85

There is a marked change of properties from carbon to lead.This gradation is of such nature, however, that there are very few similarities between the extreme members.Thus carbon and lead differ very considerably; far more, for example,

than do lithium and caesium in group IA. The electronic configurations of IVA group elements along with their physical properties are given in Table 3.4.

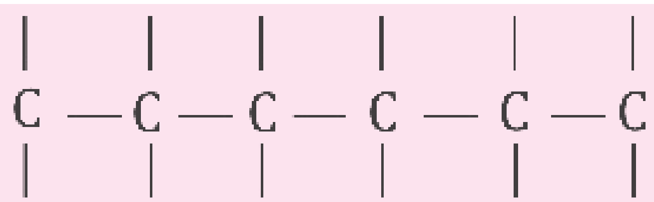
Carbon and silicon are the only non-metals in Group IVA. Carbon has the peculiar property of forming long carbon chains, silicon forms long chains of alternating silicon and oxygen atoms.

1. Carbon and silicon both form acidic oxides, whereas the oxides of germanium, tin and lead are amphoteric in nature.
2. Both carbon and silicon form covalent bonds. Their oxides are acidic and both form hydrides and chlorides.

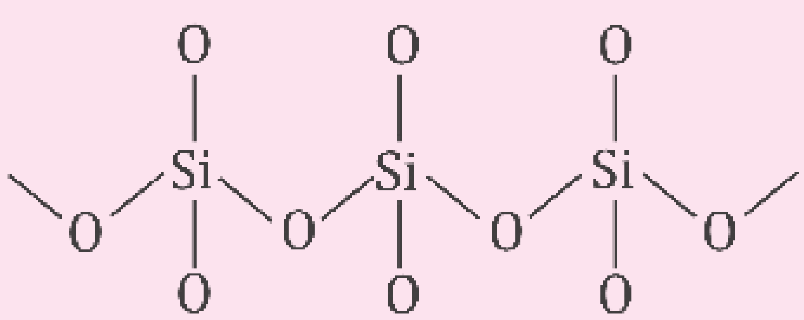
The elements of group IVA are characterized by a set of four valence electrons, which form two pairs. In the first three elements of IVA group, carbon, silicon and germanium, all the four outermost electrons are used as valency electrons, while in tin and lead either all four (stannic and plumbic compounds) or only one of the pairs of electrons (stannous and plumbous compound) is used for bonding.

The pair of valence electrons that do not readily take part in chemical combination is termed as inert pair. As in other groups, the inert pair effect is most marked in the element of highest atomic mass, namely lead.

The increase in electropositive character from carbon through silicon, tin, and lead is pronounced. This trend is shown also by the. increase in the metallic character of the elements with increased atomic mass.



Carbon and Carbon Linkages



Silicon and Oxygen Linkages

The Following are the Common Properties of Group IVA Elements:

1. All the elements of this group show a valency of four.
2. All of them form hydrides, MH_4.
3. They form tetrachlorides, MCl_4.
4. They also form the dioxides, MO_2

3.4.1 Occurrence of Carbon

Carbon occurs naturally in the two states. One is crystallline (graphite, diamond) form and the other is amourphous (coal, charcoal) form.

Minerals of Carbon	Chemical Formula
Limestone (calcite)	$CaCO_3$
Dolomite	$MgCO_3.CaCO_3$
Magnesite	$Mg\ CO_3$

3.4.2 Occurrence of Silicon

Silicon is very abundant, about 25% of the mass of the Earth's crust being due to this element. Silicon, unlike carbon, is not found in free state.

Minerals of Silicon	Chemical Formula
Analcite (a zeolite)	$NaAl(SiO_3)_2.H_2O$
Asbestos	$CaMg_3(SiO_3)_4$
Kaolin (pottery clay)	$H_2Al(SiO_4)_2.H_2O$
Zircon	$ZrSiO_4$
Talc (or soapstone)	$H_2Mg_3\ (SiO_3)_4$

Silicon is found as a major constituent of rocks either in the form of silica or silicates. Most minerals other than sulphides, sulphates, phosphates, and carbonates contain a high proportion of silicon. As oxide, it is found as quartz in the following forms:

Rock crystal, amethyst quartz, smoky quartz, rose quartz and milky quartz. Sand is largely silicon dioxide (silica). Opal is a hydrated variety of quartz.

3.4.3 Peculiar Behaviour of Carbon

Carbon differs from the remaining members of Group IV-A in the following respects:

1. Carbon and silicon are nonmetals while the other members of the family are metalloids or metals.
2. Catenation or self linkage. Carbon has a tendency to form long chains of identical atoms. The type of linkage of identical atoms with each other is called catenation or self-linkage. The property of catenation decreases on moving down the group from carbon to lead. The maximum tendency of catenation associated with carbon forms the basis of the carbon compounds which constitute organic chemistry.

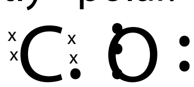
3.5 COMPOUNDS OF CARBON AND SILICON

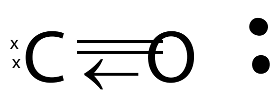
3.5.1 Structure of Oxides of Carbon

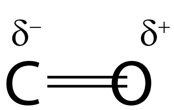
Three oxides of carbon are known:

(i) Carbon monoxide, CO (ii) Carbon dioxide, CO_2 (iii) Carbon suboxide, C_3O_2 Out of these, the last one is of little importance.

Structure of Carbon Monoxide (CO)

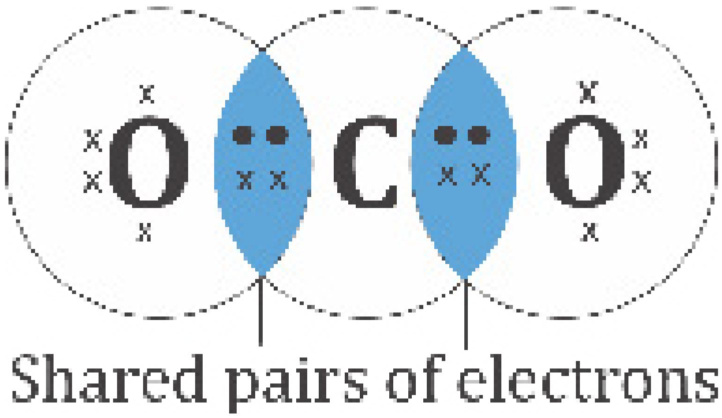
Carbon monoxide is diatomic molecule having triple bond between the two atoms. It is very slightly polar. The electronic structure of carbon monoxide can be represented as 

It is usually written as: 

It might appear from the above structure that the molecule should have a large dipole moment, but in fact the molecule has a small dipole moment (0.112D). 

Structure of the Carbon Dioxide

Carbon dioxide exists in the gaseous state as linear molecules. The observed C-O bond distance is 115 pm and is in agreement with the Structure shown. Solid CO_2 has a face-centered cubic structure. Being linear its dipole moment is zero.



3.5.2 Oxides of Silicon

Silicon Dioxide

Silicon dioxide, SiO_2 called silica, is probably the most common and the most important compound of silicon. In silica every silicon atom is attached tetrahedrally to four oxygen atoms and each oxygen atom has two close silicon neighbours.

Vitreous silica possesses the following interesting and useful properties.
1. High transparency to light.
2. Very refractory, does not soften below 1500 to 1600°C.
3. Very low thermal expansion.
4. Excellent insulator.
5. Hard, brittle and elastic.
6. Insoluble in water and inert toward many reagents.
7. It is resistant towards all acids except HF.

Quartz, the common crystalline form of silicon dioxide, is a hard, brittle, refractor, colourless solid which differs very markedly from carbon dioxide.

Both carbon and silicon have four electrons in their valence shells and both also form four covalent bonds. So, why should there be a big difference between CO_2 and SiO_2 ?

The answer lies in the fact that silicon atoms are much larger than carbon atoms and thus tend to surround themselves with more oxygen neighbours; silicon forms only single bonds to oxygen atoms whereas carbon may form double bonds. Carbon, in fact, forms double bonds to each of the two oxygen atoms to produce a small, symmetrical, linear molecule CO_2,which is volatile and reasonably reactive.

The silicon atom can be approached closely by four oxygen atoms and forms a single bond to each at tetrahedral angles. This structure can be continued in three dimensions to produce a continuous giant silicon oxygen network extending out to give the massive silicon dioxide crystal.

In the interior of the silica network every silicon atom is bonded tetrahedrally to four oxygen atoms and every oxygen atom is bonded to two silicon atoms. The overall ratio of silicon to oxygen atoms is 1:2 and the simplest formula for silica therefore is SiO_2. The silicon oxygen bonds are strong and keep the atoms firmly in place.

Note, however, that it is not the molecular formula for silica but the whole chunk of silica must be considered to be essentially one molecule. The atoms of silicon and oxygen at the surface of the chunk do not have all their valence forces satisfied, as is shown by the high surface activity of silica.

In each of the various crystalline forms of silica, there is a special pattern which is repeated throughout the crystal in a regular definite crystal lattice. The regular tetrahedral arrangement of four oxygen atoms around each silicon persists in each crystalline form but the Si-O-Si bond angles and the rotation about each Si-O bond are different in the different polymorphic species.

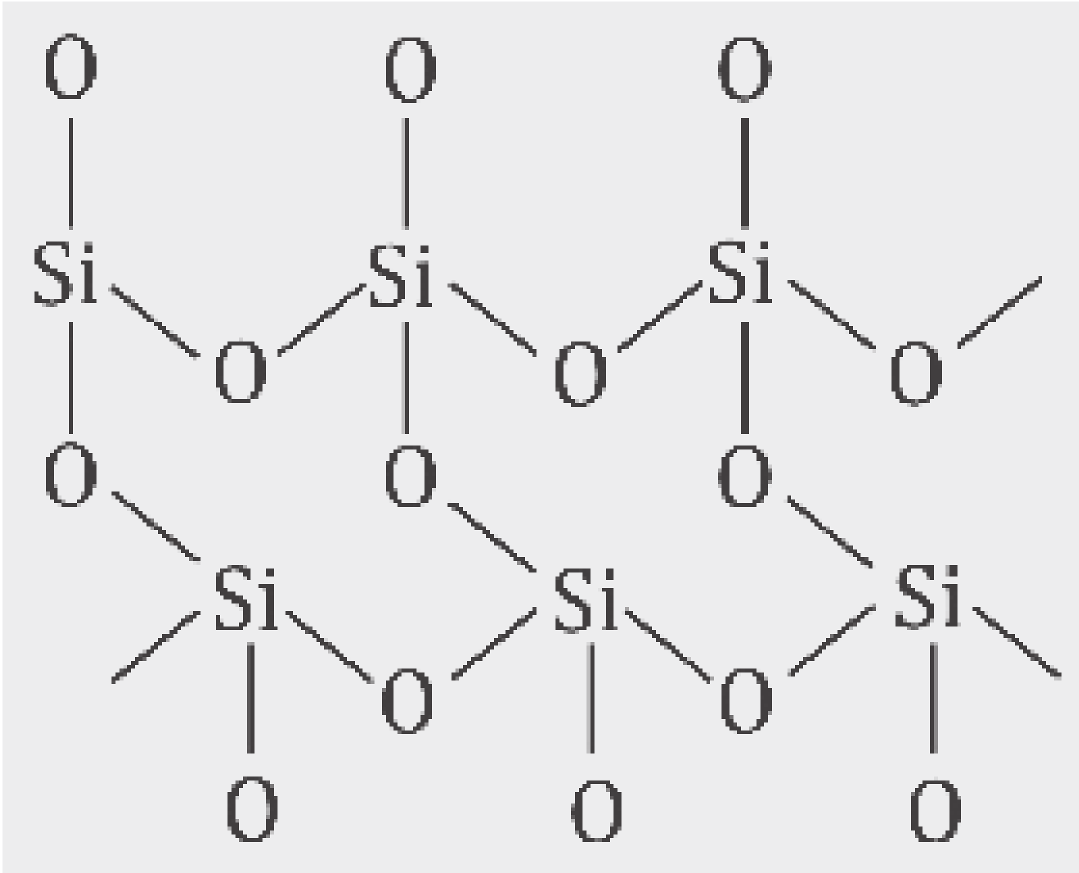


Fig. 3.1 Structure of silicon dioxide

When crystalline silica is heated sufficiently it melts to give a viscous liquid having a random structure, presumably with the silicon atoms still on the average close to four oxygen atoms and the oxygen atoms close to two silicon atoms. When this liquid silica is cooled it does not crystallize readily, but usually it under supercools tremendously and eventually becomes rigid without having undergone orientation into a regular crystal pattern. This rigid, highly under supercooled liquid is called vitreous silica or silica glass (frequently incorrectly referred to as fused quartz).

3.5.3 Silicates and their Uses

The compounds derived from silicic acids are termed as silicates.

1. Sodium silicate, Na_2SiO_3

This is a sodium salt of metasilicic acid H_2SiO_3 It is known as water glass or soluble glass. It is prepared by fusing sodium carbonate with pure sand. The process is carried out in a furnace called reverberatory furnace.

$$Na_2CO_3(s) + SiO_2(s) \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3(s)} + CO_2(g)$$

Properties:

Sodium silicate is soluble in water and its solution is strongly alkaline due to the hydrolysis.

> **Chemical Garden**
>
> When crystals of soluble coloured salts like nickel chloride, ferrous sulphate, copper sulphate or cobalt nitrate, etc. are placed in a solution of sodium silicate, they produce a very beautiful growth, like plant, which is called chemical garden.

Uses of Sodium Silicate:

1. It is used as a filler for soap in soap industry.
2. It is used in textile as a fire proof.
3. It is used as furniture polish.
4. It is also used in calico printing.

2. Aluminium Silicate

Many important silicate rocks contain aluminium. The weathering of these rocks results in the disintegration of the complex silicates which they contain. The boiling and freezing of water in the rocks, and the chemical action of water and carbon dioxide convert these compounds into potassium carbonate, sand and clay. The following reaction explains the weathering of potassium feldspar.

$$K_2O.Al_2O_3.6SiO_2(s) + H_2CO_3(aq) + H_2O(l) \longrightarrow K_2CO_3(s) + 4SiO_2(s) + Al_2O_3.(SiO_2)_2.2H_2O(s)$$

Pure clay, which has the formula shown above, is white and is called kaolin. It is used to make porcelain and china wares. Ordinary clay contains compounds of iron and other metals and it has a yellow or reddish yellow colour.

Impure clays can be more easily fused because they contain oxides of iron, calcium, magnesium and other metals which form easily fusiable silicates with sand. Such clays are used to make bricks, tiles, and stonewares. Due to the presence of ferric oxide, the articles of this clay turn reddish when heated in a kiln.

Stoneware is usually glazed to give it a less porous surface by throwing salt upon the articles while they are hot. This treatment produces sodium aluminate and sodium aluminium silicate, which melt readily and cover the entire surface. When the article cools, the covering solidifies, producing a compact, smooth, waterproof surface. China wares are made from a mixture of kaolin, bone ash, and feldspar; the mixture fuses when heated and fills the pores between the grains of kaolin.

The use of clay in making pottery and other ceramic articles depends upon the plasticity of the paste. When soaked in water the clay progressively hydrates, and the paste becomes more plastic. When the clay is heated the water of hydration is lost, and a hard rock like mass is formed.

3. Talc or Soapstone

The magnesium silicate, $Mg_3H_2(SiO_3)_4$, is commonly known as talc or soapstone. It is physically greasy to touch. Therefore it is used in making cosmetics. It is also used in making household articles.

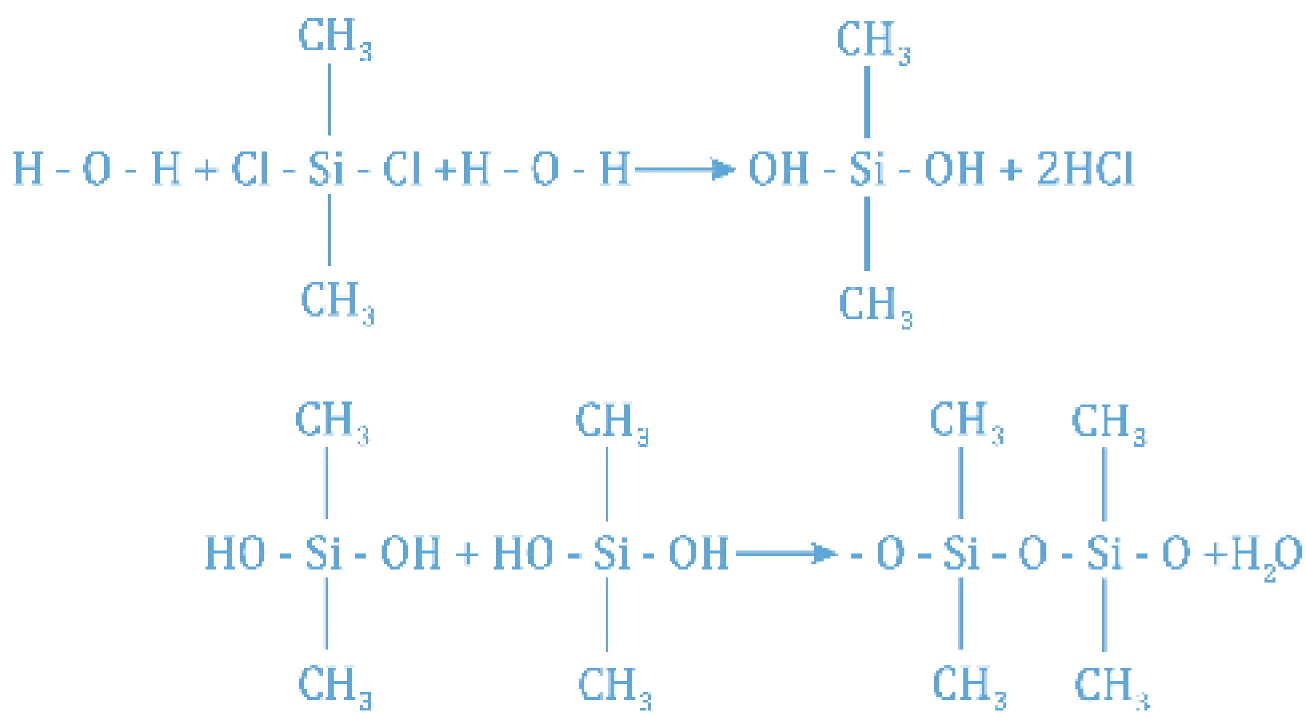
4. Asbestos

Asbestos is hydrated calcium magnesium silicate $CaMg_3(SiO_3)_4$. It is commonly used in making incombustible fabrics and hardboard, etc.

3.5.4 Silicones

The chemistry of silicon is, in many respects, very much like the chemistry of carbon. Just as carbon forms the compounds carbon dioxide (CO_2), carbon tetrachloride (CCl_4), and methane (CH_4), similarly silicon forms silicon dioxide (SiO_2), silicon tetrachloride ($SiCl_4$), and silane (SiH_4).

The silicon atom holds four methyl groups, $Si(CH_3)_4$, just as the carbon atom, $C(CH_3)_4$.If a compound of silicon containing chlorine atoms and methyl groups, $SiCl_2(CH_3)_2$, is allowed to react with water, hydrogen chloride (HCl) comes out, and the silicon atoms join together through oxygen atoms.



By this reaction we can make synthetically the silicon oxygen chains found in the mineral silicates, which we have just been discussing. A difference is that here we have $-CH_3$ groups instead of oxygen atoms joined to silicon as side chains. Such a compound is called a silicone; this particular one is a methyl silicone. Other alkyl groups may also be substituted for the methyl groups and the molecular chain can be made of various lengths.

Properties and Uses of the Silicones

Some of the methyl silicones are oily liquids and they become more viscous as the chain length increases. They are used as lubricants, either incorporated in greases or as oils, in bearings, gears, etc. They are also used in hydraulic brakes and other hydraulic systems. The outstanding physical attribute of silicone oil is its very small change in viscosity with change in temperature, compared with the behaviour of other oils of similar viscosity.

If the temperature is dropped from 100°C to 0°C the viscosity of petroleum oil may increase about one hundred folds, whereas that of silicone oil will increase less than four folds. In the presence of air or oxygen at temperature as high as 300°C, silicone oils remain free from acid formation, oxidation and similar phenomena, which frequently limit the usefulness of petroleum products and other synthetic organic liquids.

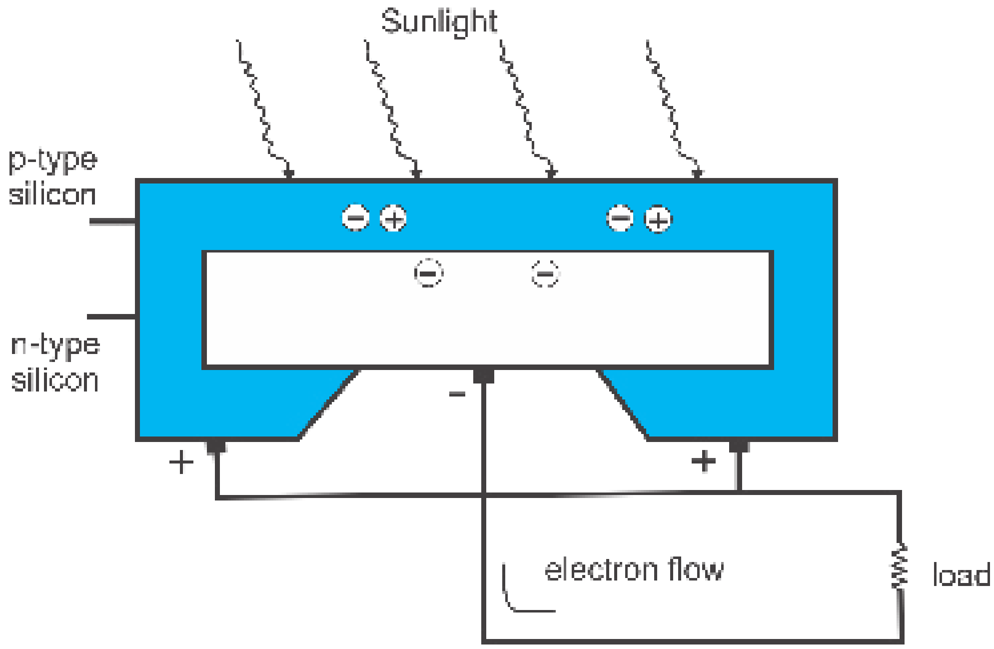
Methyl silicones of high molecular mass resemble rubber and are used in making rubber like tubing and sheets.

Silicone molecules can be made in such a way that bridges, or cross linkages bind one long molecule to another at several points along the chain. These compounds have resinous properties and are extensively used in electrical insulation.

Another interesting and important application of silicones is their use in the treatment of various surfaces to make them water repellent. A silicone film covers the surface and repels water like a grease film. Much of the leak of electricity through the moisture film on ceramic electrical insulators can be prevented by a silicone film; cloth, plastics, asbestos, glass, leather, and paper, even filter paper and blotting paper become strongly water repellent when covered with a silicone film.

3.6 SEMICONDUCTORS

A semiconductor is a substance that has different resistances to the passages of an electric current under different circumstances. Semiconductors include the elements germanium, selenium and silicon, and the compounds lead sulphide, silicon carbide, cadmium sulphide, lead telluride, gallium arsenide and indium antimonide.



Semiconductors conduct electricity better than insulators, but not as well as good conductors like metals. This gives them their name, which means "half conductors. " How well they conduct electricity depends upon their temperature. When a metal is heated, its resistance increases, when a semiconductor is heated its resistance decreases.

Semiconductors are also sensitive to light. The greater the intensity of the light that shines on them, the better they conduct electricity. The effects that light and heat energy have on semiconductors make them extremely useful. They are used in photoelectric cells and in solar batteries.

The electrons of semiconductors do not carry electric current as readily as the electrons of good electric conductors like metals. However, when the atoms of the material absorb heat or light, the electrons become less tightly bound to their atoms. They can now conduct electricity.

Another special property of semiconductors is the way they behave when they are joined to another material, which may be a metal or a different semiconductor. The junction between the different materials forms a boundary. It allows electricity to pass more properly and is used in transistors. Transistors are much smaller and less complicated than old fashioned electronic tubes. They are used in radio, television, computers and calculators.

3.7 USES OF LEAD COMPOUNDS IN PAINTS

Varoius oxides of lead, basic lead carbonate and lead chromate are commonly used as pigments in paints.

1. Lead Suboxide, Pb_2O

It is black powder, obtained on heating plumbous oxalate in the absence of air.

$$2PbC_2O_4(s) \xrightarrow{\Delta} Pb_2O(s) + 3CO_2(g) + CO(g)$$

Pb_2O is decomposed by heat into Pb and PbO.

Other than pigment, it is also used in the manufacture of lead storage batteries.

2. Lead Monoxide (Litharge, Massicot) PbO

Litharge varies in colour from pale yellow to reddish yellow, possibly owing to the existence of two forms, a rhombic (yellow) and a tetragonal (red). It is slightly soluble in water. It is usually used in preparing flint glass and paints. If litharge is boiled with water and olive oil, lead oleate which is a sticky adhesive mass is formed and glycerin passes into solution. Litharge is used in preparing oils and varnishes and in the manufacturing of flint glass.

3. Triplumbic Tetraoxide, (red lead, minium), Pb_3O_4

When lead is heated in air at about 340°C, it absorbs oxygen and forms a bright scarlet crystalline powder of read lead or minium.

$$3Pb(s) + 2O_2(g) \longrightarrow \underset{\text{Triplumbic tetraoxide}}{Pb_3O_4(g)}$$

It decomposes at 470°C

$$2Pb_3O_4(s) \longrightarrow 6PbO(s) + O_2$$

Red lead is used for a variety of purposes. Its principal uses are in the manufacture of storage batteries, as a pigment in paints applied to steel and iron to retard corrosion, and as an ingredient in the manufacture of flint glass, matches and ceramic glazes.

4. Lead Dioxide, PbO_2

When red lead is treated with concentrated nitric acid , it is decomposed into lead nitrate and lead dioxide.

$$Pb_3O_4(s) + 4HNO_3(aq) \longrightarrow 2Pb(NO_3)_2(s) + PbO_2(s) + 2H_2O$$

Lead dioxide is a reddish brown powder. It is not very soluble in water, but it does dissolve in alkaline water to yield soluble plumbates. It is not affected by dilute acids.

5. White Lead

Basic lead carbonate $2PbCO_3.Pb(OH)_2$ is an amorphous white pigment. It mixes readily with linseed oil and has a good covering power. If improperly prepared, it becomes crystalline and its covering power is reduced. White lead is not suitable for use as a good pigment since it is darkened by the hydrogen sulphide which is frequently present in the atmosphere.

6. Lead Chromate ($PbCrO_4$)

It is used as a pigment under the name of chrome yellow. Orange or red basic lead chromates are formed when lead chromate is boiled with dilute alkali hydroxide and are used as pigments. The stable yellow modification of lead chromate is monoclinic. Mixture of lead chromate with lead sulphate or barium sulphate are also used as yellow pigments.

Key Points

1. Boron occurs in traces and has been found to be important for the growth of many plants.
2. Borax ($Na_2B_3O_7$-$10H_2O$), colemanite ($Ca_2B_6O_{11}.5H_2O$), orthoboric acid (H_3BO_3) are the common minerals of boron.
3. Aluminium, after oxygen and silicon, is the third most abundant element in the earth's crust. Feldspar ($K_2O.Al_2O_3.6SiO_2$), corundum (Al_2O_3), bauxite ($Al_2O_3.2H_2O$) and cryolite (Na_3AlF_6) are the common minerals of aluminium.
4. The pair of outermost electrons that does not readily take part in chemical combination is termed as inert pair.
5. When heated, borax fuses, loses water of crystallization and swells up into a white porous mass. It is employed in borax bead test for identification of coloured salts.
6. When a hot concentrated solution of borax is treated with a calculated quantity of conc. H_2SO_4, on cooling crystals of boric acid are produced.
7. When aluminium is burnt in oxygen a brilliant light is produced.
8. The electronic configuration of group IVA elements show that they have four electrons in their valence shells, two electrons of which are in s-orbital and the remaining two are in p-orbitals.
9. Feldspar, potash mica and zircon are the famous minerals of silicon.
10. Silica has a net work structure in which every silicon atom is bonded tetrahedrally to four oxygen atoms and every oxygen atom is bond ed to two silicon atoms.
11. Sodium silicate, aluminium silicate, talc and asbestos are commercially important compounds of silicon and oxygen called silicates.
12. Methyl silicones can be used as lubricants and for water proofing.
13. Semiconductors conduct electricity better than insulators. They are also light sensitive.
14. Oxides of lead are used as pigments.

EXERCISE

Q.1. Fill in the blanks.

i) ______________________ acid has the chemical formula HBO_2.

ii) Aluminium normally occurs as____________________ minerals found in the rocks of outer portion of the earth.

iii) Aluminium gives ________________________gas with hot concentrated H_2SO_4.

iv) Boron forms-- bond in its compounds.

v) The chemical formula of white lead is ___________________ .

vi) ___________________ is the only element with less than four electrons in the outer most shell that is not a metal.

vii) In the Group IIIA of the periodic table,___________________ is a semi-metal.

viii) Borax that occurs as a natural deposit, is called________________________.

ix) Cryolite is an important mineral of aluminium and its formula is_____________________

x) A __________________________is a substance that has different resistances to the passage of an electric current under different circumstances.

Q.2. Indicate True Or False

i) Boron always uses all the three of its valence eletrons for bonding purposes.

ii) Diaspore is an ore of carbon.

iii) Emerald is an ore of aluminium that has the chemical formula $AlO_3.2SiO_2.2H_2O$.

iv) An aqueous solution of borax is feebly acidic in nature.

v) In case of borax bead test, of cupric oxide, the beads are coloured blue in the reducing flame.

vi) Boric acid can be titrated with sodium hydroxide.

vii) Carbon and silicon are the only non-metals in Group IVA.

viii) PbO is commonly known as litharge.

ix) Basic lead carbonate is a reddish brown pigment.

x) Aluminium oxide (Al_2Q_3) is also called bauxite.

Q. 4. What is the action of an aqueous solution of borax on litmus?

Q. 5. Give equations to represent the following reactions.

(a) Borax is heated with CoO

(b) Al_2O_3 is heated with NaOH solution

Q. 6. Why is aluminium not found as a free element? Explain the chemistry of borax bead test.

Q. 7. How does orthoboric acid react with:

(a) Sodium hydroxide (b) Ethyl alcohol

Q. 8. How will you convert boric acid into borax and vice versa?

Q. 9. Why are liquid silicones preferred over ordinary organic lubricants?

Q. 10. Explain:

(a) CO_2 is non-polar in nature.

(b) CO_2 is acidic in character.

Q. 11. Why is CO_2 a gas at room temperature while SiO_2 is a solid?

Q. 12. Give the names and the formulas of different acids of boron.

Q. 13. What is the importance of oxides of lead in paints?

Q. 14. Give the names, electronic configurations occurrence of Group-IIIA elements of the periodic table.

Q. 15. Discuss the peculiar behaviour of boron with respect to the other members of Group- IIIA elements.

Q. 16. (a) What is borax?

(b) Describe its commercial preparation.

(c) Outline the principal uses of borax.

(d) How does borax serve as a water softening agent?

Q. 17. (a) What is boric acid?

(b) How is boric acid prepared in laboratory?

(c) Give properties and uses of boric acid.

Q. 18.(a) Give the names alongwith the formulas of three important ores of aluminium.

(b) How and under what conditions does aluminium react with the following:

i) Oxygen ii) Hydrogen iii) Halogens iv) Acids v) Alkalies

Q. 19. Give the names, electronic configurations and occurrence of Group-IVA elements of the periodic table.

Q. 20. Discuss the peculiar behaviour of carbon with respect to the other members of Group-IVA of the periodic table.

Q.21 (a) What are silicones?

(b) Give a brief summary of the principal properties of silicones.

(c) Outline the uses pf silicones.

(d) What are silicates?

(e) Describe the important uses of silicates.

CHAPTER

4

GROUP VA AND GROUP VIA ELEMENTS

Animation 4.1 : Nitrogen-Cycle
Source and Credit: Organic

IN THIS CHAPTER YOU WILL LEARN

1. The names, electronic configuration and general characteristics of group VA and VIA elements.
2. The preparation and properties of oxides and oxyacids of nitrogen, phosphorus and halides of phosphorus.
3. Comparison of properties of oxygen and sulphur.
4. The manufacture, properties and uses of sulphuric acid.

GROUP VA ELEMENTS

4.1 INTRODUCTION

The elements of group VA of the periodic table comprises nitrogen, phosphorus, arsenic, antimony and bismuth.

Table . 4.1 Electronic Configurations and Physical Properties of Group VA Elements

Properties	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Electronic configuration	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10}4s^2 4p^3$	$[Kr]4d^{10}5s^2 5p^3$	$[Xe]5d^{10}6s^2 6p^3$
Physical appearance	Colourless gas	Black solid	Metallic solid	Metallic solid	Metallic solid
Ionization energy (kJ/mol)	1402	1012	950	830	700
Electron affinity (kJ/mol)	-7	-71.7	-77	-101	-110
Electronegativity	3.0	2.1	2.0	1.9	1.9
Atomic radius(pm)	70	110	121	141	157
Ionic radius of 3- ion (pm)	171	212	222	245	---
Melting points (°C)	-210	44	817	631	271
Boiling points (°C)	-196	280	613	1750	1560
Density (g/cm^3)	0.00125	1.83	5.73	6.68	9.80
Principal oxidation states	+3, +5	+3, +5	+3, +5	+3, +5	+3,+5

4.1.1 General Characteristics

Nitrogen and phosphorus of group VA show the typical properties of non-metals. For example, they are poor conductors of heat and electricity and give acidic oxides. Their compounds are predominantly covalent. Arsenic and antimony are metalloids. However bismuth at the bottom of the group shows definite metallic properties. The metallic character increases going down the group. Nitrogen has the greatest tendency to attract the electrons, antimony and bismuth have the least. The trend down the group also shifts from covalent bonding to ionic bonding. Phosphorus, arsenic and antimony have allotropes.

Allotropes of phosphorus i.e. red and white phosphorus are more important.

Phosphorus and other members of the group can make use of d orbitals in their bonding. This is because the energy of these orbitals is not much greater than those of the other valence shell orbitals. For example, phosphorus can make use of its 3s, 3p and the empty 3d orbitals during bonding with other elements.
In phosphorus one of the 3s electrons can be promoted to a vacant 3d orbital giving 5 unpaired electrons in the valence shell. Phosphorus can thus make three or five covalent bonds. Indeed three and five are the common valencies of the group VA elements.

4.2 NITROGEN AND ITS COMPOUNDS

4.2.1 Occurrence

Nitrogen is present in free state in air as a major constituent (78% by volume). It is an inactive gas in comparison with oxygen which is the next major constituent of air. Inorganic compounds of nitrogen are not commonly found as minerals.

In combined state nitrogen is found in all living matter including, animals and plants in the form of proteins, urea and amino acids.

Animation 4.2 : Nitrogen-Axides-Analyser
Source and Credit: Qld

4.2.2 Oxides of Nitrogen

Nitrogen forms several oxides with oxygen. Common oxides of nitrogen are N_2O, NO and NO_2. It also forms N_2O_3 and N_2O_5.

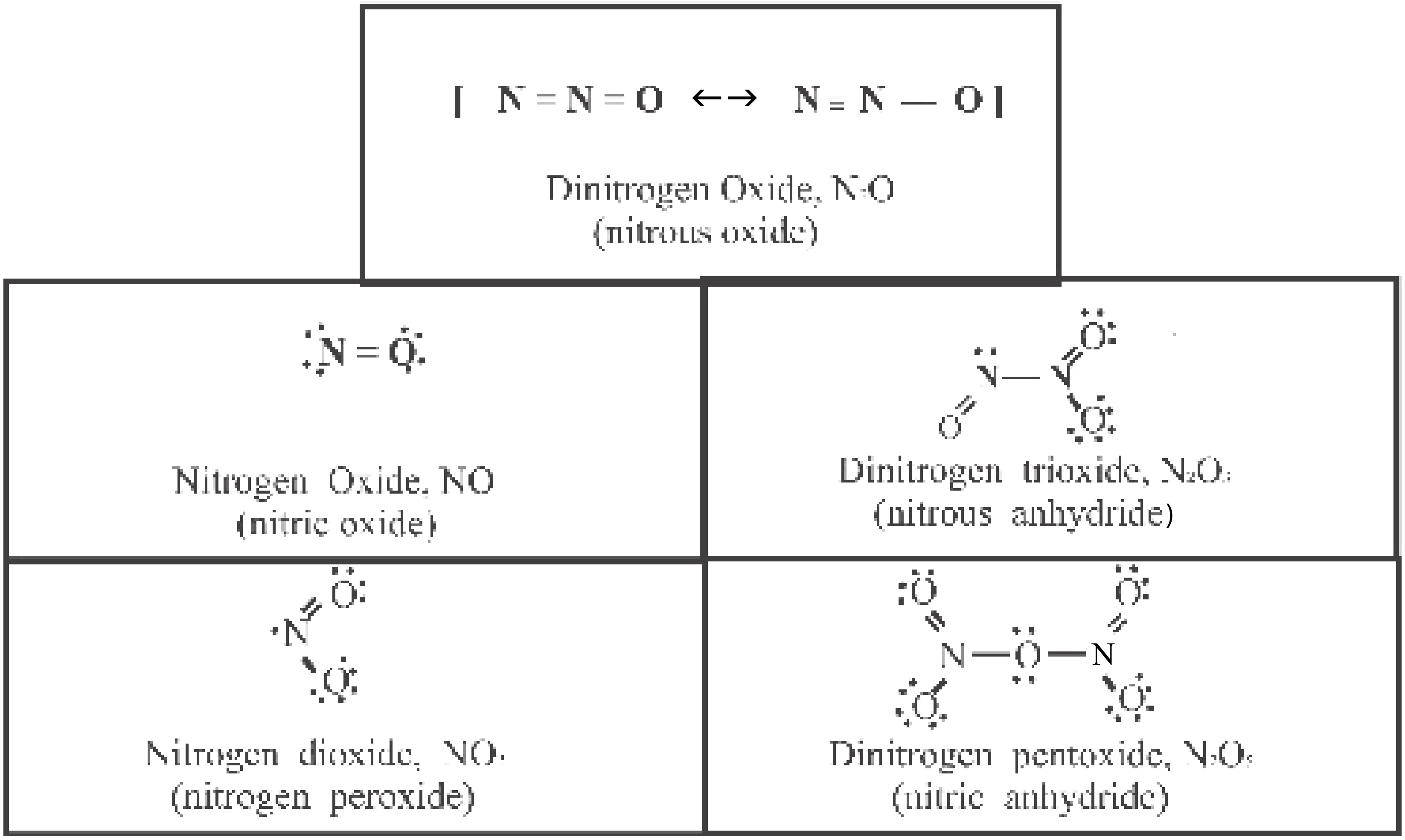


Fig. 4.1 Oxides of Nitrogen

1. Dinitrogen Oxide (N_2O)

Preparation

1.Dinitrogen oxide can be prepared by the action of dil, HNO, on metallic zinc.

$$4Zn(s)+10HNO_2(dil.)\rightarrow 4Zn(NO_3)_2(aq)+N_2O(g)+5H_2O(l)$$

2. It is usually prepared by heating ammonium nitrate to about 200°C .

$$NH_4NO_3(s)\rightarrow N_2O(g)+2H_2O(l)$$

To avoid the danger of explosion, ammonium nitrate can be replaced by a mixture of sodium nitrate and ammonium sulphate.

Properties of Dinitrogen Oxide

Dinitrogen oxide is a colourless gas with a faint, pleasant smell and a sweetish taste. It is fairly soluble in cold water. Its mixture with a little oxygen, if inhaled for a sufficiently long time, produces hysterical laughter, hence it is also known as "laughing gas".

Reactions

1. It is not combustible but resembles oxygen in rekindling a glowing splinter. Similarly, it supports combustion if burning substances, such as sulphur, phosphorus, etc. are taken in the cylinder containing this gas.

$$S(s)+2N_2O(g)\rightarrow SO_2(g)+2N_2(g)$$

$$P_4(s)+10N_2O(g)\rightarrow P_4O_{10}(s)+10N_2(g)$$

2. When N_2O is passed over red hot copper, it is reduced to nitrogen.

$$Cu(s) + N_2O(g) \rightarrow CuO(s) + N_2(g)$$

2. Nitrogen Oxide (NO)

Preparation

1. Nitrogen oxide can be prepared by the action of dil HNO_3 on copper.

$$3Cu(s) + 8HNO_3(dil.) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

2. It can also be prepared by passing air through an electric arc.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

Properties of Nitrogen Oxide

Nitrogen oxide is a colourless gas heavier than air and sparingly soluble in water.

Reactions

1. With oxygen, it forms reddish brown nitrogen dioxide.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

2. It decomposes into N_2 and O_2 at about 1000°C and supports combustion.

$$2NO(g) \rightarrow N_2(g) + O_2(g)$$

3. It forms nitrosyl chloride and nitrosyl bromide with chlorine and bromine, respectively in the presence of charcoal.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

4. It forms a brown coloured addition compound with $FeSO_4$.This test is used to confirm the presence of nitrates (Ring Test).

$$FeSO_4(aq) + NO(g) \rightarrow FeSO_4 . NO(aq)$$

5. With reducing agents, it is reduced to nitrous oxide or nitrogen.

$$H_2S(g) + 2NO(g) \rightarrow H_2O(g) + N_2O(g) + S(s)$$

$$H_2SO_3(aq) + 2NO(g) \rightarrow H_2SO_4(aq) + N_2O(g)$$

6. Oxidizing agents can oxidize NO to NO_2 or HNO_3.

$$2HNO_3(aq) + NO(g) \rightarrow H_2O(l) + 3NO_2(g)$$

$$6KMnO_4(aq) + 12H_2SO_4(aq) + 10NO(g) \longrightarrow 6KHSO_4(aq) + 6MnSO_4(aq) + 10HNO_3(aq) + 4H_2O(l)$$

3. Nitrogen Dioxide (NO_2)

Preparation

1. It can be prepared in small quantities by heating lead nitrate.

$$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$$

2. It can also be prepared by reacting conc. HNO_3 with copper.

$$Cu(s) + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$$

Animation 4.3 : Nitrogen-Cycle
Source and Credit: Organic

Properties of Nitrogen Dioxide

Nitrogen dioxide is a reddish brown gas with a pungent smell. It dissolves readily in water to form a blue acidic solution.

Reactions

1. On cooling, NO_2 is converted into a yellow liquid which can be frozen to a colourless solid dinitrogen tetraoxide (N_2O_4). If this solid is heated to 140°C, the mixture contains NO_2 and N_2O_4 but above 140°C NO_2 is converted to NO and O_2 molecules which are colourless. This decomposition is complete at 620°C.

$$\underset{\text{Pale Yellow}}{NO_2(g) \rightarrow NO_2(l) \rightarrow N_2O_4(l)} \xrightarrow{140^\circ C} \underset{\text{Reddish brown}}{2NO_2(g)} \xrightarrow{620^\circ C} \underset{\text{Colourless}}{2NO\,(g) + O_2(g)}$$

2.Elements like phosphorus, potassium and carbon continue burning in NO_2 as it yields O_2 on decomposition.

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

$$2P(s) + 5NO_2(g) \rightarrow P_2O_5(s) + 5NO(g)$$

3.In the absence of air, it dissolves in water to form nitric and nitrous acids

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

However in the presence of air or oxygen, nitric acid is the final product.

$$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$$

4.A mixture of nitrate and nitrite is formed when NO_2 is passed through strong alkalies.

$$2NaOH(aq) + 2NO_2(g) \rightarrow NaNO_3(aq) + NaNO_2(aq) + H_2O(l)$$

$$2KOH(aq) + 2NO_2(g) \rightarrow KNO_3(aq) + KNO_2(aq) + H_2O(l)$$

5. It is a strong oxidizing agent and oxidizes H_2S to sulphur, ferrous sulphate to ferric sulphate and KI to I_2.

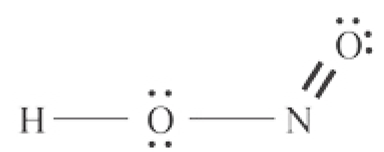
$$H_2S(g) + NO_2(g) \rightarrow H_2O(l) + S(s) + NO(g)$$

$$2FeSO_4(aq) + H_2SO_4(aq) + NO_2(g) \rightarrow Fe_2(SO_4)_3(aq) + H_2O(l) + NO(g)$$

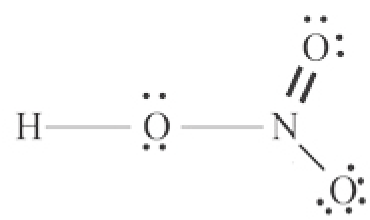
$$2KI(aq) + 2NO_2(g) \rightarrow 2KNO_2(aq) + I_2(s)$$

4.2.3 Oxyacids of Nitrogen

There are two important oxyacids of nitrogen, nitrous acid and nitric acid.



Nitrous acid, HNO_2



Nitric acid, HNO_3

1. Nitrous Acid (HNO_2)

Preparation

1. It can be prepared by dissolving dinitrogen trioxide in water at 0°C.

$$N_2O_3(g) + H_2O(l) \rightarrow 2HNO_2(aq)$$

2. Pure nitrous acid solution can be prepared by reaction between ice cold barium nitrite solution and ice cold dilute sulphuric acid.

$$Ba(NO_2)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HNO_2(aq)$$

Properties of Nitrous Acid

It is only known in the form of its salts and is stable to some extent in a dilute solution.

Reactions

1. It begins to decompose almost as soon as it is formed even at ordinary temperature.

$$3HNO_2(aq) \rightarrow HNO_3(aq) + 2NO(g) + H_2O(g)$$

2. It acts as an oxidizing agent and oxidizes HI, SO_2 and $SnCl_2$ into I_2, H_2SO_4 and $SnCl_4$, respectively.

$$2HNO_2(\text{aq}) + 2\,\text{HI(aq)} \rightarrow 2\,\text{H}_2\,O(l) + 2NO(g) + I_2(s)$$

$$2HNO_2 \rightarrow H_2O + 2NO + [O]$$

$$SO_2(g) + H_2O(l) + [O](g) \rightarrow H_2SO_4(aq)$$

$$SnCl_2(aq) + 2HCl(aq) + 2HNO_2(\text{aq}) \rightarrow SnCl_4(aq) + 2NO(g) + 2H_2O(l)$$

3. Nitrous acid decolourizes acidified $KMnO_4$ and bromine water. It readily gets oxidized to nitric acid, so it also behaves as a reducing agent.

$$2KMnO_4(aq) + 3H_2SO_4(aq) + 5HNO_2(aq) \rightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 3H_2O(l) + 5\,\text{HNO}_3(\text{aq})$$

$$HNO_2(aq) + Br_2(aq) + H_2O(\text{l}) \rightarrow \text{HNO}_3(\text{aq}) + 2\,\text{HBr(aq)}$$

4. As an acid it reacts with alkalies producing salts.

$$NaOH(aq) + HNO_2(aq) \rightarrow NaNO_2(aq) + H_2O(l)$$

5. It also reacts with organic compounds containing NH_2 group and produces nitrogen.

$$2HNO_2(aq) + \underset{Urea}{CO(NH_2)_2}(aq) \rightarrow 2N_2(g) + CO_2(g) + 3H_2O(l)$$

$$HNO_2(aq) + \underset{Aminobenzene}{C_6H_5NH_2}(l) \rightarrow \underset{Phenol}{C_6H_5OH}(l) + N_2(g) + H_2O(l)$$

Animation 4.4 : Nitric oxide binding
Source and Credit: ESRF

2. Nitric Acid (HNO_3)

Preparation

In the laboratory, nitric acid is prepared by heating potassium nitrate crystals with concentrated sulphuric acid.

$$KNO_3(s) + H_2SO_4(conc.) \rightarrow KHSO_4(aq) + HNO_3(aq)$$

Manufacture of Nitric Acid Birkeland and Eyde's process

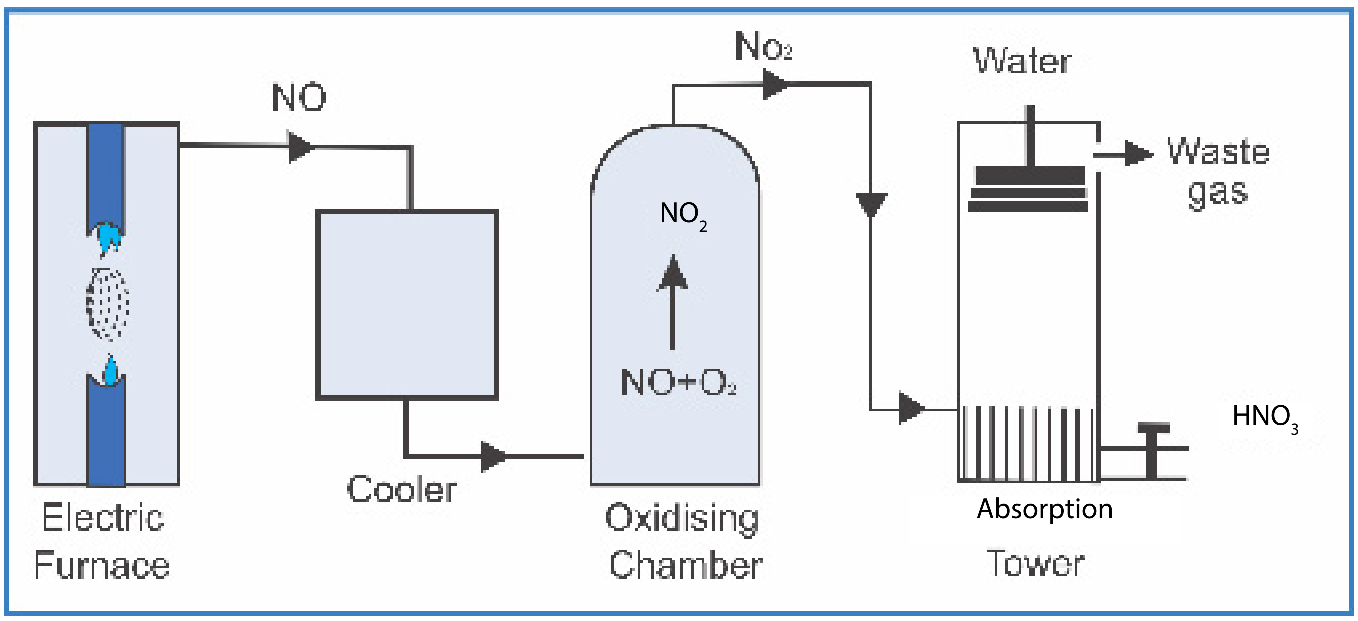
This process consists of the following steps:

(i) Formation of nitric oxide

Atmospheric nitrogen and oxygen are combined to give nitric oxide in an electric arc (3000°C).

$$N_2(g) + O_2(g) \xrightarrow{3000^\circ C} 2NO(g)$$

NO formed is cooled quickly to 1000°C at which it does not decompose.



Fiq 4.2 Manufacture of nitric acid form air

(ii) At 600°C,NO combines with O_2 to form NO_2

$$2NO(g)+O_2(g)\rightarrow 2NO_2(g)$$

(iii) Nitrogen dioxide is absorbed in water to give dilute HNO_3 along with nitrous acid.

$$2\,NO_2(g)+H_2O(l)\rightarrow HNO_3(aq)+HNO_2(aq)$$

(iv) Nitrous acid is oxidized to nitric acid and nitric oxide which is re-oxidized to NO_2.

$$3\,HNO_2(g)\rightarrow HNO_3(aq)+2\,NO(g)+H_2O(l)$$

Properties of Nitric Acid

Concentrated nitric acid is a colourless volatile liquid which fumes strongly in air . It has a pungent smell. Its specific gravity at 15°C is 1.53.

Reactions

1. Nitric acid is decomposed in the presence of light even at ordinary temperature.

$$4\,HNO_3(aq)\rightarrow 2H_2O(l)+4NO_2(g)+O_2(g)$$

2. It is a very strong acid. It exhibits all the usual general properties of acids in all reactions where its oxidizing properties are not shown. It reacts in normal way with basic oxides, hydroxides and carbonates forming respective salts.

$$2\,HNO_3(aq)+CaO(s)\rightarrow H_2\,O(l)+Ca(NO_3)_2(aq)$$

$$HNO_3(aq)+NaOH(aq)\rightarrow H_2O(l)+NaNO_3(aq)$$

$$2\,HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2\,NaNO_3(aq) + H_2\,O(l) + CO_2(g)$$

3. It acts as a strong oxidizing agent due to the ease with which it is decomposed.

$$2HNO_3(aq) \rightarrow H_2O(l) + 2NO_2(g) + [O](g)$$

(i) It oxidizes non-metals to their corresponding oxides.

$$C(s) + 4\,HNO_3(conc.) \rightarrow CO_2(g) + 4\,NO_2(g) + 2\,H_2O(l)$$

$$S(s) + 6HNO_3(conc.) \rightarrow 2H_2O(l) + 6NO_2(g) + H_2SO_4(aq)$$

$$5\,HNO_3(conc.) + P(s) \rightarrow H_3PO_4(aq) + H_2\,O(l) + 5\,NO_2(g)$$

(ii) Metalloids like arsenic and antimony can be oxidized to their corresponding acids.

$$As(g) + 5\,HNO_3(conc.) \rightarrow H_3AsO_4(aq) + 5NO_2(g) + H_2O(l)$$

$$Sb(g) \rightarrow 5HNO_3(conc.) \rightarrow H_3SbO_4(aq) + 5NO_2(g) + H_2O(l)$$

Animation 4.5 : Nitric oxide binding
Source and Credit: ESRF

(iii) Nitric acid behaves differently with different metals.

(a) Gold, platinum, iridium and titanium do not react.

(b) Iron, cobalt, nickel, chromium, aluminium are rendered passive by acid due to the formation of a film of their oxides over them .

(c) Tungsten and uranium are changed into their oxides.

(d) Magnesium, calcium and manganese give hydrogen with dilute nitric acid.

$$Mg(s) + 2HNO_3(dil) \rightarrow Mg(NO_3)_2(aq) + H_2(g)$$

$$Mn(s) + 2HNO_3(dil) \rightarrow Mn(NO_3)_2(aq) + H_2(g)$$

(e) Copper and lead give nitric oxide with dilute acid and nitrogen dioxide with concentrated acid.

$$3Cu(s) + 8HNO_3(dil) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

$$Cu(s) + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

(f) Mercury gives mercurous nitrate and nitric oxide with dilute nitric acid.

$$6Hg(l) + 8HNO_3(dil) \rightarrow 3Hg_2(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$$

With concentrated acid, it gives mercuric nitrate and NO_2

$$Hg(l) + 4HNO_3(conc) \rightarrow Hg(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

(g) Silver reacts with nitric acid to give silver nitrate and nitric oxide

$$3Ag(s) + 4HNO_3(aq) \rightarrow 3AgNO_3(aq) + NO(g) + 2H_2O(l)$$

(h) Dilute nitric acid gives ammonium nitrate, when it reacts with tin. With concentrated acid meta-stannic acid is produced.

$$4Sn(s) + 10HNO_3(dil.) \rightarrow 4Sn(NO_3)_2(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

$$\mathrm{Sn(s)} + 4HNO_3(conc.) \rightarrow H_2SnO_3(aq) + 4NO_2(g) + H_2O(l)$$

(i) Zinc gives different products depending upon the concentration of acid and temperature. Very dilute nitric acid gives NH_4NO_3. Moderately dilute nitric acid gives nitrous oxide while concentrated nitric acid gives NO_2.

$$4Zn(s) + 10HNO_3(v.\mathrm{dil.}) \rightarrow 4Z\,\mathrm{n(NO_3)_2}(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

$$4Zn(s) + 10HNO_3(dil.) \rightarrow 4Zn(NO_3)_2(aq) + N_2O(g) + 5H_2O(l)$$

$$Zn(s) + 4HNO_3(conc.) \rightarrow Zn(NO_3)_2(aq) + 2\,\mathrm{NO_2} + 2H_2O(l)$$

4 .Reducing agents like $FeSO_4$, H_2S and HI are converted to F $e_2(SO_4)_3$, S and I_2 respectively, when they react with conc. HNO_3

$$6FeSO_4(aq) + 3H_2SO_4(aq) + 2HNO_3(conc.) \rightarrow 3Fe_2(SO_4)_3(aq) + 2NO(g) + 4H_2O(l)$$

$$2HNO_3(aq) + 3H_2S(g) \rightarrow 4H_2O(l) + 2NO(g) + 3S(s)$$

$$6HI(aq) + 2HNO_3(conc.) \rightarrow 4H_2O(l) + 2NO(g) + 3I_2(s)$$

5 Aqua Regia

When one volume of concentrated HNO_3 is mixed with 3 volumes of concentrated HCl, aqua regia is formed.It is employed to dissolve gold and platinum.

$$HNO_3(conc.) + 3\,\mathrm{HCl(conc.)} \rightarrow \mathrm{NOCl(aq)} + Cl_2(g) + 2H_2O(l)$$

Animation 4.6 : Gold Coin Dissolving in Acid
Source and Credit: Makeagif

NOCl formed is decomposed giving NO and Cl_2

$$NOCl \rightarrow NO(g) + [Cl](g)$$

This liberated chlorine gas converts noble metals such as gold and platinum into their water soluble chlorides.

$$Au(s) + 3[Cl](aq) \rightarrow 2AuCl_3(aq)$$

6. Nitric acid reacts with glycerine, toluene and phenol to prepare materials used as explosives like nitroglycerine, trinitrotoluene (TNT) and picric acid, respectively.

Uses

It is used

1. as a laboratory reagent.
2. in the manufacture of nitrogen fertilizers.
3. in the manufacture of explosives.
4. for making varnishes and organic dyes.

4.3 PHOSPHORUS AND ITS COMPOUNDS

4.3.1 Occurrence

Phosphorus is the second member of group VA. Its name comes from Greek word meaning "Light bearing". Unlike, nitrogen it does not occur in free state in nature. Most of the phosphorus is found in deposits of phosphate rock, i.e.impure $Ca_3(PO_4)_2$ and apatite $Ca_5F\ (PO_4)_3$. As a constituent of plant and animal tissues, it is essential for their normal growth. It occurs especially in seeds, the yolk of eggs, the nerves, brain and bone marrows, usually in the form of lecithins. In the form of calcium phosphate, it is an essential constituent of bones. Bone ash (80% calcium phosphate) is an important source of phosphorus.

4.3.2 Allotropes of Phosphorus

Phosphorus can exist in at least six different solid allotropic forms, of which we will mention only three.

White phosphorus is a very reactive, poisonous, volatile, waxy, yellowish white substance, which is soluble in benzene and carbon disulphide. It exists in the form of tetraatomic molecules (P_4) which have a tetrahedral structure, Fig. 4.3. It boils at 280°C to P_4 vapours which dissociate above 700°C to form P_2 molecules.

Red phosphorus is much less reactive and less poisonous than white phosphorus. It is prepared by heating white phosphorus in the presence of a little iodine or sulphur as a catalyst upto 250°C in vacuum. The tetra-atomic molecules of red phosphorus combine to form macromolecules, Fig. 4.4 .

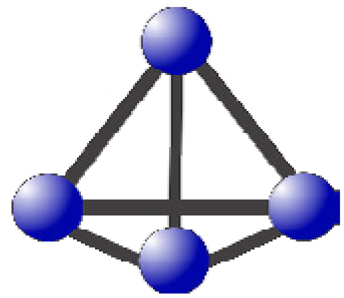


Fig.4.3 White phosphorus

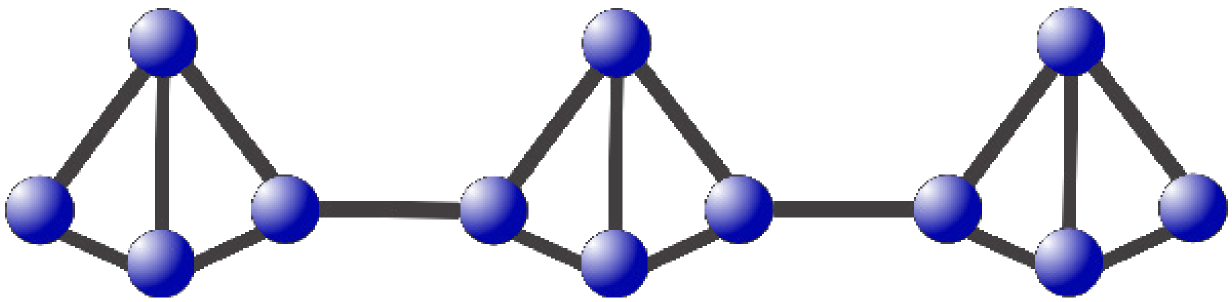


Fig. 4.4 Red phosphorus

Black phosphorus is the third form which is most stable under ordinary conditions. Black phosphorus is prepared by heating red phosphorus to high temperature and pressure.

4.3.3 Halides of Phosphorus

1. Phosphorus Trichloride (PCl_3)

Preparation

1. It is usually prepared by melting white phosporus in a retort in an inert atmosphere of CO_2 and current of dried chlorine is passed over it. The vapours of PCl_3 are collected in a flask kept in an ice-bath.

$$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l)$$

2. It may also be prepared by the action of phosphorus with thionyl chloride.

$$2P(g) + 4SOCl_2(l) \rightarrow 2PCl_3(l) + 2SO_2(g) + S_2Cl_2(s)$$

Properties of Phosphorus Trichloride

It is a colourless fuming liquid which boils at 76°C and freezes at-112°C.

Reactions

1. It combines with chlorine to form phosphorus pentachloride

$$PC1_3(l)+C1_2(g)\rightarrow PC1_5(s)$$

2. It combines with atmospheric oxygen slowly to form phosphorus oxychloride.

$$2PC1_3(l)+O_2(g)\rightarrow 2POC1_3(s)$$

3. It is soluble in organic solvents, but readily reacts with water to form phosphorus acid.

$$PC1_3(l)+3H_2O(l)\rightarrow H_3PO_3(aq)+3HC1(aq)$$

4. It reacts with alcohols and carboxylic acidsforming the respective chloro derivatives and H_3PO_3.

$$3CH_3OH(l)+PC1_3(l)\rightarrow 3CH_3C1(l)+H_3PO_3(l)$$

$$3CH_3COOH(l)+PC1_3(l)\longrightarrow 3CH_3COC1(l)+H_3PO_3(l)$$

2. Phosphorus Pentachloride ($PC1_5$)

Preparation

1. By passing dry chlorine through phosphorus trichloride.

$$PC1_3(l)+C1_2(g)\rightarrow PC1_5(s)$$

2. It may also be prepared by passing dry chlorine in a well cooled solution of phosphorus in carbon disulphide

$$2P(l)+5C1_2(g)\rightarrow 2PC1_5(s)$$

Properties of Phophorus Pentachloride

1. It is a yellowish white crystalline solid which sublimes at about 100°C. It gives fumes in moist air with an irritating smell.

Reactions

1. It decomposes on heating producing PCl_3 and chlorine.

$$PCl_5(s) \rightarrow PCl_3(l) + Cl_2(g)$$

2. It gets decomposed by water forming phosphorus oxychloride which further reacts with water to produce orthophosphoric acid.

$$PCl_5(s) + H_2O(l) \rightarrow POCl_3(l) + 2HCl(aq)$$
$$POCl_3(l) + 3H_2O(l) \rightarrow H_3PO_4(aq) + 3HCl(aq)$$
$$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$$

3. It converts metals into their chlorides.

$$Zn(s) + PCl_5(s) \rightarrow ZnCl_2(s) + PCl_3(l)$$

4.3.4 Oxides of Phosphorus

1. Phosphorus Trioxide, P_2O_3 (P_4O_6)

Preparation

1. P_2O_3 can be prepared by burning white phosphorus in a limited supply of air.

$$P_4(s) + 3O_2(g) \rightarrow 2P_2O_3(s)$$

Properties of Phoshorus Trioxide

It is a white waxy solid with garlic like odour. It melts at 22.8°C and boils at 173°C. It is highly poisonous in nature.

Reactions

1. When heated in the presence of air or oxygen, it is converted into phosphorus pentoxide.

$$P_2O_3(s) + O_2(g) \rightarrow P_2O_5(s)$$

2. It reacts with cold water to give phosphorus acid.

$$P_2O_3(s) + 3H_2O(l) \longrightarrow 2H_3PO_3(l)$$

With hot water, it forms phosphine and phosphoric acid.

$$2P_2O_3(s) + 6H_2O(l) \rightarrow 3H_3PO_4(aq) + PH_3(g)$$

Phosphorus Pentoxide, P_2O_5 or P_4O_{10}

Preparation

1. It is prepared by burning phosphorus in excess of dry air.

$$P_4(s) + 5O_2(g) \rightarrow 2P_2O_5(s)$$

Properties of Phosphorus Pentoxide

It is a white hygroscopic powder having a faint, garlic like odour due to the presence of traces of P_2O_3. It sublimes at 360°C.

Reactions

1. With cold water phosphorus pentoxide forms metaphosphoric acid.

$$P_2O_5(s) + H_2O(l) \rightarrow 2HPO_3(aq)$$

With hot water, it forms orthophosphoric acid

$$P_2O_5(s)+3H_2O(l)\rightarrow 2H_3PO_4(aq)$$

2. It is a powerful dehydrating agent, thus, with HNO_3, H_2SO_4, CH_3COOH and C_2H_5OH, it gives N_2O_5, SO_3, $(CH_3CO)_2O$ and C_2H_4 ,respectively.

$$2HNO_3(aq)+P_2O_5(s)\rightarrow N_2O_5(g)+2HPO_3(aq)$$

$$H_2SO_4(aq)+P_2O_5(s)\rightarrow SO_3(g)+2HPO_3(aq)$$

$$2CH_3COOH(aq)+P_2O_5(s)\rightarrow \underset{Aceticanhydride}{(CH_3CO)_2O(l)}+2HPO_3(aq)$$

$$C_2H_5OH(l)+P_2O_5(s)\rightarrow C_2H_4(g)+2HPO_3(aq)$$

4.3.5 Oxyacids of Phosphorus

1. Phosphorus Acid (H_3PO_3)

Preparation

1. It is prepared by dissolving phosphorus trioxide in cold water.

$$P_2O_3(s)+3H_2O(l)\rightarrow 2H_3PO_3(aq)$$

2. It is also obtained by the hydrolysis of phosphorus trichloride.

$$PCl_3(l)+3H_2O(l)\rightarrow H_3PO_3(aq)+3HCl(aq)$$

Properties of Phosphorus Acid

It is a white crystalline solid, which melts at 73.6°C.

Reactions

1. It decomposes into phosphine and orthophophoric acid on heating.

$$4H_3PO_3(s) \rightarrow 3H_3PO_4(l) + PH_3(g)$$

2. It is a powerful reducing agent and reduces $CuSO_4$, $AgNO_3$, etc. to the metallic state.

$$H_3PO_3(s) + CuSO_4(aq) + H_2O(l) \rightarrow H_3PO_4(aq) + H_2SO_4(aq) + Cu(s)$$

$$H_3PO_3(s) + 2AgNO_3(aq) + 2NH_4OH(aq) \rightarrow H_3PO_4(aq) + 2NH_4NO_3(aq) + H_2O(l) + 2Ag(s)$$

3. It reacts with oxygen to form orthophosphoric acid.

$$2H_3PO_3(s) + O_2(g) \rightarrow 2H_3PO_4(s)$$

4. Nascent hydrogen produced by Zn/HCl reduces H_3PO_3 to phosphine

$$H_3PO_3(s) + 6[H](g) \rightarrow PH_3(g) + 3H_2O(l)$$

2. Orthophosphoric Acid (H_3PO_4)

Preparation

1. It is prepared by dissolving phosphorus pentoxide in hot water.

$$P_2O_5(s) + 3H_2O(l) \rightarrow 2H_3PO_4(aq)$$

2. It is also obtained by heating red phosphorus with concentrated HNO_3.

$$P(s) + 5HNO_3(conc.) \rightarrow H_3PO_4(aq) + 5NO_2(g) + H_2O(l)$$

3. Hydrolysis of phosphorus pentachloride also gives orthophosphoric acid.

$$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$$

4. On large scale, it can be prepared by heating a mixture of phosphorite (bone ash) and sand in an electric furnace. The phosphorus pentoxide formed is treated with hot water to obtain phosphoric acid.

$$Ca_3(PO_4)_2(s) + 3SiO_2(s) \rightarrow 3CaSiO_3(s) + P_2O_5(s)$$

$$P_2O_5(s) + 3H_2O(l) \rightarrow 2H_3PO_4(aq)$$

Properties of Orthophosphoric Acid

It is a colourless, deliquescent crystalline solid which melts at 41°C. It is soluble in water.

Reactions

1. It is a weak tribasic acid. It reacts with NaOH to give three series of salts.

i. $H_3PO_4(aq) + NaOH(aq) \rightarrow NaH_2PO_4(aq) + H_2O(l)$

ii. $NaH_2PO_4(aq) + NaOH(aq) \rightarrow Na_2HPO_4(aq) + H_2O(l)$

iii. $Na_2HPO_4(aq) + NaOH(aq) \rightarrow Na_3PO_4(aq) + H_2O(l)$

2. On heating, it loses water and converted into pyro and metaphosphoric acid.

$$\underset{\text{Orthophosphoric acid}}{2H_3PO_4} \xrightarrow[-H_2O]{240^\circ C} \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} \xrightarrow[-H_2O]{316^\circ C} \underset{\text{Metaphosphoric acid}}{2HPO_3}$$

GROUP VIA ELEMENTS

4.4 Group VIA Elements

The group VIA of the periodic table consists of oxygen, sulphur, selenium, tellurium and polonium. These elements are called chalcogens from the Greek for "copper giver", because they are often found in copper ores. The electronic configuration and physical properties of group VIA elements are shown in Table 4.2

Table . 4.2 Electronic Configuration and Physical Properties of Group VIA Elements

Physical Properties	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Electronic configuration	$[He]2s^22p^4$	$[Ne]3s^23p^4$	$[Ar]4s^24p^4$	$[Kr]5s^25p^4$	$[Xe]6s^26p^4$
Ionization energy (kJ/mol)	1314	1000	941	869	813
Electron affinity (kJ/mol)	-141.1	-200.42	-195	-183	-180
Electronegativity	3.5	2.5	2.4	2.1	2.0
Atomic radius(pm)	66	104	117	137	152
Ionic radius 2-ion (pm)	140	184	198	221	-----
Melting points (°C)	-218	113	217	450	254
Boiling points (°C)	-183	444.6	684	990	962
Density (g/cm^3)	0.00143	2.06	4.8	6.25	9.4

4.4.1 General Characteristics

All the elements of group VIA are non-metals except Po which is a radioactive metal. Atomic radii, density, melting and boiling points generally increase with increase in atomic number down the group. Ionization energies of the group members are very high which shows their reluctance to lose electrons. Oxygen is the most electronegative element after fluorine. All these elements show the property of allotropy.

Oxygen has two allotropic forms (O_2 and O_3), sulphur has 3(α, β, γ), Se has two (red and grey) ,Te has two (metallic and non-metallic). They also show the property of catenation. This property decreases down the group. All the elements are polymeric in nature (they form poiy-atomic molecules). They attain the electronic configuration of the nearest noble gas by gaining 2 electrons forming O^{-2}, S^{-2}, Se^{-2}, etc. Except oxygen the other members of the group show a covalency of +2 ,+4, and +6, for example, SCl_2, SCl_4, SCl_6. +2 oxidation state is shown due to 2 unpaired electrons in the p-orbitals. +4 oxidation state is shown when 1 electron from p-orbilal is promoted to the next vacant d-orbital, while + 6 oxidation state is shown when another electron from s-orbital is also promoted to the next vacant d-orbital.

4.4.2 Occurrence

Oxygen is the most widely distributed and common of all the elements, comprising about 50% of the earth's crust. About one-fourth of the atmospheric air by weight consists of free oxygen and water contains nearly 89% of combined oxygen. The calcium carbonate which occurs as chalk, limestone, marble etc, contains 48% oxygen. Silica which is found in flint, quartz, etc, contains more than 53% oxygen by weight.

Sulphur is also widely distributed in nature both as free and in combined forms. Many important metallic ores are sulphides, e.g, galena (PbS), Zinc blende (ZnS), cinnabar (HgS), stibnite (Sb_2S_3), copper pyrite ($Cu_2S.Fe_2S_3$), iron pyrite (FeS_2), etc. Some important sulphates are also found in nature, e.g. gypsum ($CaSO_4$), heavy spar ($BaSO_4$), etc.

Sulphur also occurs in organic compounds present in animals and vegetables. Onions, garlic, mustard, hair, many oils, eggs and proteins consist of compounds containing sulphur in them . It also occurs as a constituent of coal and petroleum .

4.4.3 Comparison of Oxygen and Sulphur

Smililarities:

1. Both oxygen and sulphur have same outer electronic configuration of ns^2p^4.
2. Both oxygen and sulphur are usually divalent.
3. Both oxygen and sulphur exhibit allotropic forms.

4. Both have polyatomic molecules. Oxygen has diatomic O_2, while sulphur has S_2 and S_8 molecules.

5. Both combine with metals in the form of O^{-2} and S^{-2} with oxidation state -2.

6. Both combine with non-metals and form covalent compounds, e.g, H_2O and H_2S, CO_2 and CS_2 ,etc.

7. Both are typical non-metals.

8. Both are found in free and combined states on earth.

Dissmililarities:

Oxygen	Sulphur
1. There are two allotropic forms of Oxygen-O_2 and O_3.	There are 3 allotropic forms of sulphur, rhombic, monoclinic and plastic.
2. It is gas at ordinary temperature.	It is solid at ordinary temperature.
3. Oxygen is sparingly soluble in water.	Sulphur is not soluble in water.
4. Oxygen helps in combustion.	Sulphur is itself combustible.
5. It is paramagnetic in nature.	It is diamagnetic in nature.
6. It does not react with water.	When steam is passed through boiling sulphur a little hydrogen sulphide and sulphur dioxide are formed.
7. It does not react with acids.	It is readily oxidized by conc. sulphuric acid or nitric acid.
8. It does not react with alkalies.	It reacts with alkali solution and forms sulphides and thiosulphate.
9. It shows -2 oxidation state.	It shows oxidation states of -2, +2, +4 and +6.

4.5 SULPHURIC ACID (H_2SO_4)

Sulphuric acid was first prepared by a muslim scientist Jabir bin Hayyan in 8th century. In Europe, in 14^{th} and 15^{th} centuries, its preparation on commercial level was started due to the awareness of its properties and uses. It was called "oil of vitriol".It does not occur as such in nature , however, small quantities of H_2SO_4 are found in the waters of some springs and rivers.

4.5.1 Manufacture of Sulphuric Acid

Sulphuric acid is being manufactured commonly by contact process.

Contact Process

This method was developed by Knietsch in Germany. Basically, it involves the catalytic combination of sulphur and oxygen to form SO_2 which is then dissolved in water to form H_2SO_4.

Animation 4.8 : Sulfuric acid - contact process
Source and Credit: Dynamicscience

Principle

SO_2 obtained by burning sulphur or iron pyrites is oxidized to SO_3 in the presence of V_2O_5 which acts as a catalyst. The best yield of SO_3 can be obtained by using excess of oxygen or air and keeping the temperature between 400-500°C. SO_3 formed is absorbed in concentrated H_2SO_4 and "Oleum" ($H_2S_2O_7$) formed can be converted to sulphuric acid of any strength by mixing adequate quantities of water.

The process is completed in the steps given below.

a. Sulphur Burners

Sulphur or iron pyrites are burnt in excess of air to produce SO_2.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

b. Purifying Unit

SO_2 is purified from impurities like dust and arsenic oxide, to avoid poisoning of the catalyst. Purifying unit consists of the following parts.

(i) Dust remover

Steam is injected to remove dust particles from the gases.

(ii) Cooling Pipes

The gases are passed through lead pipes to cool them to 100°C.

(iii) Scrubbers

The cooled gases are washed by a spray of water, as SO_2 is not soluble in water at high temperature.

(iv) Drying Tower

The moisture of gases is removed by concentrated H_2SO_4 trickling down through the coke filled in this tower.

(v) Arsenic Purifier

Arsenic oxide is then removed by passing the gases through a chamber provided with shelves packed with freshly prepared ferric hydroxide.

(vi) Testing box

In this box a beam of light is introduced which indicates the presence or absence of solid particles. If present the gases are sent back for further purification.

c. Contact Tower

Preheated gases at 400-500°C are passed through vertical iron columms packed with the catalyst V_2O_5. Here SO_2 is oxidized to SO_3.

$$2SO_2(g) + O_2(g) \rightarrow \xrightarrow[V_2O_5]{400-500^\circ C} 2SO_3 \qquad \Delta H = -269.3kJ/mol.$$

The reaction is highly exothermic so no heating is required once the reaction is started.

d. Absorption Unit

The SO_3 obtained from the contact tower is dissolved in 98% H_2SO_4 to form pyrosulphuric acid (oleum), $H_2S_2O_7$. It can be diluted with water to get any required concentration of sulphuric acid.

$$H_2SO_4(aq) + SO_3(g) \rightarrow H_2S_2O_7(l)$$

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$$

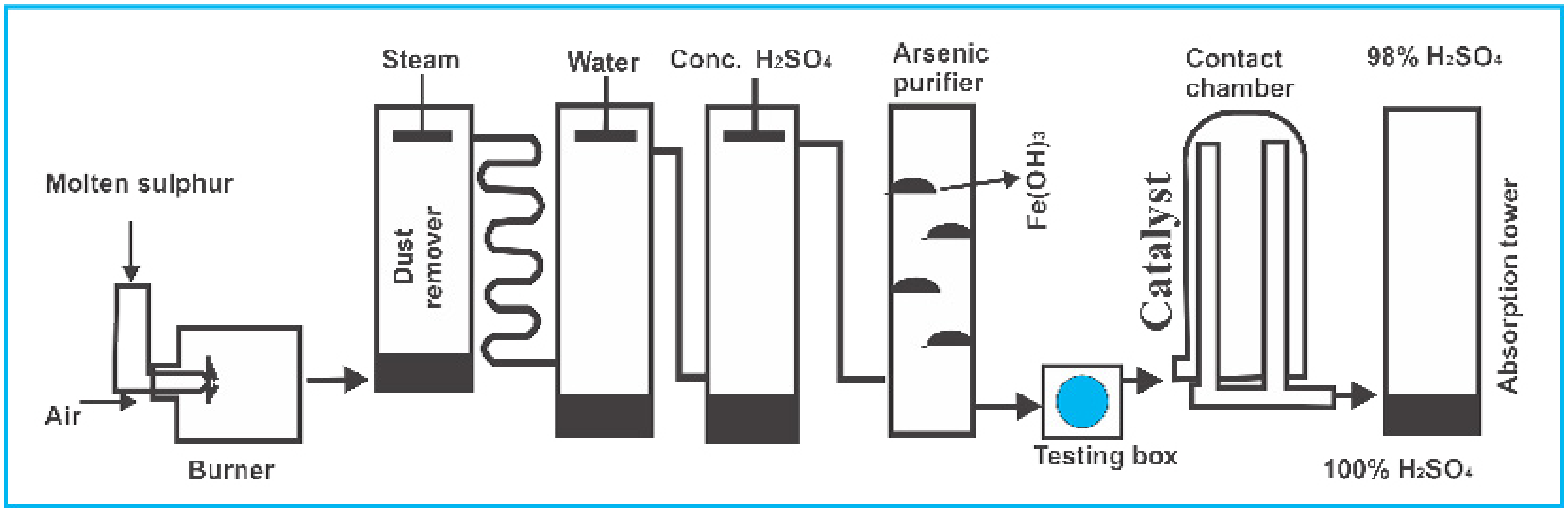


Fig.4.5 Contact Process

4.5.2 Properties

Physical Properties

1. Pure sulphuric acid is a colourless oily liquid without an odour.
2. Its specific gravity is 1.834 at 18°C.
3. It freezes at 10.5°C.
4. Its boiling point is 338°C.
5. It dissolves in water liberating a lot of heat which raises the temperature of the mixture up to 120°C. H_2SO_4 should always be poured in water in a thin stream to avoid any accident.
6. Pure acid is a nonconductor of electricity but the addition of a little water makes it a good conductor.
7. It is extremely corrosive to skin and causes very serious burns to all the tissues.

Reactions

1. It is stable at ordinary temperature but on strong heating it dissociates into SO_3 and H_2O.

$$H_2SO_4 \rightarrow SO_3 + H_2O$$

2.It is a strong acid. In an aqueous solution it completely ionizes to give hydrogen, hydrogen sulphate and sulphate ions. The dissociation take place in two steps.

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(l) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + H_3O^+(l)$$

3. Reaction as an Acid

(i) Reactions with alkalies

$$H_2SO_4(aq) + NaOH(aq) \rightarrow NaHSO_4(aq) + H_2O(l)$$

$$NaHSO_4(aq) + NaOH \rightarrow Na_2SO_4(aq) + H_2O(l)$$

(ii) Reactions with carbonates and hydrogen carbonates.

$$Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

$$2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$$

(iii) Reactions with salts

$$2NaCl(s) + H_2SO_4(Conc) \xrightarrow{\text{Strong heat}} Na_2SO_4(aq) + 2HCl(g)$$

$$KNO_3(aq) + H_2SO_4(Conc) \rightarrow KHSO_4(aq) + HNO_3(g)$$

(iv) Reaction with metals

(a) Cold dilute acid reacts with almost all metals to produce hydrogen gas and sulphate salts.

$$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$$

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

$$Sn(s) + H_2SO_4(aq) \rightarrow SnSO_4(g) + H_2(g)$$

(b) Cold concentrated H_2SO_4 does not react with most of the metals like Cu, Ag, Hg, Pb, Au.

(c) With certain metals hot concentrated sulphuric acid gives metal sulphates, water and SO_2.

$$Cu(s) + 2H_2SO_4(conc) \rightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$$

$$2Ag(s) + 2H_2SO_4(conc) \rightarrow Ag_2SO_4(aq) + 2H_2O(l) + SO_2(g)$$

$$Hg(l) + 2H_2SO_4(conc) \rightarrow HgSO_4(aq) + 2H_2O(l) + SO_2(g)$$

4. Reactions as a Dehydrating Agent

H_2SO_4 has a great affinity for water , so it acts as dehydrating agent and eliminates water from different compounds.

(i) With oxalic acid it forms CO_2 and CO.

$$\begin{array}{l} COOH \\ | \\ COOH(s) \end{array} \xrightarrow{conc.H_2SO_4} CO_2(g) + CO(g) + H_2O(l)$$

(ii) With formic acid, CO is formed.

$$HCOOH(l) \xrightarrow{conc.\ H_2SO_4} CO(g) + H_2O(l)$$

(iii) With ethyl alcohol it forms ethylene.

$$C_2H_5OH(\ell) \xrightarrow[100^\circ C]{Conc.H_2SO_4} C_2H_4(g) + H_2O(\ell)$$

(iv) With wood, paper, sugar and starch it forms carbon and water.

$$C_6H_{12}O_6(s) \xrightarrow{Conc.H_2SO} 6C(s) + 6H_2O(g)$$

$$C_{12}H_{22}O_{11}(s) \xrightarrow{Conc.H_2SO_4} 12C(s) + 11H_2O(g)$$

$$(C_6H_{10}O_5)n \xrightarrow{Conc.H_2SO_4} 6nC + 5nH_2O$$

5. As an Oxidizing Agent

H_2SO_4 acts as a strong oxidizing agent.

(i) It oxidizes C and S giving CO_2 and SO_2 , respectively.

$$C(s) + 2H_2SO_4(conc) \rightarrow CO_2(g) + 2SO_2(g) + 2H_2O(g)$$

$$S(s) + 2H_2SO_4(conc) \rightarrow 3SO_2(g) + 2H_2O(l)$$

(ii) H_2S is oxidized to S .

$$H_2S(g) + H_2SO_4(aq) \rightarrow S(s) + SO_2(g) + 2H_2O(g)$$

(iii) Reactions of H_2SO_4 with HBr and HI produces bromine and iodine respectively.

$$2HBr(aq) + H_2SO_4(aq) \rightarrow Br_2(g) + SO_2(g) + 2H_2O(g)$$

$$2HI(aq) + H_2SO_4(aq) \rightarrow I_2(g) + SO_2(g) + 2H_2O(g)$$

6 . Reactions with Gases.

(i) It absorbs SO_3 and forms oleum

$$H_2SO_{4\,(Conc)} + SO_3(g) \rightarrow H_2S_2O_7(l)$$

(ii) It reacts with ammonia forming ammonium sulphate.

$$2\,NH_3(g) + H_2\,SO_4(aq) \rightarrow (NH_4)_2\,SO_4(aq)$$

7. Reaction with Benzene

Benzene sulphonic acid is produced when H_2SO_4 reacts with benzene.

$$C_6H_6(l) + H_2SO_{4\,(conc)} \rightarrow \underset{\text{Benzenesulphonic acid}}{C_6H_5SO_2OH(l)} + H_2O(l)$$

8. Precipitation Reactions

White precipitates are produced when H_2SO_4 reacts with solutions of $BaCl_2$, $Pb(NO_3)_2$ and $Sr(NO_3)_2$.

$$BaCl_2\,(aq) + H_2SO_4\,(aq) \rightarrow BaSO_4\,(s) \downarrow + 2\,HCl(aq)$$

$$Pb(NO_3)_2\,(aq) + H_2SO_4\,(aq) \rightarrow PbSO_4\,(s) \downarrow + 2\,HNO_3\,(aq)$$

9. Reactions with Oxidizing Agents

It reacts with oxidizing agents like $KMnO_4$ and $K_2Cr_2O_7$ to liberate oxygen which may oxidize other compounds.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$10FeSO_4 + 5H_2SO_4 + 5[O] \rightarrow 5Fe_2(SO_4)_3 + 5H_2O$$

$$2KMnO_{4\,(aq)} + 8H_2SO_{4\,(aq)} + 10FeSO_{4\,(aq)} \rightarrow K_2SO_{4\,(aq)} + 2MnSO_{4\,(aq)} + 5Fe_2(SO_4)_{3\,(aq)} + 8H_2O_{(l)}$$

4.5.3 Uses of Sulphuric Acid

It is used

1. in the manufacture of fertilizers like ammonium sulphate and calcium superphosphate.
2. in refining of petroleum to remove nitrogen and sulphur compounds.
3. in the manufacture of HCl, H_3PO_4, HNO_3 and sulphates.
4. in the manufacture of many chemicals, dyes, drugs, plastics, disinfectants, paints, explosives, synthetic fibers, etc.
5. in electrical batteries and storage cells.
6. as a dehydrating agent for drying gases.
7. as a laboratory reagent.
8. in textile, iron, steel, leather and paper industries.

KEY POINTS

1. In group VA the metallic character increases down the group. Nitrogen and phosphorus are non-metals, arsenic and antimony are metalloids while bismuth is a metal.
2. Phosphorus and other members of VA group can make use of d-orbitals in bonding.
3. Common oxides of nitrogen are N_2O, NO, NO_2,N_2O_3 and N_2O_5.
4. Nitrogen forms two oxyacids, HNO_2 and HNO_3, HNO_2 is an unstable acid and exists only in solution.
5. HNO_3 is not only a strong acid but it also acts as a strong oxidising agent.
6. Aqua regia is a mixture of one volume of concentrated HNO_3 and three volumes of concentrated HCl.
7. Phosphorus exists in six allotropic forms. White phosphorus is very reactive as compared to red phosphorus.
8. Phosphorus forms two types of chlorides PCl_3, PCl_5 and two types of oxides P_2O_3 andP_2O_5
9. Just like nitrogen, phosphorus also gives two types of oxyacids; phosphorus acid (H_3PO_3) and phosphoric acid (H_3PO_4).
10. Posphoric acid is a weak tribasic acid and it gives three series of salts with strong base.

11. Group VIA of the periodic table contains only one metal, polonium, the rest of members are non-metals. All these elements show the property of allotropy and they are polymeric in nature

12. Oxygen and sulphur are the most abundant elements of groupVIA. Oxygen is the most widely distributed of all the elements. Sulphur is widely distributed in nature in both free and combined forms

13. Sulphuric acid is commercially prepared by oxidation of SO_2 in the presence of a catalyst to SO_3 in a process called Contact Process.

14. H_2SO_4 is a very strong acid. It acts as a dehydrating agent as well as an oxidizing agent.

EXERCISE

Q.1 Fill in the blanks.

(i) The elements________ of group VA are called metalloids.

(ii) In Birkeland and Eyde's process is prepared from atmospheric oxygen and nitrogen.

(iii) The tendency to form long chain of atoms is called ________ .

(iv) All the elements of group VIA show the property of________ .

(v) Selenium shows two allotropic forms which are called ___ forms.

vi) Specific gravity of H_2SO_s at 18°C is _________ .

vii) H_2 is produced by reacting H_2SO_4 with metals, like_________ .

viii) The elements of group VIA exhibit maximum oxidation state of _________ .

ix) The outermost shell of group________ elements contain six electrons.

x) Oxygen shows______behaviour due to the presence of unpaired electrons.

xi) Conc.phosphoric acid acts as a___________.

xii) Nitrogen is a gas while other elements of the same group are _______ .

xiii) Noble metals like gold and platinum are dissolved in _______ .

xiv) Sulphur is different from oxygen because it shows _________ oxidation states.

xv) HNO_3 is used in the manufacture of _________ fertilizers.

Q.2 Indicate True or False.

i) The metallic character in groups VA and VIA elements increases down the group.

ii) The elements of group VA exhibit maximum oxidation state of +5.

iii) Ionization energy of phoshorus is greater than that of nitrogen.

iv) The electronegativity of oxygen is greater than all other elements of groups VA and VIA.

v) V_2O_5 is used as a catalyst for the oxidation of SO_2 to SO_3.

vi) The oxides of nitrogen are basic in nature.

vii) Aqua regia is prepared by mixing 3 parts of conc. HNO_3 with one part of conc. HCl.

viii) TNT is prepared by the reaction of nitric acid with toluene.

ix) P_2O_3 when reacts with cold water gives phosphorus acid and with hot water it gives phosphoric acid.

x) Sulphur occurs in many organic compounds of animal and vegetable origins.

Q.3 Multiple choice question. Encircle the correct answer.

(i) Out of all the elements of group VA, the highest ionization energy is possessed by

(a) N (b) P (c) Sb (d) Bi

ii) Among group VA elem ents, the most electronegative element is

(a) Sb (b) N (c) P (d) As

iii) Oxidation of NO in air produces

(a) N_2O (b) N_2O_3 (c) N_2O_4 (d) N_2O_5

iv) The brown gas formed, when metal reduces HNO_3 to

(a) N_2O_5 (b) N_2O_3 (c) NO_2 (d) NO

v) Laughing gas is chemically

(a) NO (b) N_2O (c) NO_2 (d) N_2O_4

(vi) Out of all the elements of group VIA, the highest melting and boiling points is shown by the element

(a) Te (b) Se (c) S (d) Pb

vii) SO_3 is not absorbed in water directly to form H_2SO_4 because
(a) the reaction does not go to completion.
(b) the reaction is quite slow.
(c) the reaction is highly exothermic.
(d) SO_3 is insoluble in water.

ix) Which catalyst is used in contact process?
(a) Fe_2O_3 (b) V_2O_5 (c) SO_3 (d) Ag_2O

x) Which of the following specie has the maximum number of unpaired electrons?
(a) O_2 (b) O_2^+ (c) O_2^- (d) O_2^{2}

Q.4 Short questions.

(i) How does nitrogen differ from other elements of its group?

ii) Why does aqua regia dissolve gold and platinum?

iii) Why the elements of group VIA other than oxygen show more than two oxidation states?

iv) Write down a comparison of the properties of oxygen and sulphur.

v) Write down the equation for the reaction between conc. H_2SO_4 and copper and explain what type of reaction is it.

Q.5 (a) Explain the Brikeland and Eyde's process for the manufacture of nitric acid.

(b) Which metals evolve hydrogen upon reaction with nitric acid? Illustrate alongwith chemical equations.

(c) What is meant by fuming nitric acid?

Q.6 (a) Sulphuric acid is said to act as an acid, an oxidizing agent and a dehydrating agent, describe two reactions in each case to illustrate the truth of this statement.

(b) Give the advantages of contact process for the manufacture of sulphuric acid.

Q.7 (a) Describe the chemistry of the industrial preparation of sulphuric acid from sulphur by the contact process.

(b) Why is SO_3 dissolved in H_2SO_4 and not in water?

(c) Explain the action of sulphuric acid on metals alongwith chemical equations.

Q.8 Describe the preparation of NO_2 gas. Also give its reactions.

Q.9 How PCl_3 and PCl_5 can be used for the preparation of other chemical compounds.

Q.10 Answer the following question.

i) Describe "Ring test" for the confirmation of the presence of nitrate ions in solution.

ii) NO_2 is a strong oxidizing agent. Prove the truth of this statement giving examples.

iii) Write down the chemical equations and names of the products formed as a result of the reaction of HNO_3 with arsenic and antimony.

iv) Give the methods of preparation of PCl_3.

v) P_2O_5 is a powerful dehydrating agent. Prove giving example.

Q.11 Complete and balance the following chemical equation:

i) $P + NO \longrightarrow$

ii) $NO + Cl_2 \longrightarrow$

iii) $H_2S + NO \longrightarrow$

iv) $Pb(NO_3)_2 \longrightarrow$

v) $NO_2 + H_2O \longrightarrow$

vi) $NO_2 + H_2SO_4 \longrightarrow$

vii) $HNO_2 + HI \longrightarrow$

viii) $HNO_2 + NH_3 \longrightarrow$

ix) $HNO_2 + CO(NH_2)_2 \longrightarrow$

x) $KNO_3 + H_2SO_4 \longrightarrow$

Q. 12 Describe the methods of preparation of phosphorus pentoxide and explain its reactions.

Q.13 Discuss the trends in physical properties of group VIA elements.

CHAPTER

7 Fundamental Principles of Organic Chemistry

Animation 7.1 : Organic Chemistry
Source and credit : Stackexchange

In This Chapter You Will Learn:

1. The special features of carbon chemistry with reference to its ability to form chains, rings and isomers.
2. The importance of organic chemistry in daily life.
3. About the sources of carbon and its compounds like coal, petroleum and natural gas with reference to their availability in Pakistan.
4. Refining, reforming and cracking of petroleum and to enlist products in a tabular form.
5. How can petroleum serve as a source of different type of fuels.
6. About the classification of organic compounds based on the carbon skeleton.
7. About functional groups and the dependence of chemical properties on functional groups.
8. About the structural isomerism in organic compounds.
9. That cis-trans isomerism arises due to restricted rotation around a carbon-carbon double bond.
10. How the hybridization theory can help us understand the type of bonding and the shapes of organic compounds.

7.1 INTRODUCTION

More than 200 years ago, early chemists recognized organic compounds distinct from inorganic compounds because of the differences in their origin and properties. Organic compounds were considered as those obtained from living things, plants or animals, and inorganic compounds were those obtained from non-living or mineral sources.

The early chemists never succeeded in synthesizing organic compounds and their failure led them to believe that organic compounds could be manufactured only by and within living things and these compounds could never be synthesized from inorganic materials. This theory was referred to as vital force theory. This theory was rejected by Friedrick Wohler when he obtained urea $(NH_2)_2CO$, an organic compound in the urine of mammals, from ammonium cyanate, NH_4CNO, a substance of known mineral origin.

$$NH_4CNO \rightarrow (NH_2)_2CO$$

7.1.1 Modern Definition of Organic Chemistry.

Since the synthesis of urea from ammonium cyanate, millions of organic compounds have been prepared and analyzed. All these compounds contain carbon as an essential element. Apart from carbon, most of the organic compounds also contain hydrogen. Other elements which may also be present include oxygen, nitrogen, sulphur, etc. For historical and conventional reasons a few of the carbon compounds such as CO,CO_2, carbonates, bicarbonates, etc are studied as inorganic compounds. It also has been recognized that the chemical forces in organic compounds are similar to those, which exist, in inorganic compounds. Thus it was felt that organic chemistry should be redefined. According to the modern definition, organic chemistry is that branch of chemistry which deals with the study of compounds of carbon and hydrogen (hydrocarbons) and their derivatives.

7.2 SOME FEATURES OF ORGANIC COMPOUNDS

Following are some features of organic compounds.

(1) Peculiar Nature of Carbon

Carbon forms a large number of compounds. There are millions of organic compounds known at present. The main reason for such a large number of compounds is its unique property of linking with other carbon atoms to form long chains or rings. This selflinking property of carbon is called catenation. Carbon also forms stable single and multiple bonds with other atoms like oxygen, nitrogen and sulphur, etc. It can thus form numerous compounds of various sizes, shapes and structures.

(2) Non-ionic Character of Organic Compounds

Organic compounds are generally covalent compounds, therefore, do not give ionic reactions.

(3) Similarity in Behaviour

There exists a close relationship between different organic compounds. This is exemplified by the existence of homologous series.
This similarity in behaviour has reduced the study of millions of compounds to only a few homologous series.

(4) Complexity of Organic Compounds

Organic molecules are usually large and structurally more complex. For example, starch has the formula $(C_6H_{10}O_5)_n$ where n may be several thousands. Proteins are very complex molecules having molecular masses ranging from a few thousands to a million.

(5) Isomerism

Isomerism is a very common phenomenon in organic compounds. Very often more than one compounds are represented by the same molecular formula. However, they have different structural formulas.

(6) Rates of Organic Reactions

The reactions involving organic compounds are slow and in general the yields are low. The slow rate of the organic reactions is due to the molecular nature of organic compounds.

(7) Solubility

Most organic compounds are insoluble in water and dissolve readily in non-polar organic solvents, such as, benzene, petroleum ether, etc.

7.3 IMPORTANCE OF ORGANIC CHEMISTRY

The importance of organic chemistry can hardly be over emphasized. Almost all the chemical reactions that take place in living systems, including our own bodies, are organic in nature because they involve such life molecules like proteins, enzymes, carbohydrates, lipids, vitamins and nucleic acids, all contain thousand of carbon atoms.

We have become dependent upon organic compounds that occur in nature for our food, medicines and clothing. Over the years,the chemists have learned to synthesize plastics, synthetic rubber, medicines, preservatives, paints, varnishes, textile fibres, fertilizers, pesticides, detergents, cosmetics, dyes, etc. Many of these synthetic compounds prevent the shortages of naturally occurring products.

7.4 SOURCES OF ORGANIC COMPOUNDS

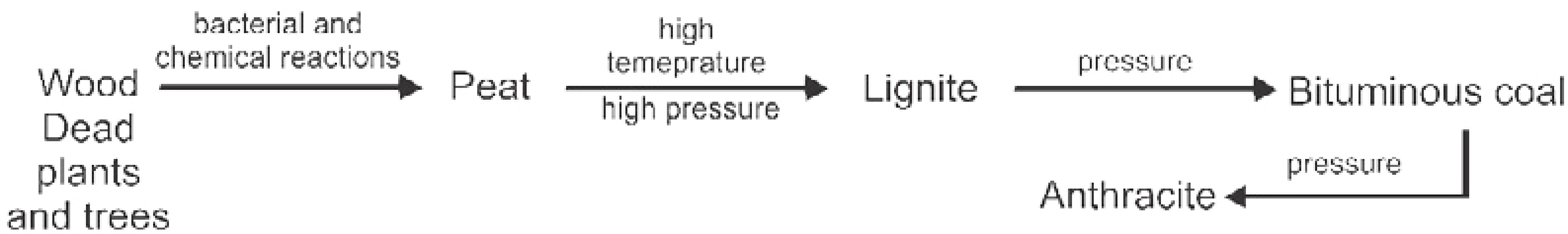
Petroleum, coal and natural gas are vast reservoirs from which many organic compounds are obtained. These are called fossil fuels and are formed, over long period of time, from the decay of plants and animals.

Coal

It is believed that coal in nature was formed from the remains of the trees buried inside the earth crust some 500 millions years ago. Due to the bacterial and chemical reactions on wood it got converted into peat. Then, as a result of high temperature and high pressure inside the earth crust, peat got transformed into coal.

Coal is an important solid fuel and becomes a source of organic compounds when subjected to carbonization or destructive distillation. When coal is heated in the absence of air (temperature ranging form 500-1000° C); it is converted into coke, coal gas and coal tar. Coal tar contains a large number of organic compounds, which separate out on fractional distillation.

The total coal resources of Pakistan are estimated by the geological survey of Pakistan to be 184 billion tonnes. About 80% of this coal is used to bake bricks in lime kilns; besides, some quantity is used for domestic purposes. Conscious efforts are being made by the government to induct coal into industry by setting up coal based powrer units. The Sindh Coal Authority and the directorates of Mineral Developments of the Punjab, Baluchistan and Khyber Pakhtunkhwa are all keen to expand coal utilization in power generation for which many incentives have been made available.



Animation 7.2 : What is coal seam gas
Source and credit: Aplng

Natural Gas

Natural Gas is an important means of energy especially for countries like Pakistan, which are deficient in the production of mineral oil and coal. It is a mixture of low boiling hydrocarbons. Major portion of the natural gas is methane. It is also formed by the decomposition of organic matter. In Pakistan the gas, being cheaper, is used for power generation, in cement and fertilizer industries; as a fuel in general industries and for domestic purposes.

Animation 7.3 : Coal fired power station
Source and credit: Gif2fly

Petroleum

Mineral oil is called petroleum when it is in the refined form. It is thought to have been formed by slow chemical and biochemical decomposition of the remains of organic matters found between the sedimentary rocks. When extracted from rocks it appears like a liquid of blackish colour known as 'crude oil'.

Table 7.1 Principal Fractions Obtained from Petroleum

Fraction	Boiling Point Rang (°C)	Composition	Uses
Natural gas	< 20	CH_4 - C_4H_{10}	Fuel, petrochemicals
Petroleum Ether	20 - 60	C_5H_{12}, C_6H_{14}	Solvent
Ligroin, or naphtha	60 - 100	C_6H_{14}, C_7H_{16}	Solvent, raw material
Gasoline	40- 220	C_4H_{10} - $C_{13}H_{28}$ mostly C_6H_{14} - C_8H_{18}	Motor fuel
Kerosene	175 - 325	C_8H_8 . $C_{14}H_{30}$	Heating fuel
Gas oil	> 275	$C_{12}H_{26}$. $C_{18}H_{38}$	Diesel and heating fuel
Lubricating oils and greases	Viscous liquids	> $C_{18}H_{38}$	Lubrication
Paraffin	M.p. 50 - 60	$C_{23}H_{48}$ - $C_{29}H_{60}$	Wax products
Asphalt, or petroleum coke	Solids	Residue	Roofing, paving, fuel reducing agent

It is refined to get different petroleum fractions. At present four oil refineries are in operation in our country. One oil refinery known as Attock Oil Refinery is located at Morgah near Rawalpindi. It has about 1.25 million tonnes oil refining capacity. Similarly, two oil refineries have been established at Karachi which have about 2.13 million tonnes of oil refining capacity. Another refinery known as Pak-Arab refinery is located at Mahmud Kot near Multan.

The crude petroleum is separated by fractional distillation into a number of fractions each corresponding to a particular boiling range, Table 7.1.

7.5 CRACKING OF PETROLEUM

The fractional distillation of petroleum yields only about 20% gasoline. Due to its high demand this supply is augmented by converting surplus supplies of less desirable petroleum fractions such as kerosene oil and gas oil into gasoline by a process called cracking. It is defined as breaking of higher hydrocarbons having high boiling points into a variety of lower hydrocarbons, which are more volatile (low boiling). For example, a higher hydrocarbons $C_{16}H_{34}$ splits according to the following reaction.

$$\underset{\text{Alkane}}{C_{16}H_{34}} \xrightarrow[700^{o}]{\text{Heat}} C_7H_{16} + 3CH_2{=}CH_2 + CH_3\text{-}CH{=}CH_2$$

This is the process in which C-C bonds in long chain alkane molecules are broken, producing smaller molecules of both alkanes and alkenes. The composition of the products depends on the condition under which the cracking takes place. Cracking is generally carried out in the following ways.

(1) Thermal Cracking

Breaking down of large molecules by heating at high temperature and pressure is called Thermal Cracking. It is particularly useful in the production of unsaturated hydrocarbons such as ethene and propene.

(2) Catalytic Cracking

Higher hydrocarbons can be cracked at lower tem perature (500°C) and lower pressure (2 atm), in the presence of a suitable catalyst. A typical catalyst used for this purpose is a mixture of silica (SiO_2) and alumina (Al_2O_3). Catalytic cracking produces gasoline of higher octane number and, therefore, this method is used for obtaining better quality gasoline.

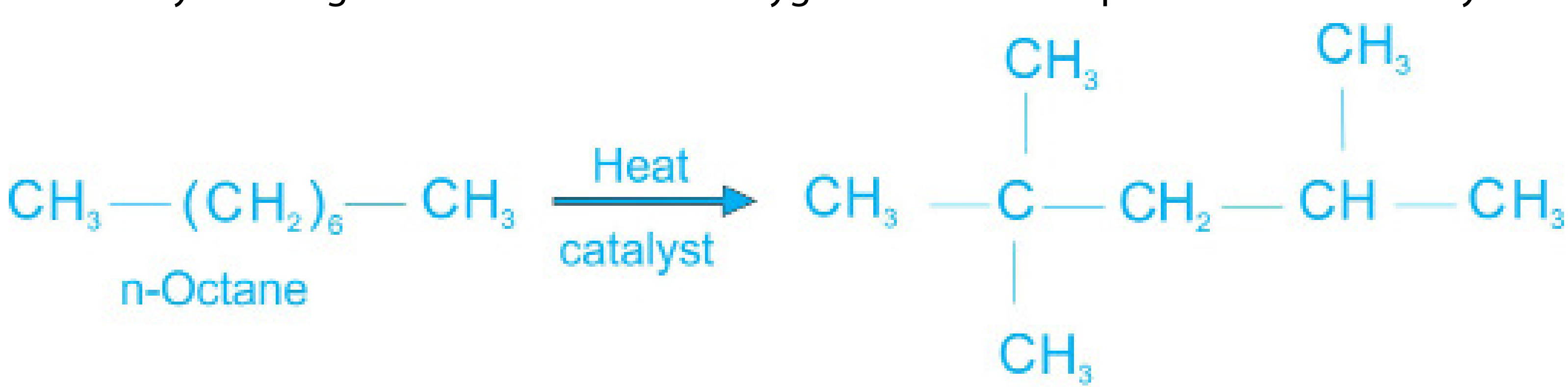
(3) Steam Cracking

In this process, higher hydrocarbons in the vapour phase are mixed with steam, heated for a short duration to about 900°C and cooled rapidly. The process is suitable for obtaining lower unsaturated hydrocarbons.

Besides increasing the yield of gasoline, cracking has also produced large amounts of useful by-products, such as ethene, propene, butene and benzene. These are used for manufacturing drugs, plastics, detergents, synthetic fibres, fertilizers, weed killers and important chemicals like ethanol, phenol and acetone.

7.6 REFORMING

The gasoline fraction present in petroleum is generally not of good quality. When it burns in an automobile engine, combustion can be initiated before the spark plug fires. This produces a sharp metallic sound called knocking which greatly reduces the efficiency of an engine. The quality of a fuel is indicated by its octane number. As the octane number increases, the engine is less likely to produce knocking. Straight- chain hydrocarbons have low octane numbers and make poor fuels. Experiments have shown that isooctane or 2,2,4- trimethyl pentane burns very smoothly in an engine and has been arbitrarily given an octane number of 100. The octane number of gasoline is improved by a process called reforming. It involves the conversion of straight chain hydrocarbons into branched chain by heating in the absence of oxygen and in the presence of a catalyst.



2.2.4-Trimethylpentane

The octane number of a poor fuel can also be improved by blending it with a small amount of additive like tetraethyl lead (TEL). Tetraethyl lead $(C_2H_5)_4$ Pb, is an efficient antiknock agent but has one serious disadvantage; its combustion product, lead oxide, is reduced to metallic lead which is discharged into the air through the exhaust pipe and causes air pollution.

7.7 CLASSIFICATIONS OF ORGANIC COMPOUNDS

There are millions of organic compounds. It is practically not possible to study each individual compound. To facilitate their study, organic compounds are classified into various groups and subgroups. They may be broadly classified into the following classes.

1. Open chain or Acyclic compounds.
2. Closed chain or Cyclic (or ring) compounds.

(1) Open Chain or Acyclic Compounds

This type of compounds contain an open chain of carbon atoms. The chains may be branched or non-branched (straight chain). The open chain compounds are also called aliphatic compounds.

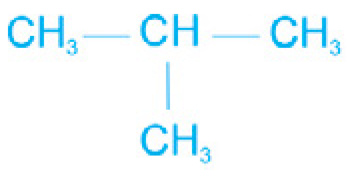
Straight Chain (or non- branched) Compounds

Those organic compounds in which the carbon atoms are connected in series from one to the other.

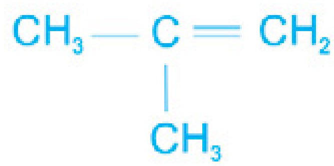
$CH_3-CH_2-CH_2-CH_3$ (n-Butane) $H_2C=CH-CH_2-CH_3$ (1-Butene) $CH_3-CH_2-CH_2-CH_2-OH$ (1-Butanol)

Branched chain compounds

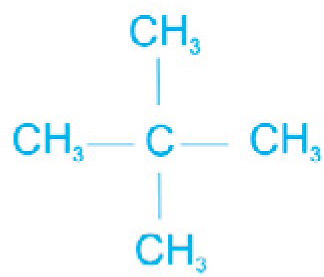
Those organic compounds in which the carbon atoms are attached on the sides of chain.



2-Methylpropane
Isobutane



2-Methylpropene
(Isobutylene)



2.2 Dimethylpropane(neo-Pentane)

(2) Closed Chain Compounds or Cyclic Compounds

These compounds contain closed chains or rings of atoms and are known as cyclic or ring compounds. These are of two types;

(a) Homocyclic or carbocycli compounds

(b) Heterocyclic compounds

The classification of organic compounds into various classes is shown in Fig. 7.1.

(a) Homocyclic or Carbocyclic Compounds

The compounds in which the ring consists of only carbon atoms, Homocyclic or carbocyclic compounds.

Homocyclic compounds are further classified as :

1. Alicyclic compounds
2. Aromatic compounds

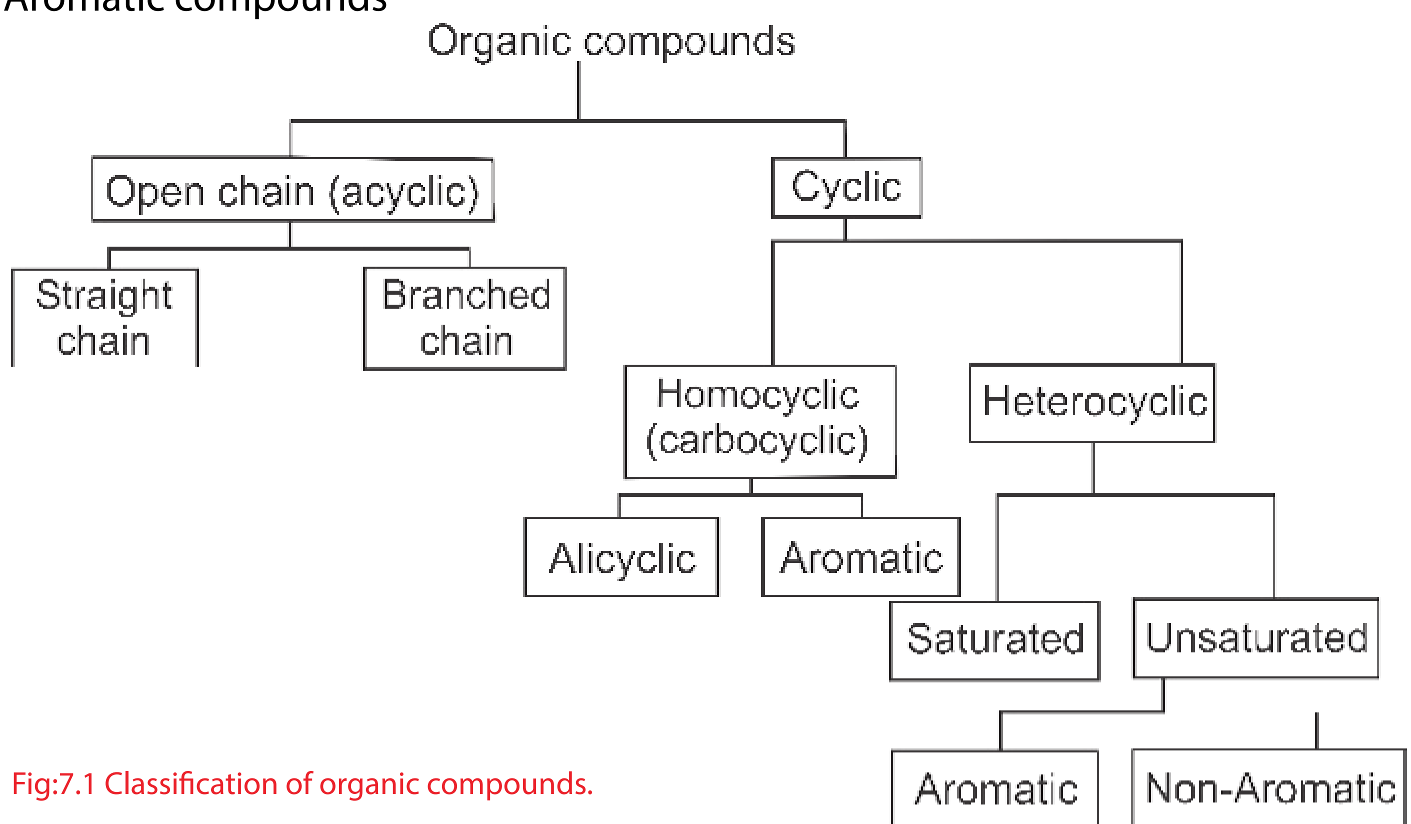
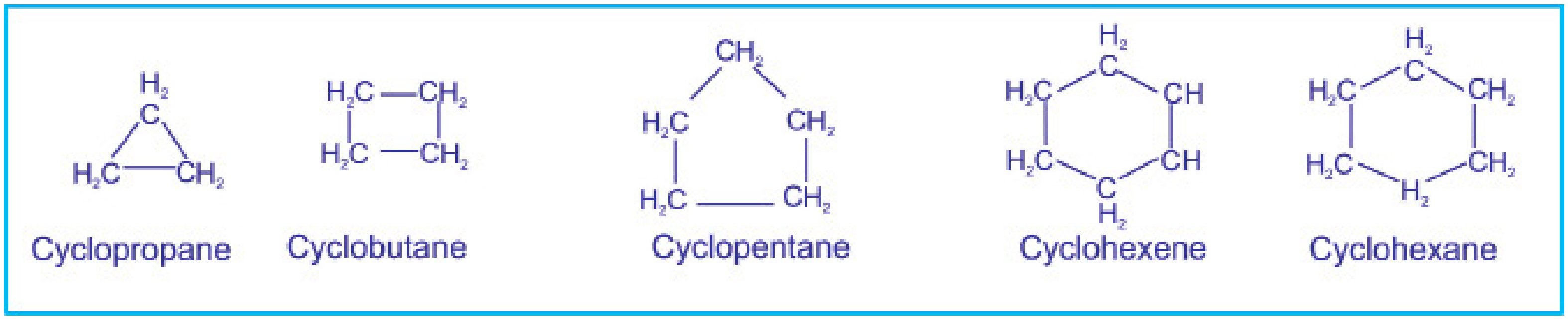


Fig:7.1 Classification of organic compounds.

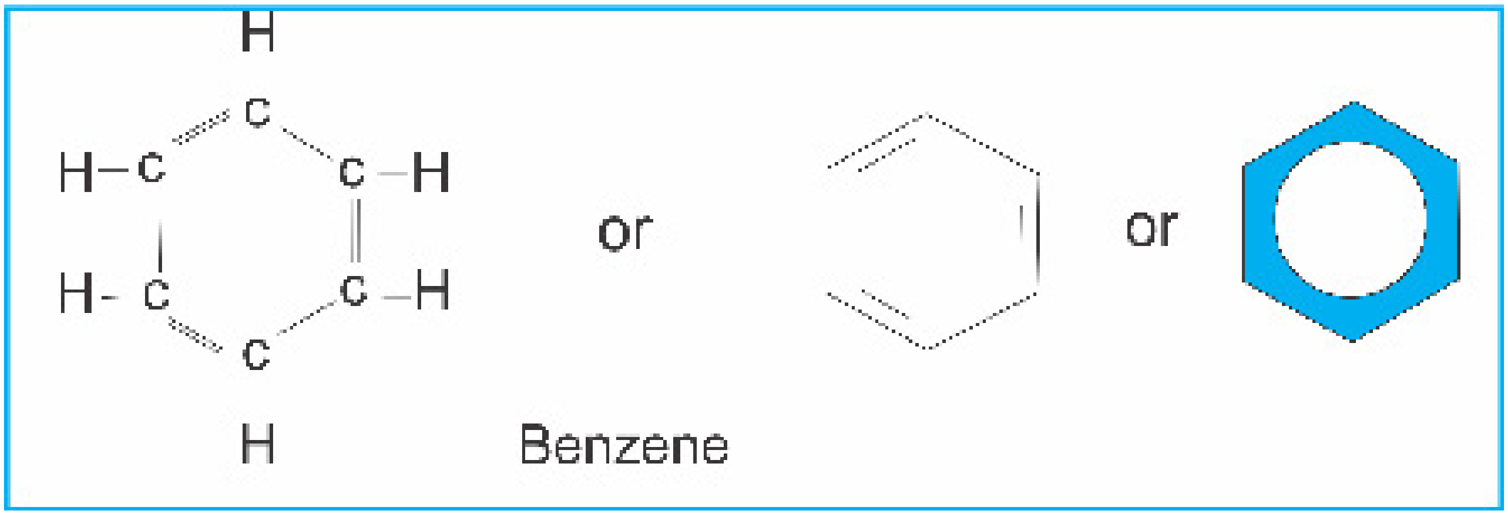
(1) Alicyclic Compounds

The homocyclic compounds which contain a ring of three or more carbon atoms and resembling aliphatic compounds are called alicyclic compounds. The saturated alicyclic hydrocarbons have the general formula C_nH_{2n}. Typical examples of alicyclic compounds are given below. One or more hydrogen atoms present in these compounds may be substituted by other group or groups.

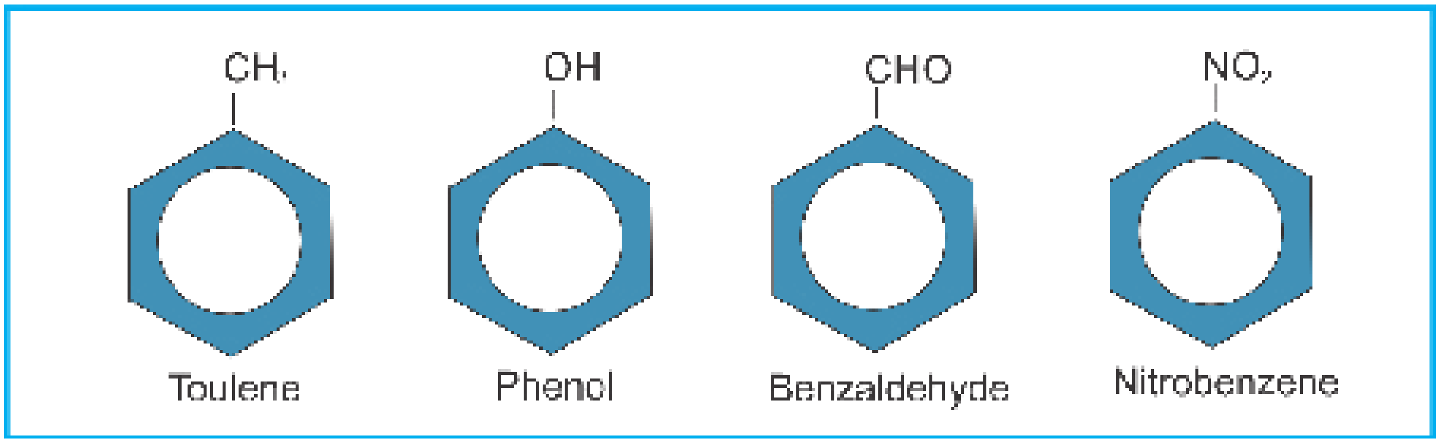


(2) Aromatic Compounds

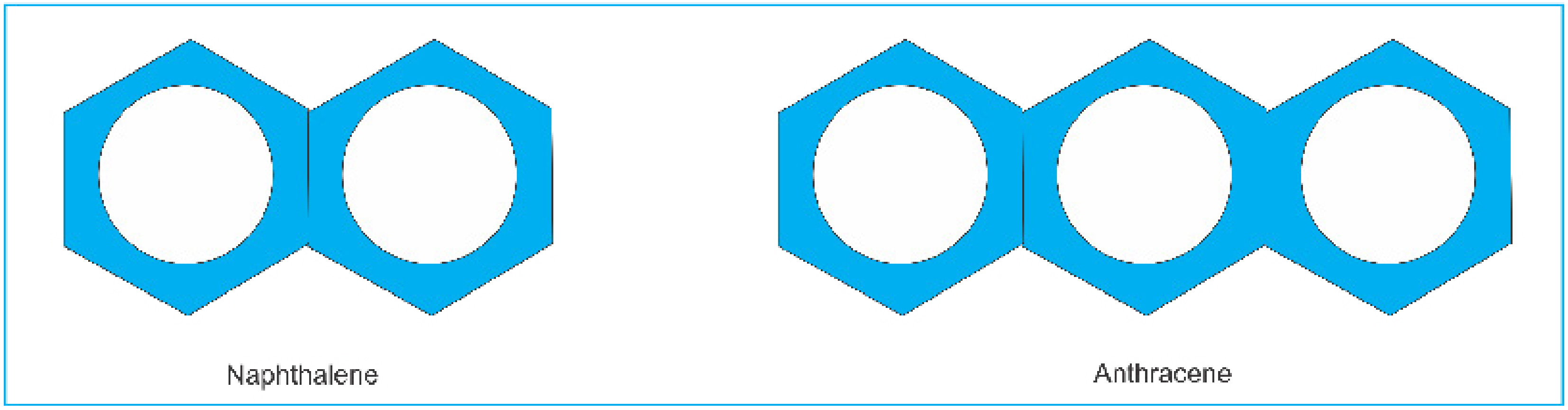
These carbocyclic compounds contain at least one benzene ring, six carbon atoms with three alternate double and single bonds.These bonds are usually shown in the form of a circle. Typical examples of aromatic compounds are given below.



The aromatic compounds may have a side-chain or a functional group attached to the ring. For example:

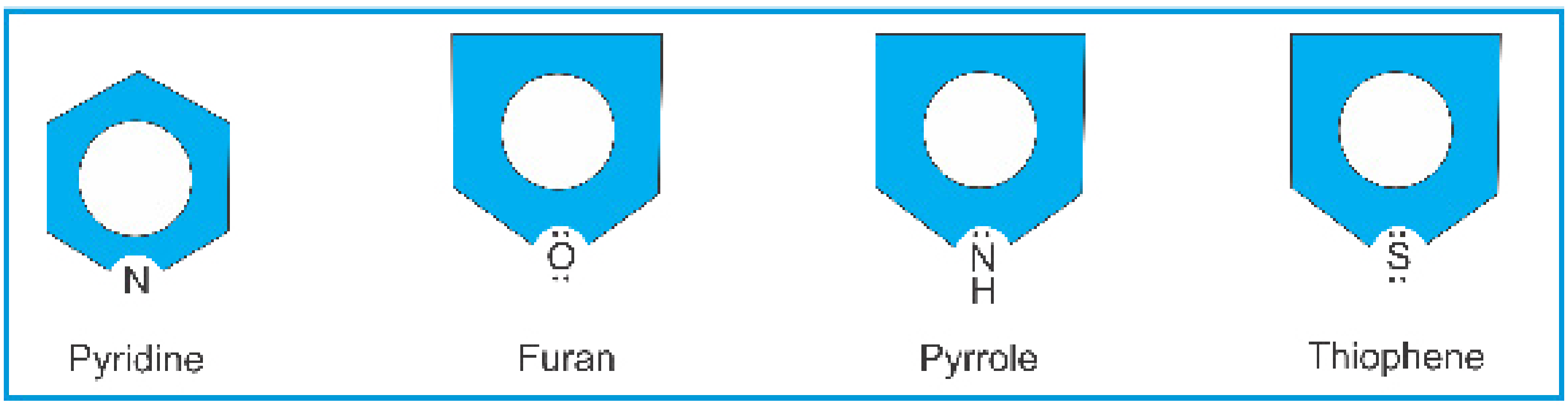


The aromatic compounds may also contain more than one benzene rings fused together.



(b) Heterocyclic Compounds

The compounds in which the ring consists of atoms of more than one kind are called heterocyclic compounds or heterocycles. In heterocyclic compounds generally one or more atoms of elements such as nitrogen (N), oxygen (O) or sulphur (S) are present. The atom other than carbon viz, N, 0, or S, present in the ring is called a hetero atom.

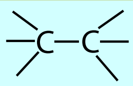
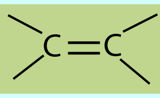
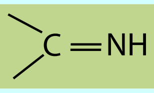
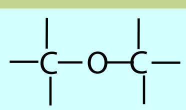
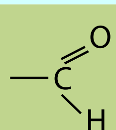
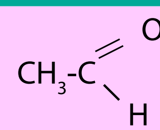
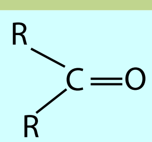
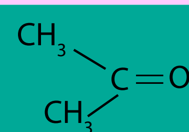


7.8 FUNCTIONAL GROUP

An atom or a group of atoms or a double bond or a triple bond whose presence imparts specific properties to organic compounds is called a functional group, because they are the chemically functional parts of molecules.

The study of organic chemistry is organized around functional groups. Each functional group defines an organic family. Although over six million organic compounds are known, there are only a handful of functional groups, and each one serves to define a family of organic compounds. The examples of functional groups are outlined in Table 7.2.

TABLE 7.2 FUNCTIONAL GROUPS

Functional group		Class of compounds	Example
Formula	Name		
	None	Alkane	CH — CH_3
	Double bond	Alkene	$H_2C = CH_2$
—C≡C—	Triple bond	Alkyne	HC=CH
-X(X=F,Cl,Br,I)	Halo (fluoro, chloro, bromo, iodo)	Alkyl halide	CH_3-CH_2-Cl
—OH —NH_2	Hydroxyl group Amino group	Alcohol or alkanol Amine	CH_3-CH_2-OH CH_3-CH_2-NH_2
	Imino group	Imine	CH_2=NH
	Ether linkage	Ether	CH_3-CH_2-O-CH_2-CH_3
	Formyl group	Aldehyde or alkanal	
	Carbonyl	Ketone or alkanohe	

$—C(=O)OH$	Carboxyl group	Carboxylicacid (oralkanoicacid)	$CH_3-C(=O)OH$
$—C(=O)—X$	Acid halide	Acid halide	$CH_3—C(=O)—Cl$
$—C(=O)NH_2$	Acid amide	Acid amide	$CH_3—C(=O)—NH_2$
$R—C(=O)OH$	Ester group	Ester	$CH_3-C(=O)OCH_3$
—SH	Mercapto	Thioalcohol or Thiol	CH_3-CH_2-SH
—C≡N	Cyano	Alkyl cyanide or alkane nitrile	$CH_3-C≡N$
$—NO_2$	Nitro	Nitro compounds	$C_6H_5NO_2$

7.9 HYBRIDIZATION OF ORBITALS AND THE SHAPES OF MOLECULES

Although the most stable electronic configuration of a carbon atom (having two partially filled 2p orbitals) requires it to be divalent, carbon is tetravalent in the majority of its compounds. In order to explain this apparent anamoly, it is assumed that an electron from the 2s orbital is promoted to an empty $2p_z$ orbital, giving the electronic configuration:

Ground state electronic configuration of carbon = $1s^2\ 2s^2\ 2p^1_x\ 2p^1_y\ 2p^o_z$
Excited state electronic configuration of carbon = $1s^2\ 2s^1\ 2p^1_x\ 2p^1_y\ 2p^1_z$

The excited state configuration can explain the tetravalency of carbon but these four valencies will not be equivalent. Orbital hybridization theory has been developed to explain the equivalent tetravalency of carbon.

According to this theory the four atomic orbitals of carbon belonging to valence shell may be mixed in different ways to explain the bonding and shapes of molecules formed by carbon atoms.

sp^3 Hybridization

In order to explain the bonding and shapes of molecules in which carbon is attached with four atoms, all these four atomic orbitals are mixed together to give rise to four new equivalent hybrid atomic orbitals having same shape and energy. This mode of hybridization is called tetrahedral or sp^3 hybridization.

All these four sp^3 hybrid orbitals are degenerate (having equal energy) and are directed at an angle of 109.5^0 in space to give a tetrahedral geometry.

When a carbon atom forms single bonds with other atoms, these hybrid orbitals overlap with the orbitals of these atoms to form four sigma bonds. This type of hybridization explains the bonding and shapes of all those compounds in which carbon atom is saturated.

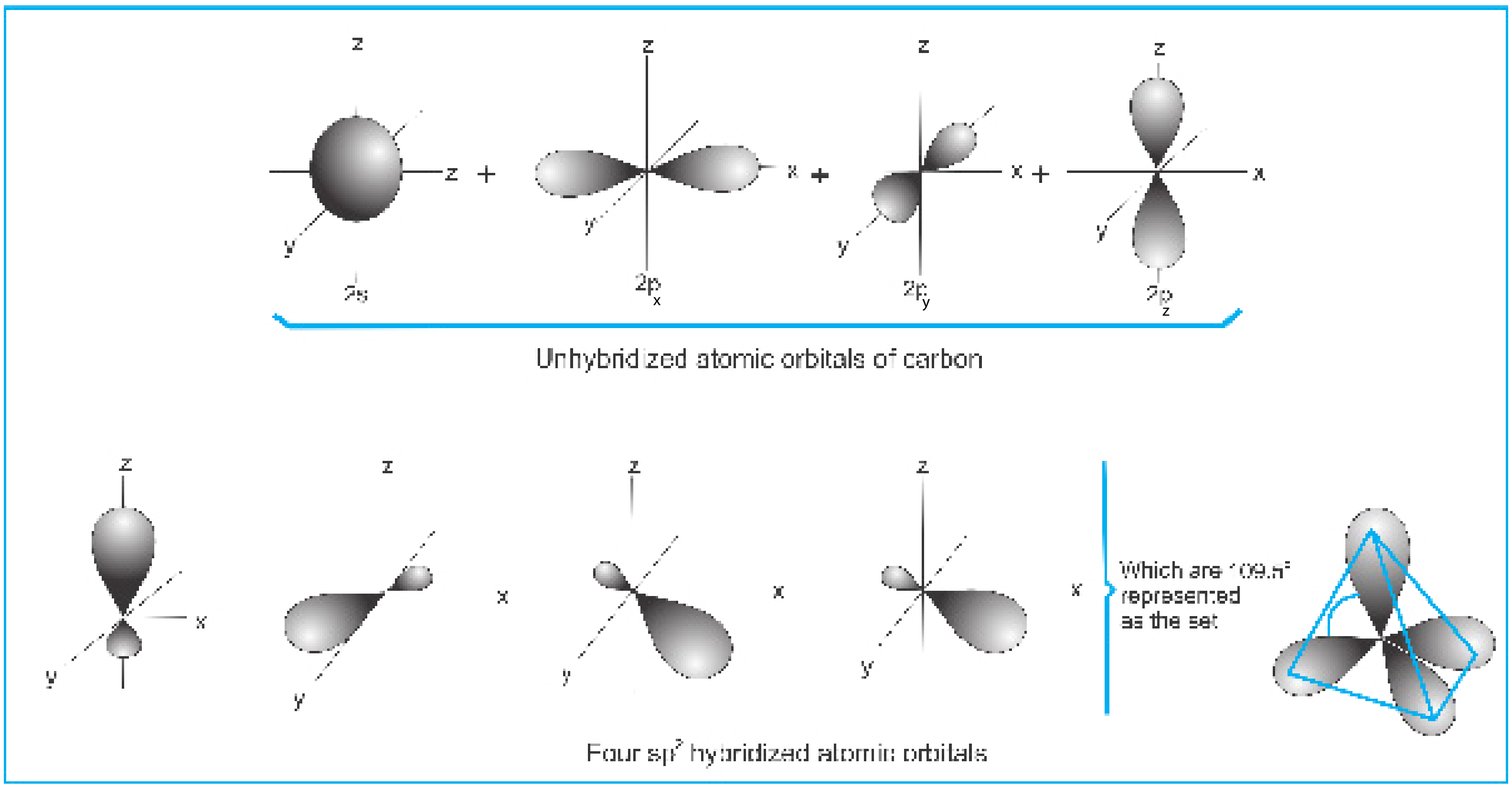
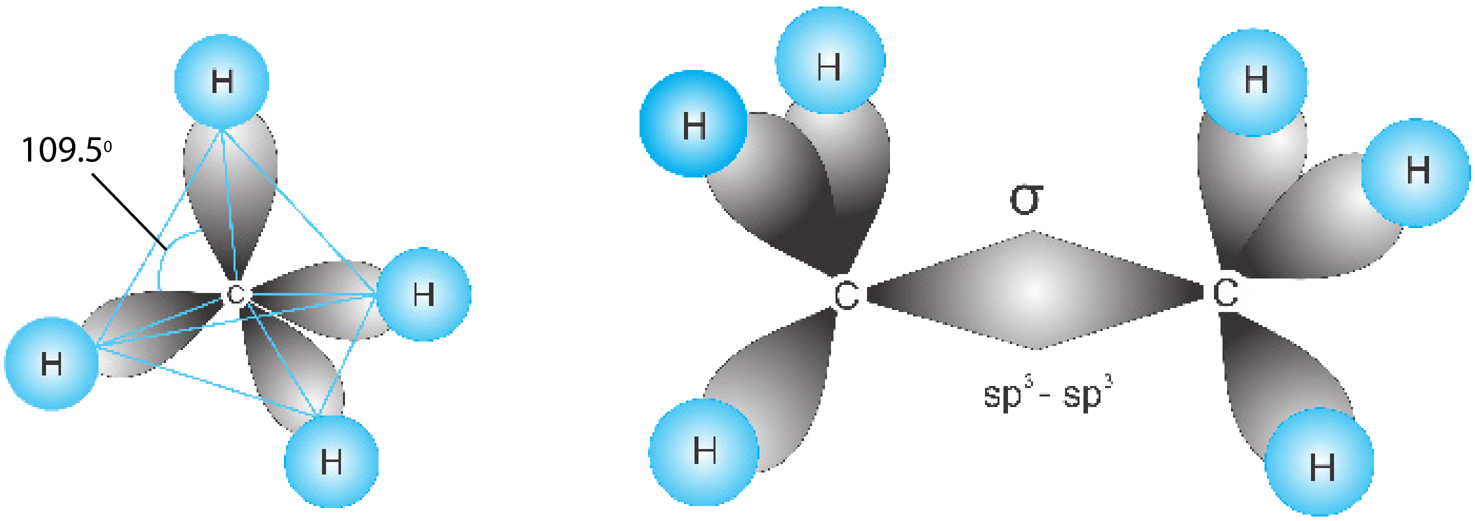


Fig. 7.2 sp^3 hybridization of carbon to give methane (CH_4)

In the formation of methane, the four hybrid atomic orbitals of carbon overlap separately with four 1s atomic orbitals of hydrogen to form four equivalent C-H bonds. The shape of methane thus formed is very similar to the actual methane molecule. All the four hydrogen atoms do not lie in the same plane.

sp^3-hybridization in ethane



Ethane

In ethane, CH_3 - CH_3, the two tetrahedrons of each carbon are joined together as shown in the above figure. Further addition of a carbon atom with ethane will mean the attachment of another tetrahedron. At this stage, it is necessary to answer an important question.From where does the energy come to excite the carbon atom?

The answer to this question is simple. Before excitation the carbon should make two covalent bonds releasing an adequate amount of energy. After excitation, however, it will form four covalent bonds releasing almost double the amount of energy. This excess energy is more than that needed to excite the carbon atom. So a tetravalent carbon atom is expected to be more stable than a divalent carbon atom.

sp^2 Hybridization

In order to explain the bonding in unsaturated compounds, two more modes of hybridization have been developed.

The structure of alkenes can be explained by sp^2 mode of hybridizaton. In this type one 2s and two 2p orbitals of carbon are mixed together to give three equivalent and coplanar sp^2 hybridized orbitals, Fig. 7.3.

Each sp^2 hybrid orbital is directed from the centre of an equilateral triangle to its three corners. The bond angle between any two sp^2 hybrid orbitals is 120°.The unhybridized $2p_z$ orbital will remain perpendicular to the triangle thus formed.

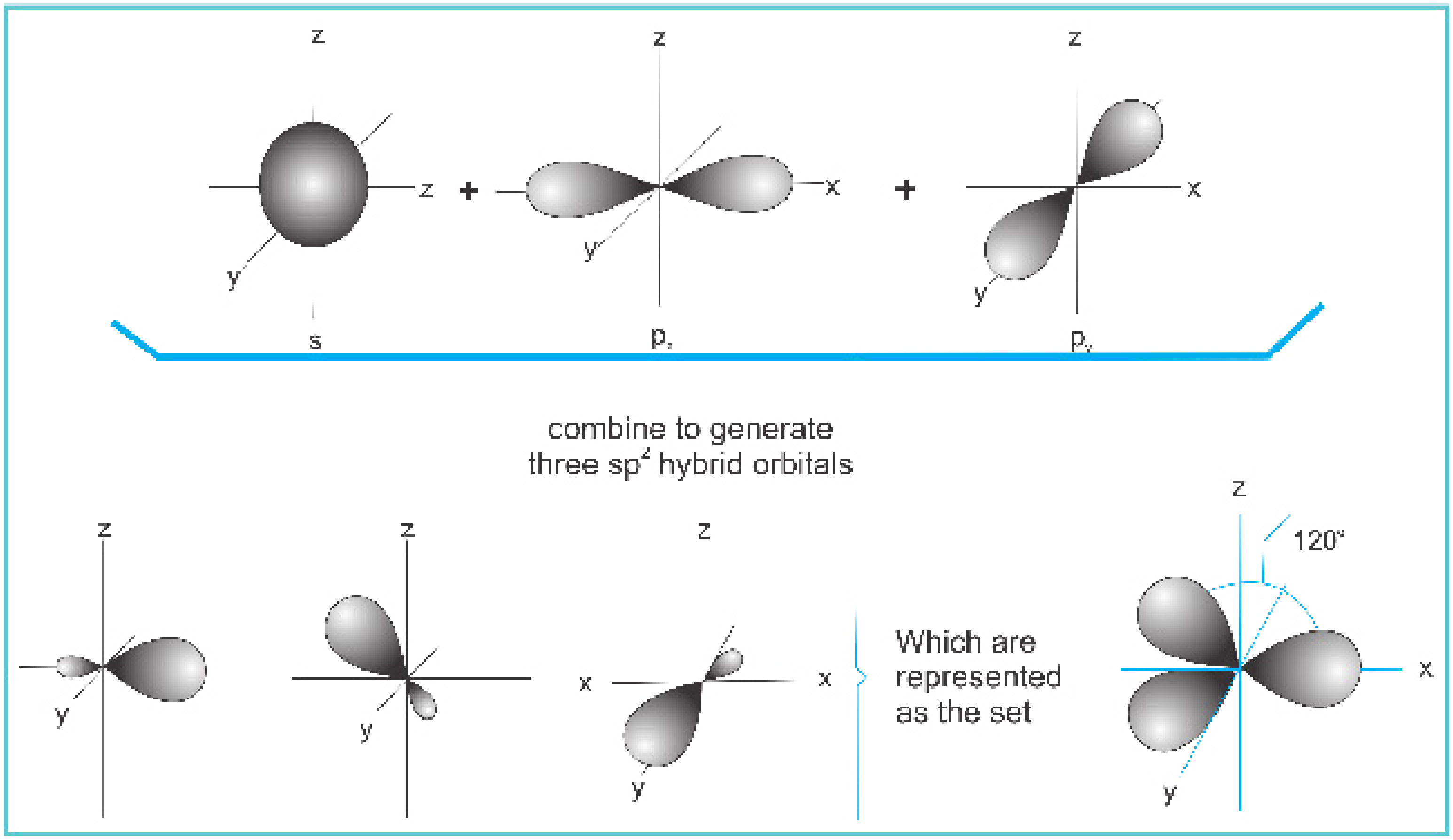


Fig. 7.3 sp^2-hybridization of carbon.

In the formation of ethene molecule, three sp^2 orbitals of each carbon atom overlap separately with sp^2 orbital of another carbon and 1s orbitals of two hydrogen atoms to form three s bonds. This gives rise to what is called the s-frame work of ethene molecule. The unhybridized orbitals of each carbon atom will then overlap in a parallel fashion to form a π - bond, Fig. 7.4

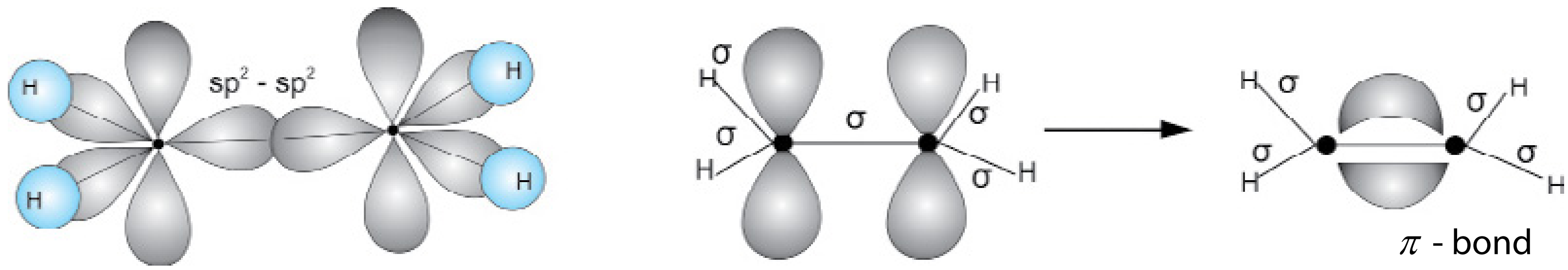
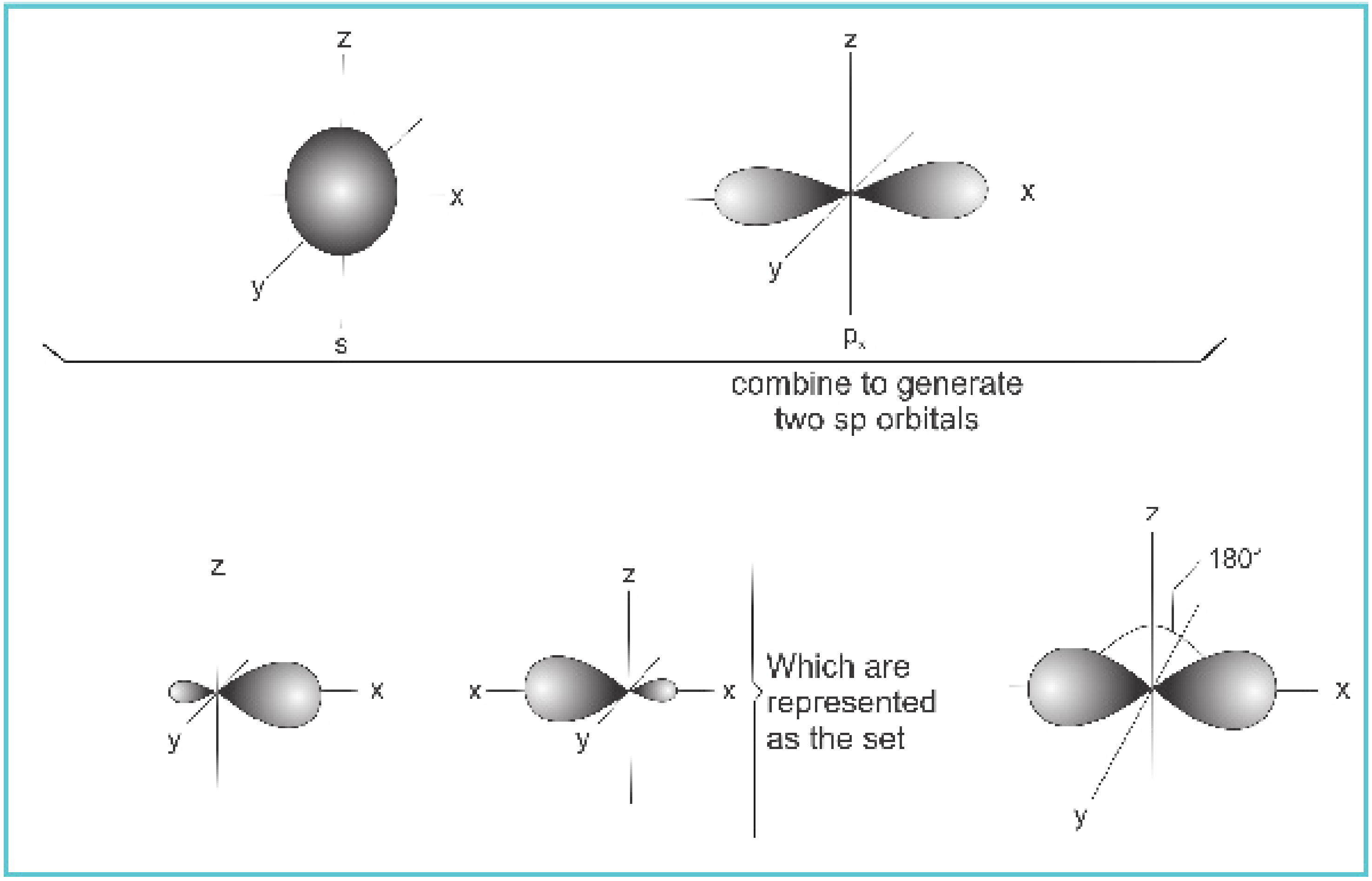


Fig. 7.4 Formation of ethene.

sp-Hybridization

The structure of alkynes can be explained by yet another mode of hybridization called sp hybridization. In this type one 2s and one 2p orbitals of the carbon atom mix together to give rise to two degenerate sp hybridized atomic orbitals. These orbitals have a linera shape with a bond angle 180°.



The two unhybridized atomic orbitals, $2p_y$ and $2p_z$ are perpendicular to these sp hybridized orbitals.

Ethyne molecule is formed when two sp hybridized carbon atoms join together to from a σ-bond by sp-sp overlap. The other sp orbital is utilized to form a σ- bond with 1s orbital of hydrogen atom.

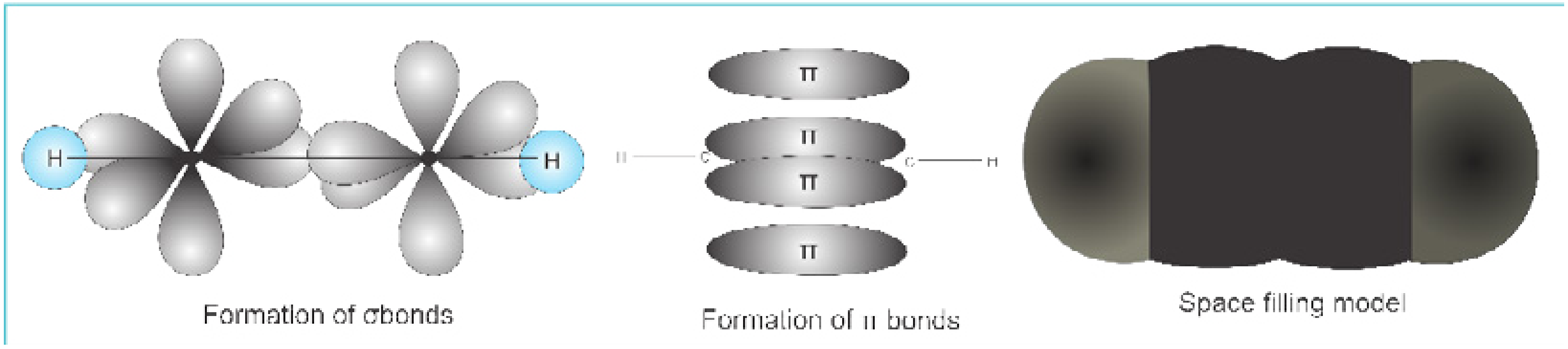


Fig. 7.6 Formation of ethyne

The two unhybridized p orbitals on a carbon atom will overlap separately with the p orbitals of the other carbon atom to give two π-bonds both perpendicular to the σ -framework of ethyne. The presence of a σ and two π bonds between two carbon atoms is responsible for shortening the bond distance.

7.10 ISOMERISM

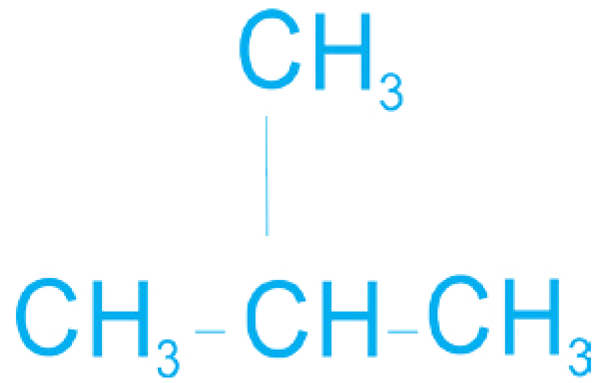
The concept of isomerism is an important feature of organic compounds. Two or more compounds having the same molecular formula but different structural formulas and properties are said to be isomers and the phenomenon is called isomerism. The structural formula of a compound shows the arrangement of atoms and bonds present in it.

The simplest hydrocarbon to have structural isomers is butane (C_4H_{10}). The alkanes, methane, ethane and propane do not show the phenomenon of isomerism because each exists in one structural form only. If we study the structural formula of butane or other higher hydrocarbons of the alkane family, we will observe that it is possible to arrange the atoms present in the molecule in more than one way to satisfy all valencies.

This means that it is possible to have two or more different arrangements for the same molecular formula.For example, butane molecule can have two different arrangements as represented by the following structural formulas:

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

n-Butane



Isobutane

This fact has been supported by an experimental evidence that there are two compounds with different physical properties but with the same molecular formula of C_4H_{10}.

Isomerism is not only possible but common if the compound contains more than three carbon atoms. As the number of carbon atoms in a hydrocarbon increases, the number of possible isomers increase very rapidly. The five carbon compound, pentane, has three isomers. When the number of carbon atoms increases to thirty, the number of isomers amount to over four billions.

7.10.1 Types of Isomerism

(1) Structural Isomerism

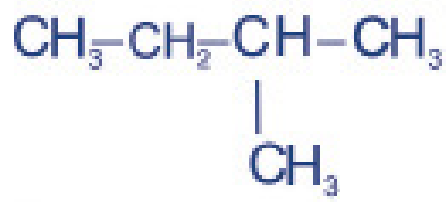
The structural isomerism is not confined to hydrocarbons only. In fact, all classes of organic compounds and their derivatives show the phenomenon of structural isomerism. The structural isomerism arises due to the difference in the arrangement of atoms within the molecule. The structural isomerism can be exhibited in five different ways. These are :

(i) The Chain Isomerism.

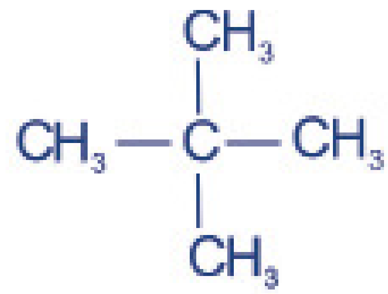
This type of isomerism arises due to the difference in the nature of the carbon chain. For example, for pentane (C_5H_{12}), the following arrangements are possible.

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

n-Pentane



Isopentane



Neopentane

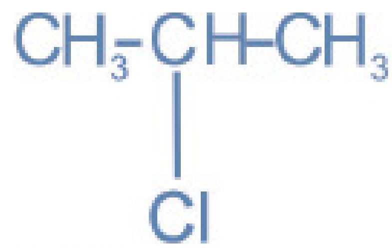
(ii) Position Isomerism.

This type of isomerism arises due to the difference in the position of the same functional group on the carbon chain. The arrangement of carbon atoms remains the same. For example,

(a) Chloropropane can have two positional isomers given below.

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}Cl$$

1-Chloropropane



2-Chloropropane

(b) Butene (C_4H_8) can have two positional isomers.

$$CH_3\text{-}CH_2\text{-}CH{=}CH_2 \qquad CH_3\text{-}CH{=}CH\text{-}CH_3$$

I-Butene 2-Butene

(iii) Functional Group Isomerism

The compounds having the same molecular formula but different functional groups are said to exhibit functional group isomerism. For example, there are two compounds having the same molecular formula C_2H_6O , but different arrangement of atoms.

$$CH_3\text{-}O\text{-}CH_3 \qquad CH_3\text{-}CH_2\text{-}OH$$

Dimethyl ether Ethyl alcohol

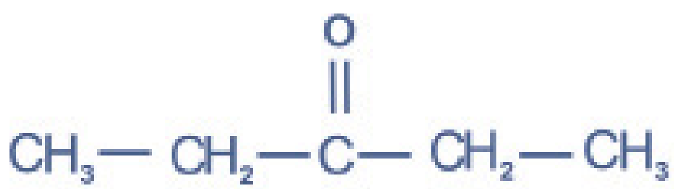
(iv) Metamerism

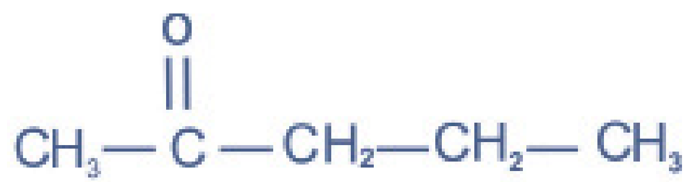
This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group. Such compounds belong to the same homologous series. For example, diethyl ether and methyl n-propyl ether are metamers.

$$CH_3-CH_2-O-CH_2-CH_3$$
Diethyl ether

$$CH_3-O-CH_2-CH_2-CH_3$$
Methyl n-propyl ether

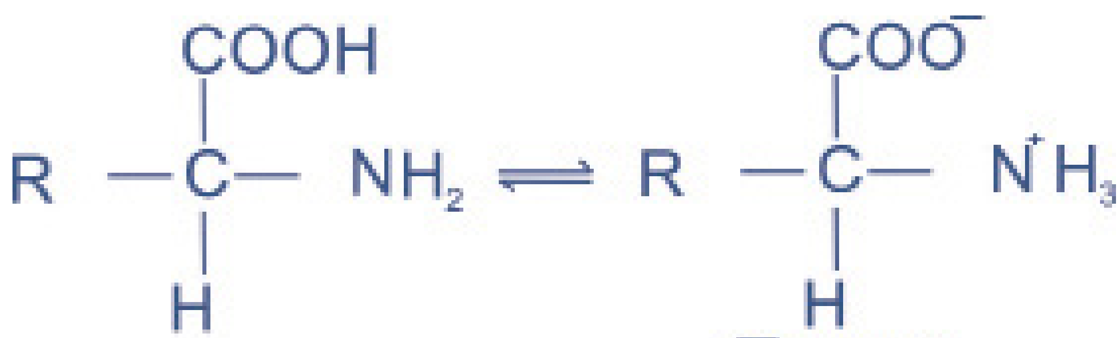
For a ketonic compound having the molecular formula $C_5H_{10}O$, the following two metamers are possible.


Diethyl ketone


Methyl n-propyl ketone

(v) Tautomerism

This type of isomerism arises due to shifting of proton from one atom to other in the same molecule.


Zwitterion

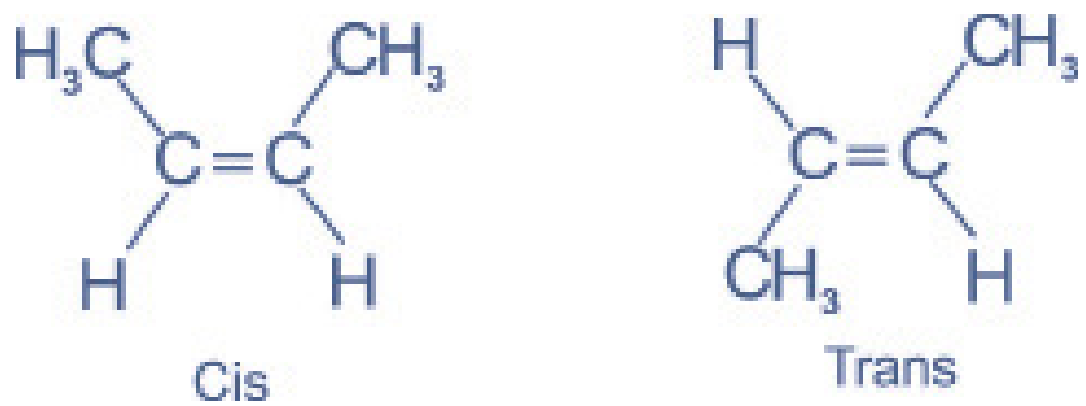
(2) Cis-trans Isomerism or Geometric Isomersim

Two carbon atoms joined by a single bond are capable of free rotation about it. However, when two carbon atoms are joined by a double bond, they cannot rotate freely. As a result, the relative positions of the various groups attached to these carbon atoms get fixed and gives rise to cis- trans isomers.

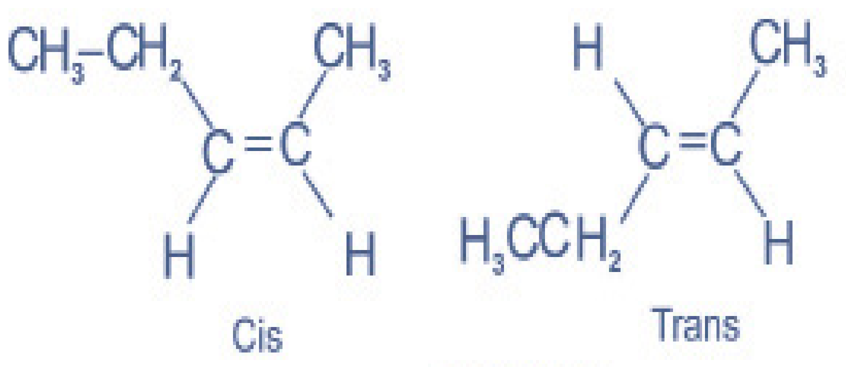
Such compounds which possess the same structural formula, but differ with respect to the positions of the identical groups in space are called cis-trans isomers and the phenomenon is known as the cis-trans or geometric isomerism.

The necessary and sufficient condition for a compound to exhibit geometric isomerism is that the two groups attached to the same carbon must be different.

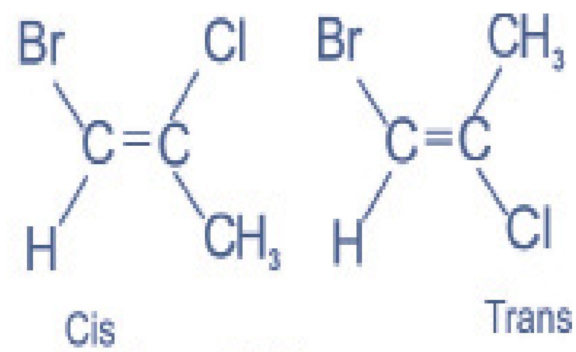
2-Butene can exist in the form of cis and trans isomers.



Similarly 2-pentene and l-bromo-2-chloropropene also show cis-trans isomerism.



2-Pentene



1-bromo-2-chlororpopene

In the cis-form, the similar groups lie on the same side of the double bond whereas in the trans-form, the similar groups lie on the opposite sides of the double bond.

The rotation of two carbon atoms joined by a double bond could happen only if the π bond breaks.This ordinarily costs too much energy, making geometric isomers possible.

KEY POINTS

1. Chemical compounds were classified as organic and inorganic compounds based upon their origin. Organic compounds are obtained from living things whereas inorganic compounds are obtained from mineral sources.
2. It was thought that organic compounds could not be synthesized in the laboratory from inorganic sources.
3. Organic chemistry is now-a-days defined as the chemistry of carbon compounds.
4. Most of the commercially important compounds we use everyday are organic in nature.
5. Coal, petroleum and natural gas are important sources of organic compounds.
6. The process of cracking is developed to increase the yield of lower hydrocarbons which serve as important fuels commercially.
7. Organic compounds are classified into acyclic and cyclic compounds.
8. The study of organic chemistry is organized around functional groups. Each functional group defines an organic family.
9. The type of bonding and the shapes of different type of compounds formed by carbon can be explained by sp^3, sp^2 and sp modes of hybridization.
10. Compounds having the same molecular formula but different structural formulas are called isomers. There are four different type of structural isomers.
11. Isomerism arises due to restricted rotation around a carbon- carbon double bond is called cis-trans isomerism.

EXERCISE

Q I. Fill in the blanks

i) Organic compounds having same molecular formula but different _______are called isomers.

ii) The state of hybridization of carbon atom in _______ is sp^2.

iii) Alkenes show_______ due to restricted rotation around a carbon-carbon double bond.

iv) Heating an organic compound in the absence of oxygen and in the presence of_________as a catalyst is called cracking.

v) A group of atoms which confers characteristic properties to an organic compound is called __________ .

vi) 2-Butene is_________of 1-butene.

vii) Carbonyl functional group is present in both__________and ketones.

viii) A heterocyclic compound contains an atom other than_______ in its ring.

ix) The quality of gasoline can be checked by finding out its______ .

x) A carboxylic acid contains____________ as a functional group.

Q.2 Indicate true or false.

(i) There are three possible isomers forpentane.

(ii) Alkynes do not show the phenomenon of cis-trans isomerism.

(iii) Organic compounds can not be synthesized from inorganic compounds.

(iv) All close chain compounds are aromatic in nature.

(v) The functional group present in amides is called an amino group.

(vi) Government of Pakistan is trying to use coal for power generation.

(vii) Crude petroleum is subjected to fractional sublimation in order to separate it into different fractions,

(viii) A bond between carbon and hydrogen serves as a functional group for alkanes.

(ix) o-Nitrotoluene and p-nitrotoluene are the examples of functional group isomerism.

(x) Almost all the chemical reactions taking place in our body are inorganic in nature.

Q 3. Multiple choice questions. Encircle the correct answer.

(i) The state of hybridization of carbon atom in methane is:

(a) sp^3 (b) sp^2 (c) sp (d) dsp^2

(ii) In t-butyl alcohol, the tertiary carbon is bonded to:

(a) two hydrogen atoms (b) three hydrogen atoms

(c) one hydrogen atom (d) no hydrogen atom

(iii) Which set of hybrid orbitals has planar triangular shape.

(a) sp^3 (b) sp (c) sp^2 (d) dsp^2

(iv) The chemist who synthesized urea from ammonium cyanate was:

(a) Berzelius (b)Kolbe (c) Wholer (d) Lavoisier

(v) Linear shape is associated with which set of hybrid orbitals?
(a) sp (b) sp^2 (c) sp^3 (d) dsp^2

(vi) A double bond consists of:
(a) two sigma bonds (b) one sigma and one pi bond
(c) one sigma and two pi bonds (d) two pi bond

(vii) Ethers show the phenonenom of:
(a) position isomerism (b) functional group isomerism
(c) metamerism (d) cis-trans isomerism

(viii) Select From the following the one which is alcohol:
(a) CH_3-CH_2-OH (b) CH_3-O-CH_3
(c) CH_3COOH (d) CH_3-CH_2-Br

Q 4. How organic compounds are classified? Give suitable example of each type.
Q 5. What are homocyclic and heterocyclic compounds? Give one example of each.
Q 6. Write the structural formulas of the two possible isomers of C_4H_{10}.
Q 7. Why is ethene an important industrial chemical?
Q 8. What is meant by a functional group? Name typical functional groups containing oxygen.
Q 9. What is an organic compound? Explain the importance of Wohler's work in the developrnent of organic chemistry.
Q 10. Write a short note on cracking of hydrocarbons.
Q 11. Explain reforming of petroleum with the help of suitable example.
Q 12. Describe important sources of organic compounds.
Q13. What is orbital hybridization? Explain sp^3 sp^2 and sp modes of hybridization of carbon.
Q14. Explain the type of bonds and shapes of the following molecules using hybridization approach.
$CH_3 - CH_3$, $CH_2 = CH_2$, $CH \equiv CH$, HCHO, CH_3Cl
Q 15. Why there is no free rotation around a double bond and a free rotation around a single bond ? Discuss cis-trans isomerism.

CHAPTER

8

ALIPHATIC HYDROCARBONS

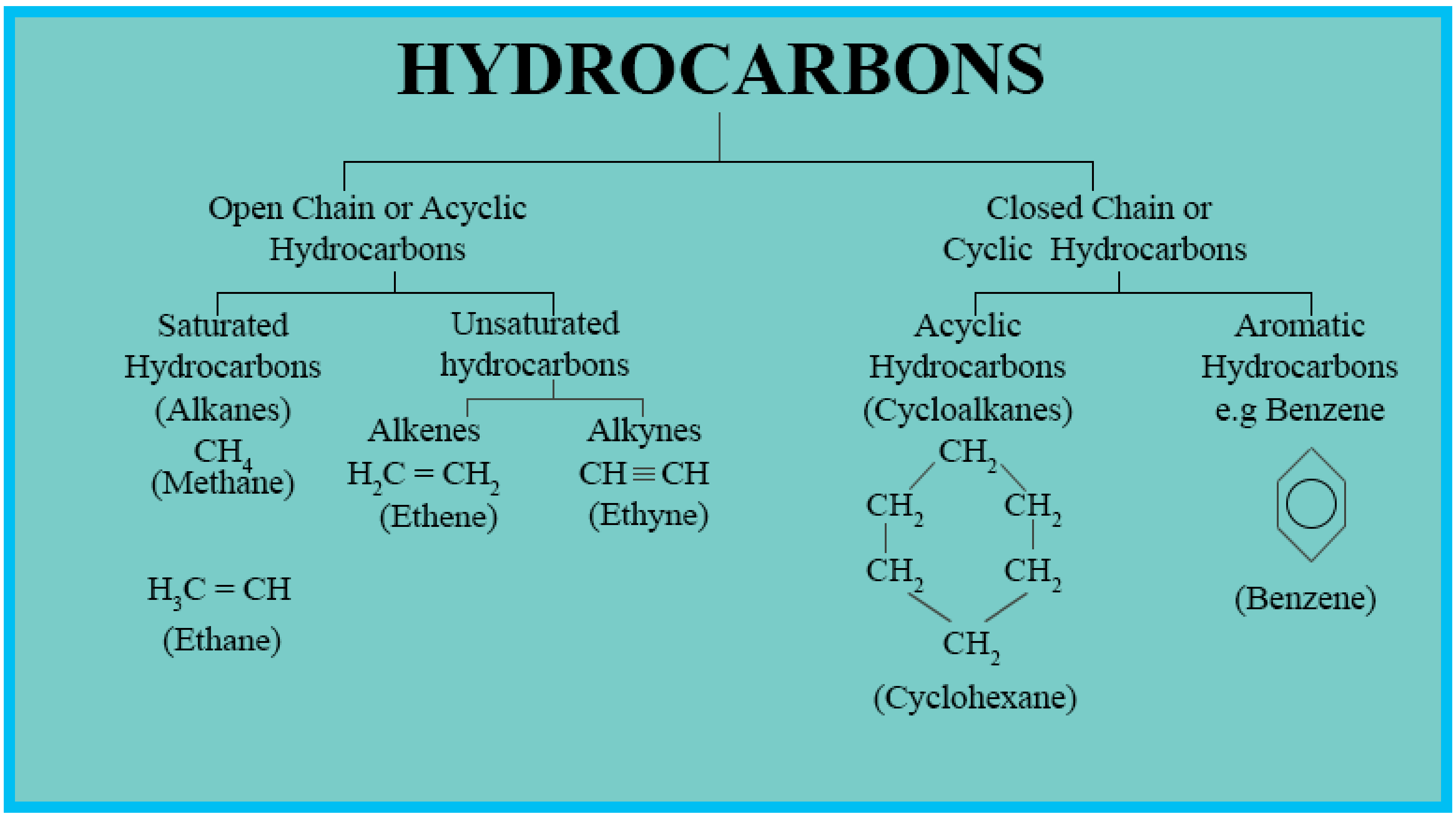
Animation 8.1 : Cycloalkanes
Source and credit : Stackexchange

In This Chapter You Will Learn:

1. How to name the aliphatic hydrocarbons according to IUPAC rules.
2. The synthesis of alkanes, alkenes and alkynes and their important reactions.
3. The comparison of reactivity of s bond and p bond.
4. About the free radical nature of reactions of alkanes and electrophilic addition of alkenes and alkynes.
5. The comparison of reactivities of alkanes, alkenes and alkynes.

8.1 INTRODUCTION

Hydrocarbons are organic compounds which contain carbon and hydrogen only. The number of such compounds is very large because of the property of catenation. Hydrocarbons have been divided into various classes on the basis of structure of the chain or size and nature of the ring.



If all the valencies of the carbon atoms in a molecule are fully satisfied and these cannot further take up any more hydrogen atoms, then the hydrocarbons are named as saturated hydrocarbons or alkanes. The compounds of carbon and hydrogen in which all the four valencies of carbon are not fully utilized and they contain either a double or a triple bond, such compounds are called unsaturated hydrocarbons.

Those unsaturated hydrocarbons which contain a double bond are called alkenes while those containing a triple bond are called alkynes. Classification of hydrocarbons has been' shown at page 136.

8.2 NOMENCLATURE

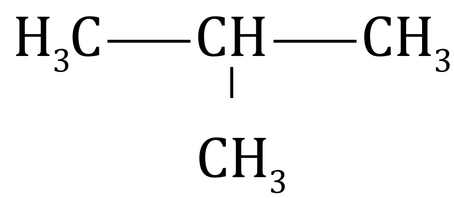
8.2.1 Common or Trivial Names:

In the early days, the compounds were named on the basis of their history, the method of preparation or name of the person working on it, e.g., the name marsh gas was given to methane because it was found in marshy places. Acetic acid derives its name from vinegar (Latin, acetum means vinegar). Organic compounds were named after a person, like barbituric acid after Barbara. Such a system may have a certain charm but is never manageable.

For alkanes with five or more carbon atoms, the root word is derived from the Greek or Latin numerals indicating the number of carbon atoms in a molecule, and the name is completed by adding 'ane' as a suffix, e.g. pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), etc. The common or trivial names are applicable to all isomers of a given molecular formula. The prefixes n, iso, neo are, however, to differentiate between isomers.

$$CH_3—CH_2—CH_2—CH_3$$

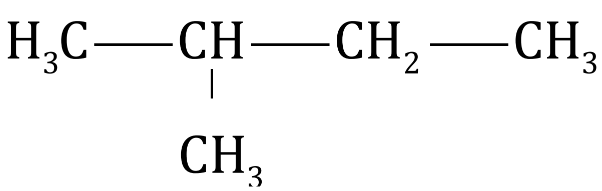
n-butane



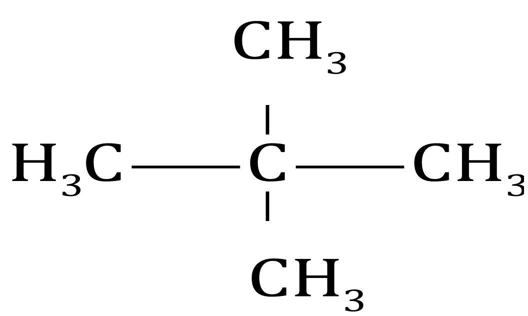
Isobutane

$$CH_3—CH_2—CH_2—CH_2—CH_3$$

n-pentane



Isopentane



Neophentane

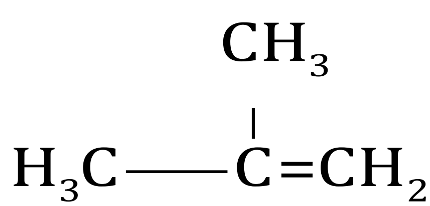
These prefixes have only limited use, as they are not workable with complex molecules. Moreover, common names give only minimum information about the structure of the compounds.Alkenes are similarly named by replacing the ending -ane of the name of alkane with ylene. e.g.

$$H_2C=CH_2$$

Ethylene

$$H_3C—CH=CH_2$$

Propylene



Isobutylene

8.2.2 IUPAC Names

In 1889 the solution for naming the organic compounds systematically was sought by International Chemical Congress. A report was accepted in 1892 in Geneva but it was found incomplete. In 1930, International Union of Chemistry (IUC) gave a modified report which is also referred as Liege Rules. This report was further modified by International union of Pure and Applied Chemists (IUPAC) in the year 1947. Since that date the union has issued periodic reports on rules for the systematic nomenclature of organic compounds, the most recent of which was published in the year 1979. IUPAC system of nomenclature is based on the following principle.

'Each different compound should have a different name'.

Thus through a systematic set of rules, the IUPAC system provides different names for more than 7 million known organic compounds.

Nomenclature of Alkyl Groups:

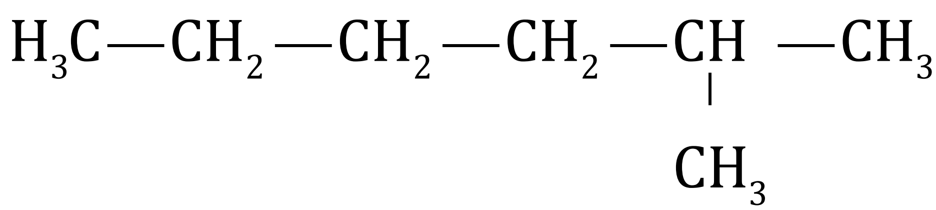
If we remove one hydrogen atom from an alkane, we obtain what is called an alkyl group. These alkyl groups have names that end in —yl.When the alkane is unbranched and the hydrogen atom that is removed is a terminal hydrogen atom, the names are straight forward:

Alkane	Alkyl Group	Abbreviation
$CH_3—H$	$CH_3—$	Me-
Methane	Methyl	
$CH_3—CH_2—H$	$CH_3CH_2—$	Et-
Ethane	Ethyl	
$CH_3—CH_2—CH_2—H$	$CH_3CH_2CH_2—$	Pr-
Propane	n-propyl	
$CH_3—CH_2—CH_2—CH_2—H$	$CH_3CH_2CH_2CH_2—$	n-Bu-
n-Butane	n-Butyl	

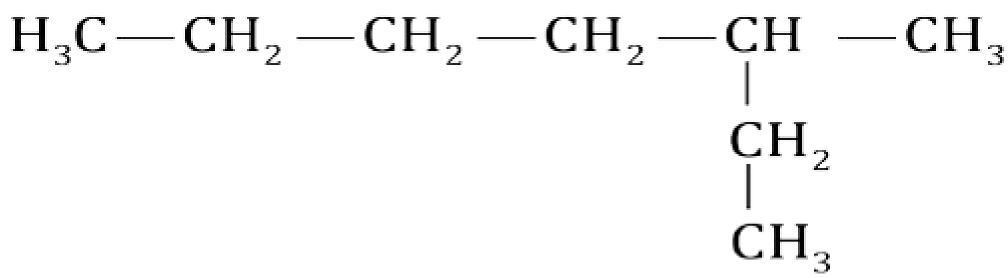
8.2.3 Nomenclature of Alkanes

Branched-chain alkanes are named according to the following rules.

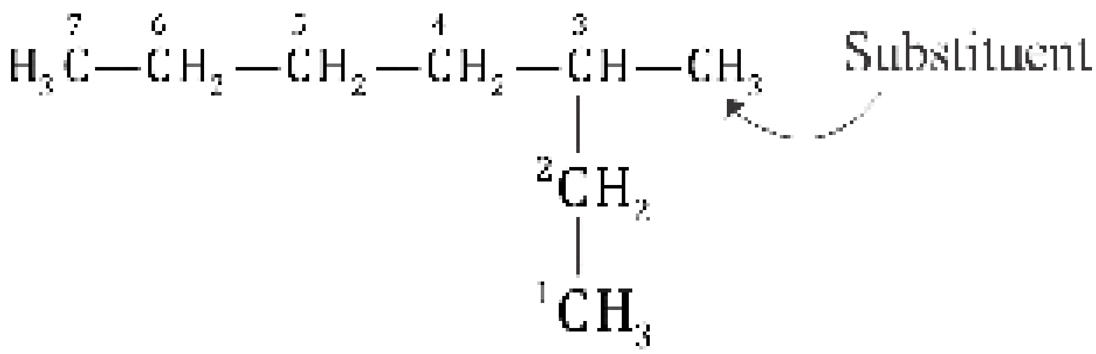
1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkane. We designate the following compound as a hexane because the longest continuous chain contains six carbon atoms.

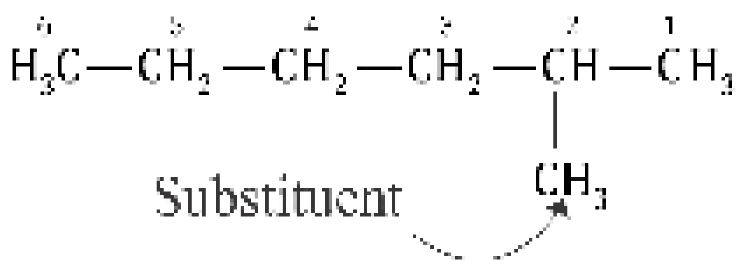


The longest continuous chain may not always be obvious from the way the formula is written. Notice, for example, that the following alkane is designated as a heptane because the longest chain contains seven carbon atoms.

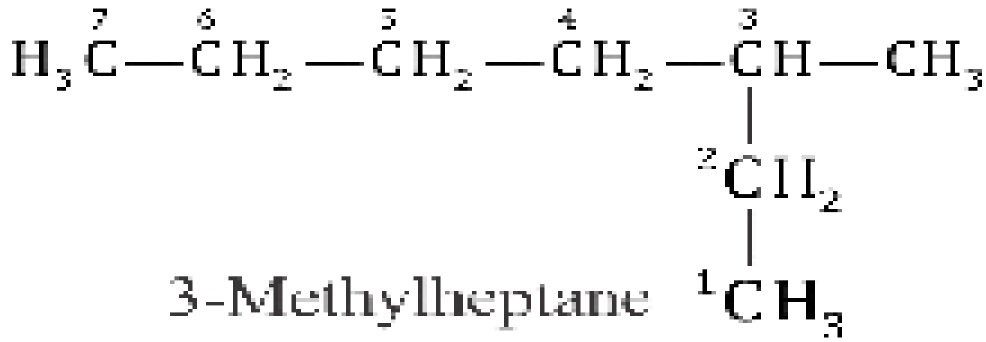


2. Number the longest chain beginning from the end of the chain nearer the substituent. Applying this rule, we number the two alkanes shown above in the following way.

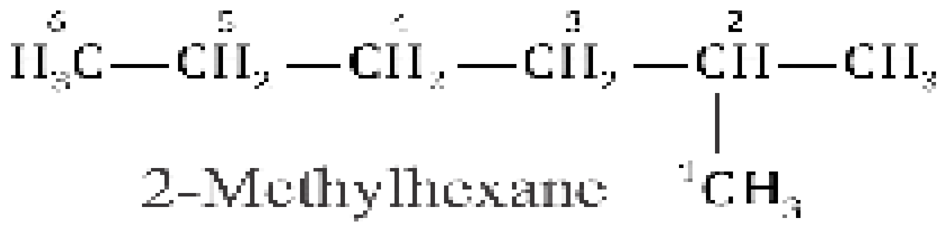




3.Use the numbers obtained by the application of rule 2 to designate the location of the substituent group. The parent name is placed last, and the substituent group, preceded by the number designating its location on the chain, is placed first. Numbers are separated from words by a hyphen. The systematic names ot the two compounds shown above will then be:

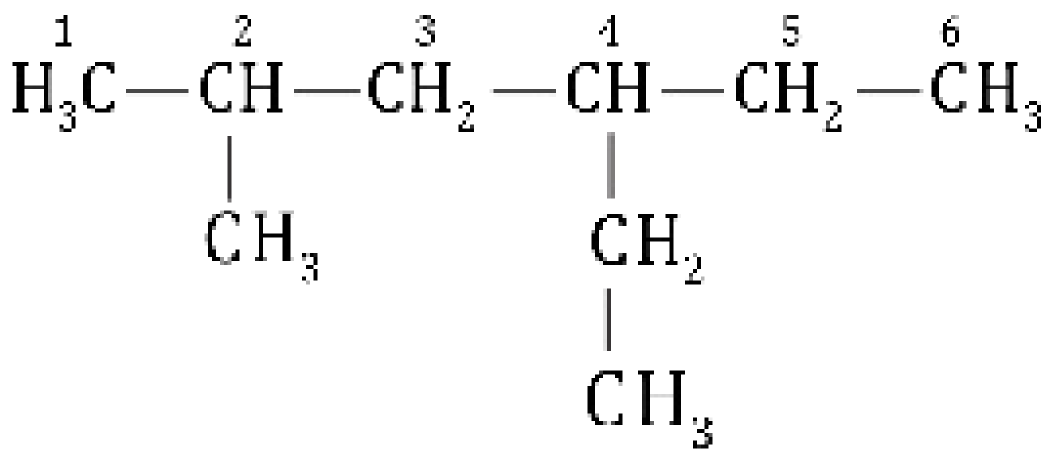


3-Methylheptane



2-Methylhexane

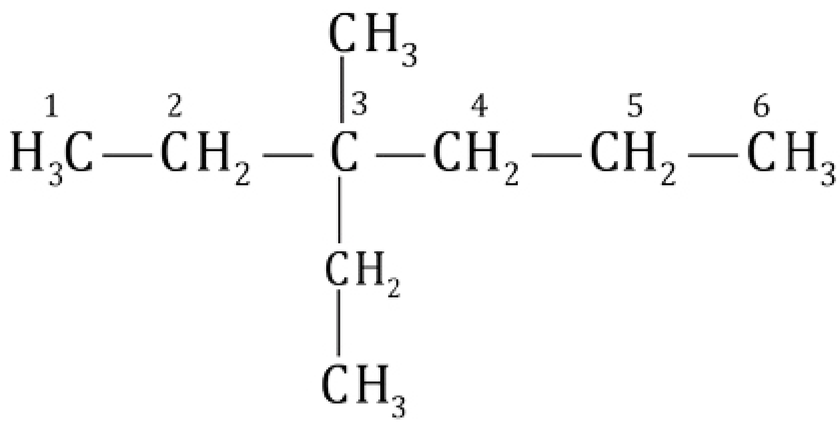
4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. For example, we designate the following compound as 4 -ethyl-2 -methylhexane.



4-Ethyl-2-methylhexane

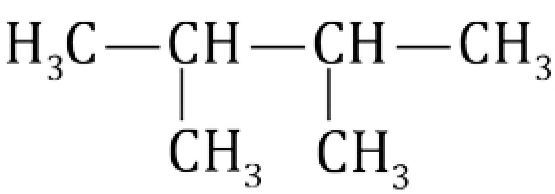
The substituent groups should be listed alphabetically (i.e. ethyl before methyl). In deciding on alphabetical order disregard multiplying prefixes such as “di” and “tri”.

5. When two substituents are present on the same carbon atom, use that number twice.

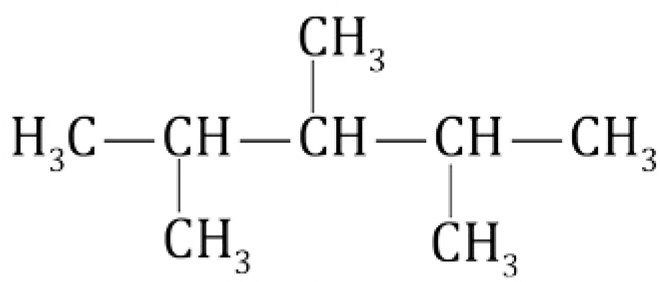


3-Ethyl-3-methylhexane

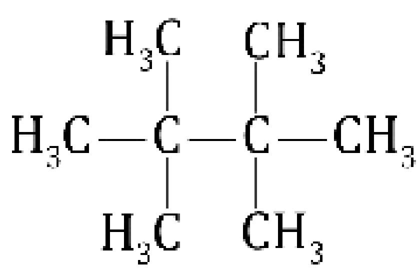
6.When two or more substituents are identical, indicate this by the use of the prefixes di, tri , tetra , and so on. Then make certain that each and every substituent has a number. Commas are used to separate numbers from each other.



2, 3-Dimethylbutane



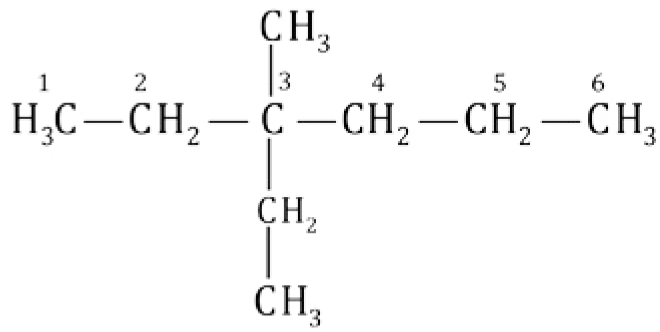
2, 3, 4-Trimethylpentane



2, 2, 3, 3-Tetramethylbutane

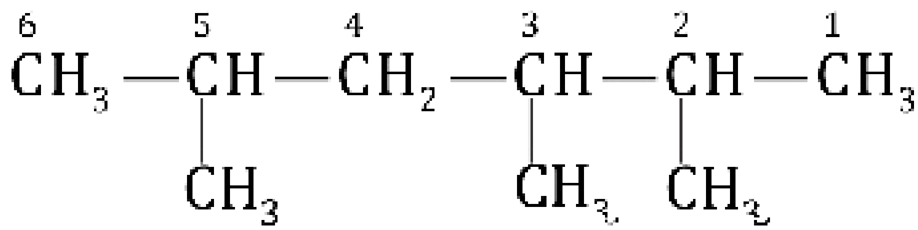
Application of these six rules allows us to name most of the alkanes that we shall encounter. Two other rules, however, may be required occasionally.

7.When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents.



3-Ethyl-3-methylhexane

8. When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.

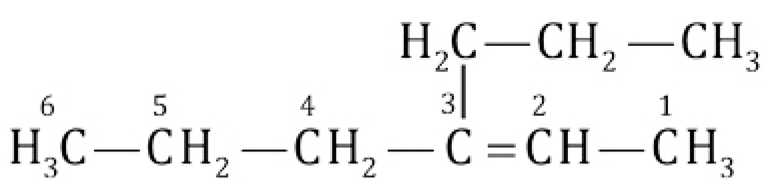


2, 3, 5-Trimethylhexane (not 2,4,5-Trimethylhexane)

8.2.4 Nomenclature of Alkenes:

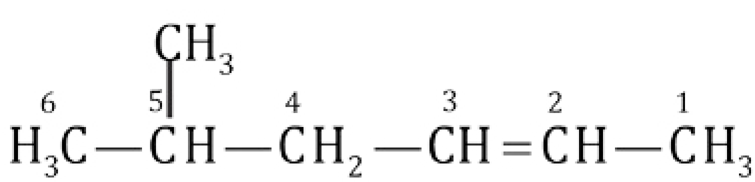
The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes.

1.Select the longest continuous chain that contains the C = C as the parent chain. Change the ending of the name of the alkane of identical length from — ane to — ene, e.g.,



3- n - Propyl-2-hexene

2.Number the chain so as to include both carbon atoms of the double bond. Numbering begins from the end nearer to the double bond.



5-Methyl-2-hexene

3. Designate the location of the double bond by using the number of the first atom of the double bond as a prefix.

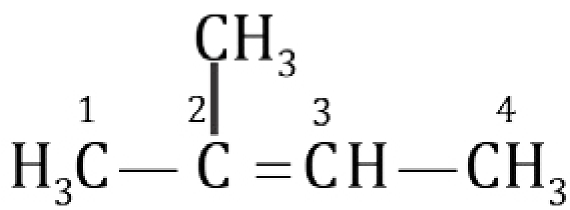
$$\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

1-Butene

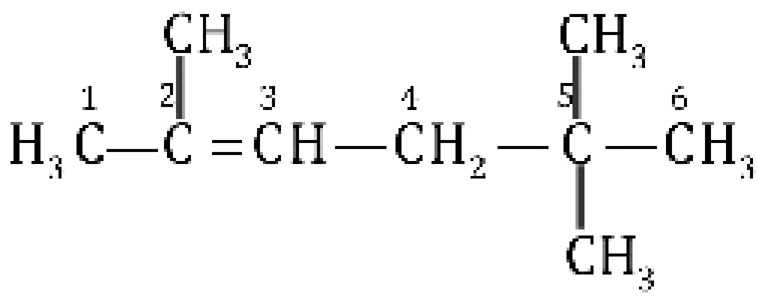
$$\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

1-Pentene

4. Indicate the locations of the substituent groups by the numbers of the carbon atoms to which they are attached.



2-Methyl-2-butene



2, 5, 5-Trimethyl-2-hexene

5. If the parent chain contains more than one double bonds, they are alkadienes for two, alkatrienes for three and so on.

$$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$$

1,3-Butadiene

8.2.5 Nomenclature of Alkynes:

1. The largest continuous carbon chain containing triple bond is selected. The name of the identical alkane is changed from ane to — yne. e.g.

$$\overset{2}{CH}\equiv\overset{1}{CH}$$

Ethyne

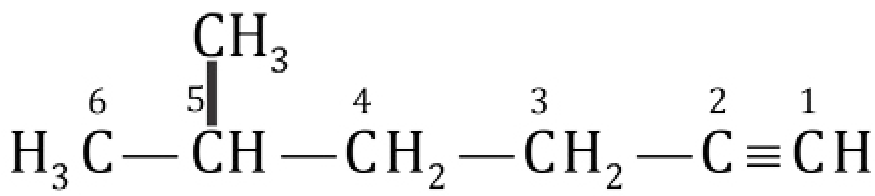
$$\overset{3}{H_3C}-\overset{2}{C}\equiv\overset{1}{CH}$$

Propyne

2.The position of triple bond is shown by numbering the alkyne, so that minimum number is assigned to the triple bond.

$$\overset{4}{H_3C}-\overset{3}{CH_2}-\overset{2}{C}\equiv\overset{1}{CH}$$

1-Butyne



5-Methyl-1-hexyne

3.If a hydrocarbon contains more than one triple bonds, it is named as alkadiyne and triyne, etc. depending on the number of triple bonds.

$$H\overset{6}{C}\equiv\overset{5}{C}-\overset{4}{CH_2}-\overset{3}{CH_2}-\overset{2}{C}\equiv\overset{1}{CH}$$

1,5 - Hexadiyne

4.If both double and triple bonds are present in the compound then ending enyne is given to the root.

a.Lowest possible number is assigned to a double or a triple bond irrespective of whether ene or yne gets the lower number.

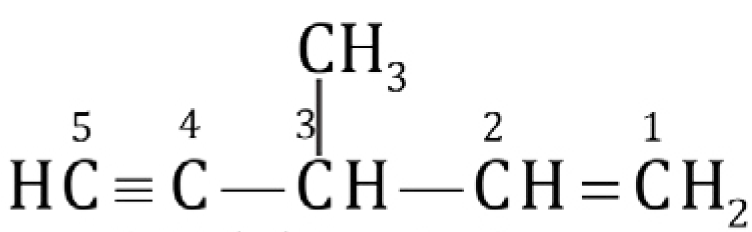
$$H\overset{1}{C}\equiv\overset{2}{C}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH_3}$$

3 - Penten - 1 - yne

$$H_2\overset{1}{C}=\overset{2}{CH}-\overset{3}{C}\equiv\overset{4}{C}=\overset{5}{CH_3}$$

1 - Penten - 3 - yne

b.In case a double and a triple bond are present at identical positions, the double bond is given the lower number.



3-Methyl-1-penten-4-yne

8.3 ALKANES OR PARAFFINS

Alkanes are the simplest organic compounds made up of carbon and hydrogen only. They have a general formula of C_nH_{2n+2}. In these compounds the four valencies of carbon atoms are satisfied by single bonds to either other carbon atoms or hydrogen atom. They are, therefore known as Saturated Hydrocarbons. Methane (CH_4) is the simplest member of this family. Each carbon atom in alkane is sp^3 hybridized and has a tetrahedral geometry.

8.3.1 General Methods of Preparations

(1) Hydrogenation of Unsaturated Hydrocarbons (Sabatier-Sendem's Reaction)

Hydrogenation of alkenes or alkynes in the presence of nickel at 200-300°C yields alkanes.

$$R-CH=CH_2 + H_2 \xrightarrow[200-300^\circ C]{Ni} R-CH_2-CH_3$$

Alkene

$$\text{e.g } CH_2=CH_2 + H_2 \xrightarrow[200-300^\circ C]{Ni} CH_3-CH_3$$

Ethane

The hydrogenation can also be carried out with platinum or palladium at room temperature but they are expensive than nickel. The method is of industrial importance. Production of vegetable ghee by the catalytic hydrogenation of vegetable oil (unsaturated fatty acids) is an example of the application of this method on industrial scale.

(2) From Alkyl Halides:

An alkane is produced when an alkyl halide reacts with zinc in the presence of an aqueous acid.

$$\underset{\text{Alkyl halide}}{R-X} + Zn + H^+ + X^- \longrightarrow \underset{\text{Alkane}}{R-H} + ZnX_2$$

$$\underset{\text{Methyl iodide}}{CH_3-I} + Zn + H^+ + I^- \longrightarrow \underset{\text{Methane}}{CH_4} + ZnI_2$$

$$\underset{\text{2-Bromo-butane}}{CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3} + Zn + H^+ + Br^- \longrightarrow \underset{\text{n-Butane}}{CH_3-CH_2-CH_2-CH_3} + ZnBr$$

Alkanes can also be prepared from alkyl halides using palladium-charcoal as acatalyst. The method is known as Hydrogenolysis (hydrogenation accompanied by bond cleavage)

$$R-X + H_2 \xrightarrow[\Delta]{Pd/C} R-H + H-X$$

(3) Decarboxylation of Monocarboxylic Acids

i) When sodium salts of fatty acids are heated with soda-lime (prepared by soaking quick lime (CaO) with caustic soda solution and drying the product). They eliminate a molecule of CO_2 to form alkanes.

$$\underset{\text{Sod. salt of an acid}}{R-\overset{\overset{\displaystyle O}{||}}{C}-O^-Na^+} + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

e.g $$\underset{\text{Sod. Propionate}}{H_3C-CH_2-\overset{\overset{\displaystyle O}{||}}{C}-O^-Na^+} + NaOH \xrightarrow[\Delta]{CaO} \underset{\text{Ethane}}{H_3C-CH_3} + Na_2CO_3$$

ii) Kolbe's Electrolytic Method

When a concentrated solution of sodium or potassium salt of a mono carboxylic acid is electrolysed, an alkane is produced. This method is only suitable for the preparation of symmetrical alkanes i.e. those of the type R—R. Methane cannot be prepared by this method.

$$2RCOO^-Na^+ + 2H_2O \xrightarrow{\text{Electrolysis}} R—R + 2CO_2 + 2NaOH + H_2$$

It is known to involve the following mechanism.
When potassium salt of acetic acid is electrolysed, acetate ion migrates towards the anode gives up one electron to produce acetate free radical ($CH_3CO\dot{O}$), which decomposes to give a methyl free radical ($\dot{C}H_3$) and CO_2.Two such methyl radicals combine to give ethane.

$$2H_3C—\overset{\overset{O}{\|}}{C}—O^-K^+ \xrightleftharpoons{H_2O} 2H_3C—\overset{\overset{O}{\|}}{C}—O^- + 2K^+$$

At Anode

$$2H_3C—\overset{\overset{O}{\|}}{C}—O^- \xrightarrow{\text{Electrolysis}} 2H_3C—\overset{\overset{O}{\|}}{C}—\dot{O} + 2e'$$

$$2H_3C—\overset{\overset{O}{\|}}{C}—\dot{O} \longrightarrow 2\dot{C}H_3 + 2CO_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow H_3C—CH_3$$

At Cathode

$$2H_2O + 2e^- \longrightarrow 2O\overline{H} + H_2$$

$$2K^+ + 2O\overline{H} \longrightarrow 2KOH$$

This reaction has limited synthetic applications as it forms a number of side products.

(4) From Carbonyl Compounds (Aldehydes or Ketones)

The carbonyl groups of aldehydes or ketones are reduced to methyl or methylene group respectively by either Clemmensen or Wolf-Kishner's reduction. In the former reaction a ketone is reduced to an alkane using zinc amalgam and hydrochloric acid whereas in the later an aldehyde is reduced to alkane with hydrazine in the presence of KOH.

$$\underset{\text{Acetone}}{H_3C-\overset{\overset{\displaystyle O}{||}}{C}-CH_3} + 4[H] \xrightarrow{\text{Zn-Hg/HCl}} \underset{\text{Propane}}{H_3C-CH_2-CH_3} + H_2O$$

$$H_3C-\overset{\overset{\displaystyle O}{||}}{C}-H + 4[H] \xrightarrow[200^{o}C]{N_2H_4/KOH} H_3C-CH_3 + H_2O$$

(5) From Grignard Reagents

Alkyl halides react in anhydrous ether with magnesium to form alkyl magnesium halides, known as Grignard Reagent. They decompose on treatment with water or dilute acid to give alkanes.

$$\overset{\delta-}{CH_3}\overset{\delta+}{Mg}Br + \overset{\delta+}{H_3}-\overset{\delta-}{OH} \xrightarrow[H^+]{\text{ether}} CH_4 + Mg\begin{matrix}Br\\OH\end{matrix}$$

$$H_3C-\overset{\delta-}{CH_2}-\overset{\delta+}{Mg}Br + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow[H^-]{\text{ether}} H_3C-CH_3 + Mg\begin{matrix}Br\\OH\end{matrix}$$

8.3.2. Physical Properties

1. Alkanes containing upto four carbon atoms are colourless, odourless gases while pentane to heptadecane (C_5 to C_{17}) are colourless, odourless liquids. The higher members from C_{18} onwards are waxy solids which are also colourless and odourless.

2. Alkanes are non-polar or very weakly polar and are insoluble in polar solvents like water, but soluble in non-polar solvents like benzene, ether, carbon tetra chloride,etc.

3. Their physical constants like boiling .points, melting points, density, etc increase with the increase in number of carbon atoms, whereas solubility decreases with increase in molecular mass. The boiling point increases by 20 to 30°C for addition of each CH_2 group to the molecule. The boiling points of alkanes having branched chain structures are lower than their isomeric normal chain alkanes, e.g. n-butane has a higher boiling point-0.5^0 C than isobutane (-1 1 .7°C).

4. The melting points of alkanes also increase with the increase in molecular mass but this increase is not so regular.

8.3.3. Reactivity of Alkanes

The alkanes or paraffins (Latin: parum = little, affins = affinity) under ordinary condition are inert towards acids, alkalis, oxidizing and reducing agents. However, under suitable conditions, alkanes do undergo two types of reactions.

1. Substitution Reactions
2. Thermal and Catalytic Reactions

These reactions take place at high temperature or on absorption of light energy through the formation of highly reactive free radicals.

The unreactivity of alkanes under normal conditions may be explained on the basis of the non-polarity of the bonds forming them. The eletronegativity values of carbon (2.5) and hydrogen (2.1) do not differ appreciably and the bonding electrons between C-H and C-C are equally shared making them almost non-polar. In view of this, the ionic reagents such as acids, alkalies, oxidizing agents, etc find no reaction site in the alkane molecules to which they could be attached.

Inertness of σ-bond

The unreactivity of alkanes can also be explained on the basis of inertness of a σ-bond. In a σ -bond the electrons are very tightly held between the nuclei which makes it a very stable bond. A lot of energy is required to break it. Moreover the electrons present in a σ-bond can neither attack on any electrophile nor a nucleophile can attack on them. Both these facts make alkanes less reactive.

8.3.4 Reactions

1. Combustion

Burning of an alkane in the presence of oxygen is known as Combustion. Complete combustion of an alkane yields CO_2, H_2O and heat.

The amount of heat evolved when one mole of a hydrocarbon is burnt to CO_2 and H_2O is called heat of combustion, e.g;

$$CH_4(g) + 2O_2(g) \xrightarrow{\text{Flame}} CO_2(g) + 2H_2O(g) + 891\,kJmol^{-1}$$

Although the reaction is highly exothermic, it requires very high temperature to initiate it, e.g. by a flame or a spark.

Combustion is the major reaction occurring in the internal combustion engines of automobiles. A compressed mixture of alkanes and air burns smoothly in the internal combustion engine and increases its efficiency.

2. Oxidation

Oxidation of methane under different conditions gives different products.

i) Incomplete oxidation occurs in a limited supply of oxygen or air and results in the formation of CO and carbon black.

$$3CH_4(g) + 4O_2(g) \xrightarrow{\text{Flame}} 2CO(g) + 6H_2O(g) + C(s)$$

ii) Catalytic Oxidation: Lower alkanes when burnt in the presence of metallic catalysts, at high temperature and pressure, result in the formation of useful products.

$$CH_4 + [O] \xrightarrow[400^oC/200atm]{Cu} H_3C-OH$$

Methyl alcohol

$$H_3C-OH + [O] \xrightarrow[400^oC/200atm]{Cu} HCHO + H_2O$$

Formaldehyde

$$HCHO + [O] \xrightarrow[400^oC/200atm]{Cu} HCOOH$$

Formic acid

$$HCOOH + [O] \xrightarrow[400^oC/200atm]{Cu} CO_2 + H_2O$$

Catalytic oxidation of alkanes is used industrially to prepare higher fatty acids used in soap and vegetable oil industries.

3. Nitration:

It is a substitution reaction of alkanes in which a hydrogen atom of an alkane is replaced by nitro group ($-NO_2$). Alkanes undergo vapour-phase nitration under drastic condition (at 400-500°C) to give nitroalkanes, e.g.

$$CH_4 + HONO_2 \xrightarrow{450^oC} CH_3NO_2 + H_2O$$

Nitromethane

Nitroalkanes generally find use as fuels, solvents, and in organic synthesis.

4. Halogenation

Alkanes react with chlorine and bromine in the presence of sunlight or UV light or at high temperature resulting in the successive replacement of hydrogen atoms with halogens called halogenation. Extent of halogenation depends upon the amount of halogen used. Reaction of alkanes with fluorine is highly violent and results in a mixture of carbon, fluorinated alkanes and hydrofluoriq acid. Iodine does not substitute directly because the reaction is too slow and reversible. The order of reactivity of halogens is $F_2 > Cl_2 > Br_2 > I_2$.

Halogenation is believed to proceed through free radical mechanism. It involves the following three steps.

Step I $$Cl{-}Cl \xrightarrow{h\upsilon} Cl^{-} + Cl^{-}$$ (Initiation)

Step 2 (Propagation)
$$H_3C{-}H + Cl^{\cdot} \xrightarrow{h\upsilon} CH^{\cdot}_3 + HCl$$
$$CH^{\cdot}_3 + Cl{-}Cl \xrightarrow{h\upsilon} CH_3{-}Cl + Cl^{\cdot}$$

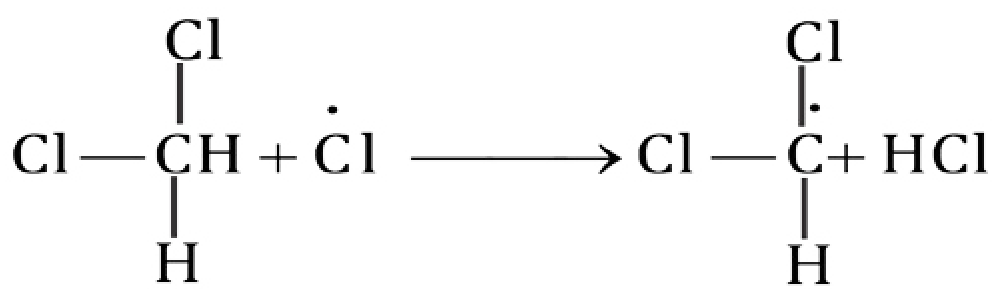
Step 3 $$CH^{\cdot}_3 + Cl^{\cdot} \longrightarrow CH_3{-}Cl$$ (Termination)

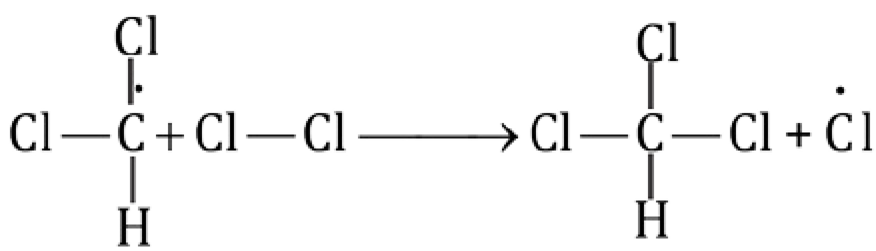
By repetition of step II, a mixture of halogen substituted products are obtained.The reaction is not synthetically so important.

$$H{-}\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}{-}Cl + Cl^{\cdot} \longrightarrow Cl{-}\dot{C}H_2 + HCl$$

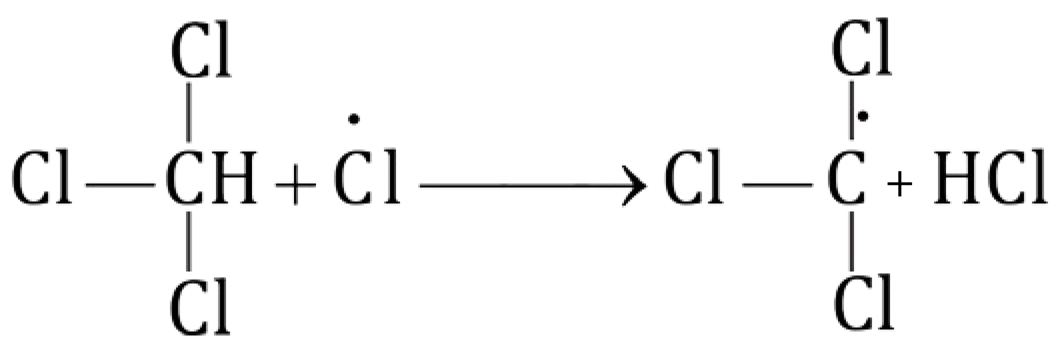
$$Cl—\dot{C}H_2 + Cl—Cl \longrightarrow Cl—CH_2—Cl + \dot{C}l$$

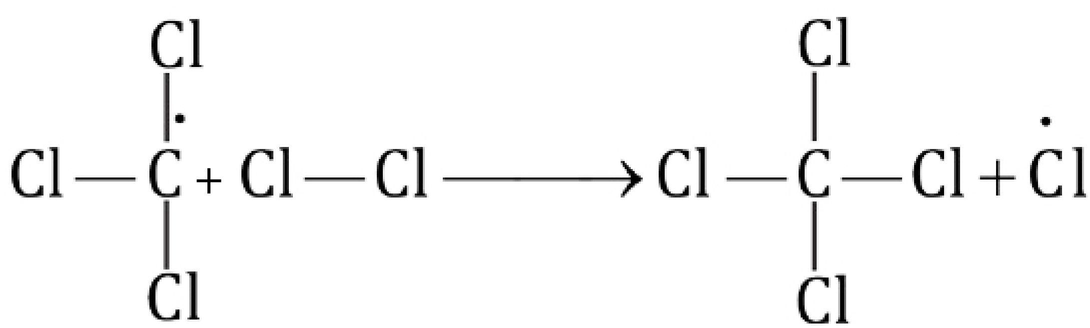
Dichloromethane





Chloroform





Tetrachloromethane or
carbon tetrachloride

8.3.5 Uses of Methane

Methane is used:

(i) as a fuel and as an illuminating gas.
(ii) for the preparation of methylchloride, dichloromethane, chloroform and carbon tetrachloride.

(iii) for the industrial preparation of methyl alcohol, formaldehyde and hydrogen cyanide.
(iv) for the preparation of carbon black used in paints, printing inks and automobile tyres.
(v) is used to manufacture urea fertilizer.

8.4 ALKENES

Alkenes have two hydrogen atoms less than the coresponding saturated hydrocarbons. They are also known as Olefins (derived from Latin word olefiant meaning oil forming) because lower members form oily products on treatment with chlorine or bromine. The simplest olefin is C_2H_4, ethene.

Alkene having one double bond are known as mono-enes with general formula C_nH_{2n}. Alkenes containing two double bonds are called dienes.

8.4.1 General Methods of Preparation

1. Dehydrohalogenation of Alkyl Halides

Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenation i.e. elimination of a halogen atom together with a hydrogen atom from adjacent carbon atoms.

$$R-CH_2-\underset{\displaystyle X}{\underset{|}{CH_2}} \xrightarrow{\text{Alc. KOH}} R-CH=CH_2 + KX + H_2O$$

$$\underset{\displaystyle H}{\underset{|}{H_2C}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} + KOH \xrightarrow{\text{Alcohol}} H_2C=CH_2 + KBr + H_2O$$

$$H_3C-CH_2-CH_2-Br + KOH \xrightarrow{\text{Alcohol}} H_3C-CH=CH_2 + KBr + H_2O$$

2. Dehydration of Alcohols

Alcohols when dehydrated in the presence of a catalyst give alkene . The best procedure is to pass vapours of alcohol over heated alumina.

$$\underset{\text{Alcohol}}{R-CH_2-\underset{\displaystyle OH}{\underset{|}{CH_2}}} \xrightarrow[340-450^{\circ}C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2 + H_2O}$$

P_4O_{10}, (conc)H_2SO_4 and H_3PO_4 are also used for dehydration. The ease of dehydration of various alcohols is in the order. Ter. alcohol > Sec. alcohol > Pri .alcohol

Thus

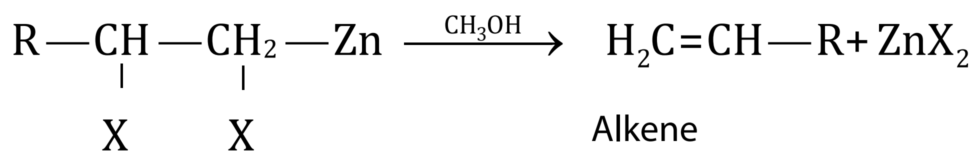
$$\underset{\text{Primary Alcohol}}{R-CH_2-\underset{\displaystyle OH}{\underset{|}{CH_2}}} \xrightarrow[140-170^{\circ}C]{75\%\ H_2SO_4} R-CH=CH_2 + H_2O$$

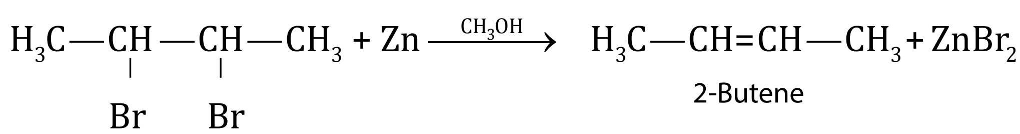
$$\underset{\text{Secondary Alcohol}}{R-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3} \xrightarrow[100^{\circ}C]{60\%\ H_2SO_4} R-CH=CH-CH_3 + H_2O$$

$$\underset{\text{Tertiary Alcohol}}{R-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH} \xrightarrow[85^{\circ}C]{20\%\ H_2SO_4} R-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 + H_2O$$

3. Dehalogenation of Vicinal Dihalides

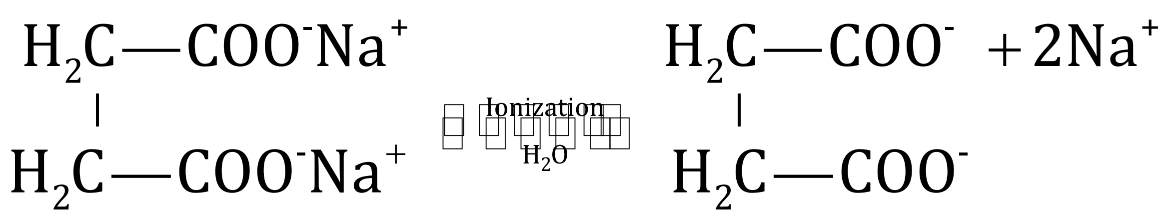
Vicinal dihalides have two halogens on adjacent carbon atoms. Dehalogenation occurs when dihalide is treated with Zinc dust in an anhydrous solvent like methanol or acetic acid.





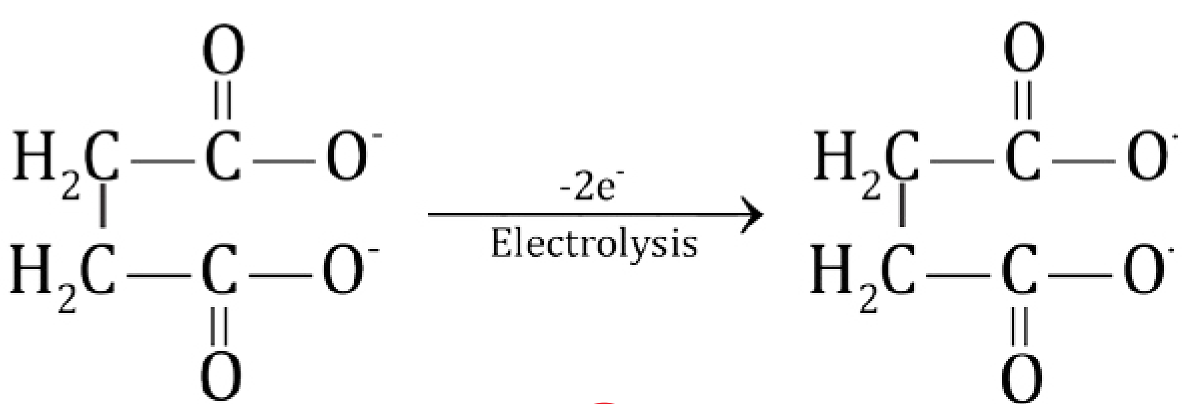
4. Electrolysis of Salts of Dicarboxylic acid (Kolbe's Electrolytic Method)

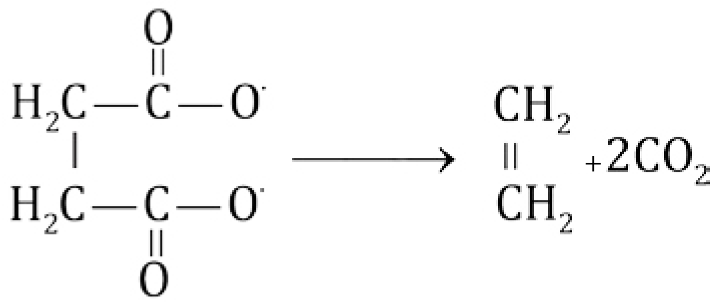
When sodium or potassium salts of the dicarboxylic acid like succinic acid are subjected to electrolysis in an aqueous solution, alkenes are formed.



Disodium Succinate

At Anode





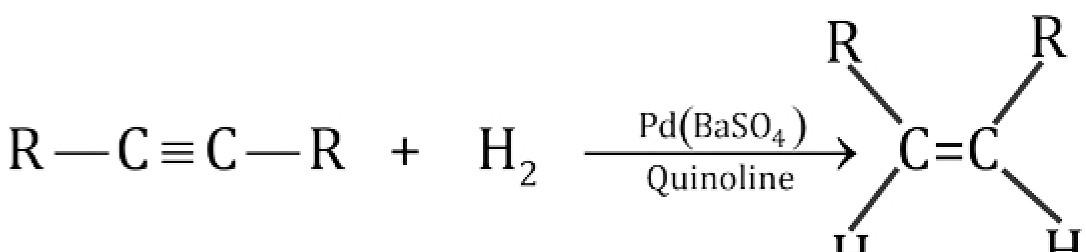
At Cathode

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

$$2Na^+ + 2OH^- \longrightarrow 2NaOH$$

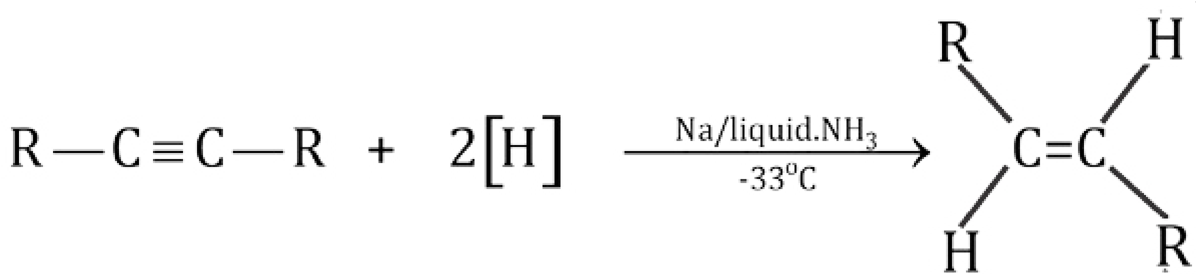
5. Partial Hydrogenation of Alkynes: -

Controlled hydrogenation of alkynes with hydrogen gas in an equimolar ratio over heated catalysts, gives alkenes. The catalyst is finely divided palladium supported on $BaSO_4$ and poisoned by treatment with quinoline (Lindlar's catalyst).



Cis-Alkene

A trans alkene can be obtained by treating an alkyne with Na in liquid NH_3 at -33°C.



trans-Alkene

8.4.2 Physical Properties

1. First three members i.e. ethene, propene and butene are gases at room temperature while C_5 to C_{15} are liquids and the higher members are solids.
2. They are insoluble in water but soluble in alcohol.
3. They have characteristic smell and burn with luminous flame.
4. Unlike alkanes, they show weakly polar properties because of sp^2 hybridization.

8.4.3 Reactivity of a π-bond

In the formation of a π-bond, the partially filled p-orbitals overlap in a parallel fashion. The probability of finding electron is thus away from the line joining the two nuclei. Due to this reason π-electrons are less firmly held between the nuclei. A π-bond is, therefore, a weak bond as compared to a σ-bond. During a reaction it breaks comparatively easily rendering alkenes as reactive group of compounds. Moreover, the loosely held π-electrons are more exposed to attack by the electrophilic reagents. Alkenes, therefore, undergo electrophilic reactions very easily.

8.4.4 Reactions of Alkenes

A. Addition Reactions

1. Addition of Hydrogen (Hydrogenation)

Hydrogenation is a process in which a molecule of hydrogen is added to an alkene in the presence of a catalyst and at moderate pressure (1-5 atm.) to give a saturated compound. The process is known as Catalytic Hydrogenation.

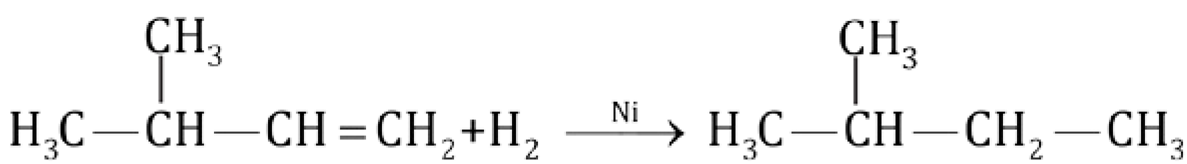
It is a highly exothermic process and the amount of heat evolved when one mole of an alkene is hydrogenated is called Heat of Hydrogenation. The heat of hydrogenation of most alkenes is about 120kJmole^{-1} for each double bond present in a molecule. The catalysts employed are Pt, Pd and Raney nickel.

Raney Nickel

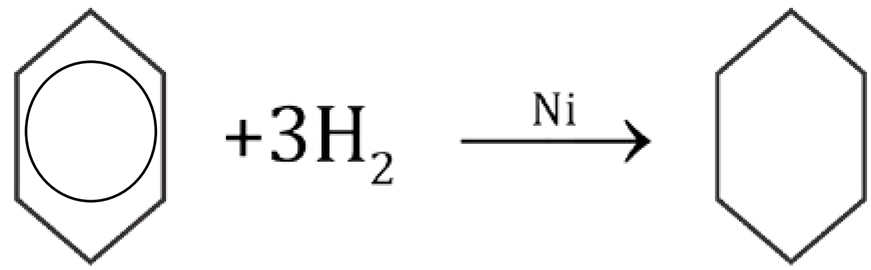
It is prepared by treating a Ni — Al alloy with caustic soda.

$$Ni{-}Al + NaOH + H_2O \longrightarrow Ni + NaAlO_2 + {}^{3}\!/_{2}\,H_2$$

Most alkenes are hydrogenated over Raney nickel at about 100°C and upto 3-atmosphere pressure.



3-Methyl-l-butene iso Bentane



Benzene Cyclohexane

Catalytic hydrogenation of alkenes is used in the laboratory as well as in industry. In industry, it is used for the manufacture of vegetable ghee from vegetable oils. In the laboratory, it is used as a synthetic method as well as an analytical tool, as the reaction is generally quantitative.

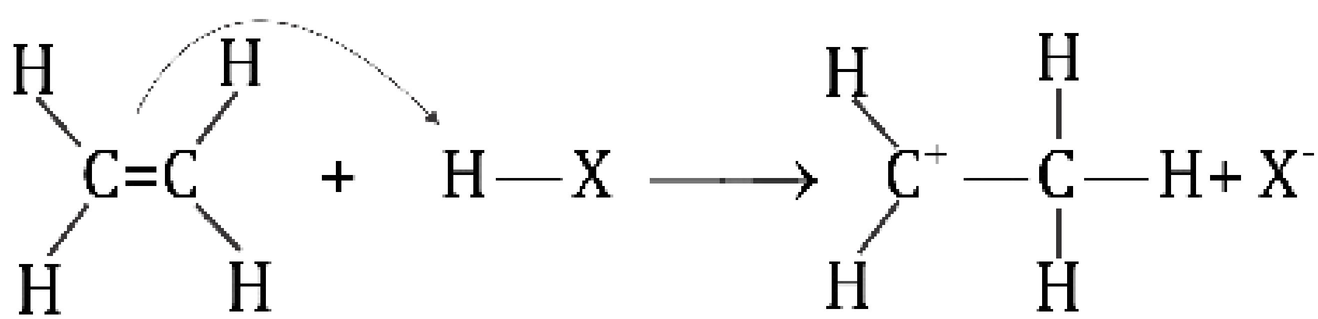
2. Addition of Hydrogen Halides

Alkenes react with dry gaseous hydrogen halides to form alkyl halides. The order of reactivity of halogen aicds is HI > HBr > HC1.

$$R—CH=CH_2 + HX \longrightarrow R—\underset{\substack{|\\X}}{CH}—CH_3$$

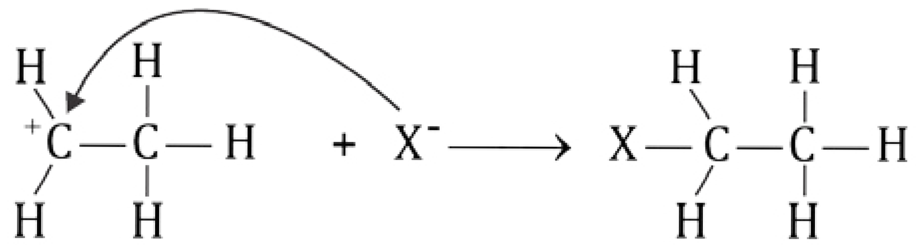
$$H_2C=CH_2 + HCl \longrightarrow H_3C—\underset{\substack{|\\Cl}}{CH_2}$$

The addition of a hydrogen halide to an alkene takes place in two steps. Alkene accepts the proton of hydrogen halide to form a carbocation.

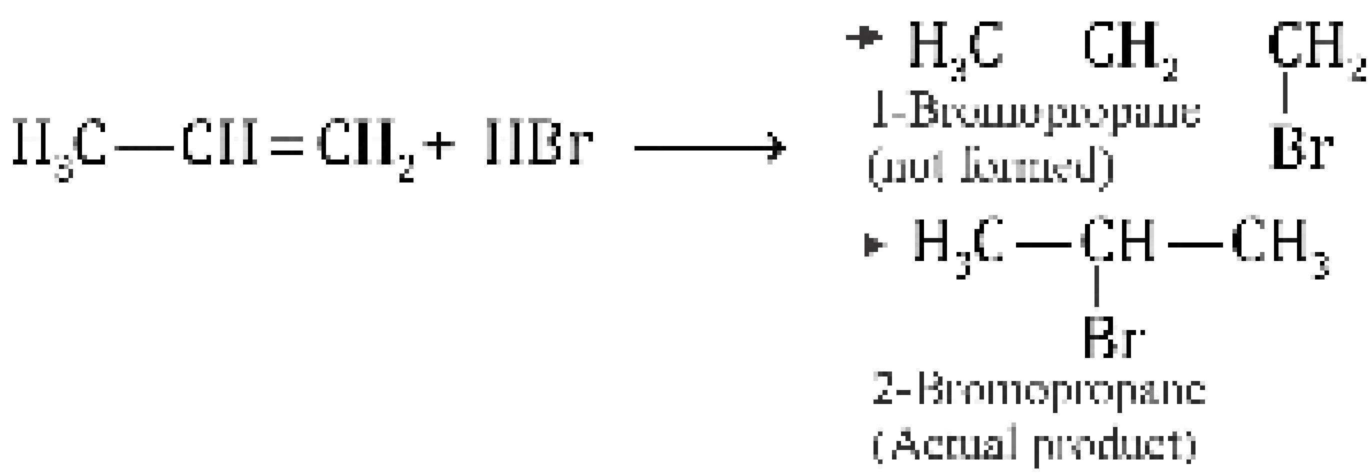


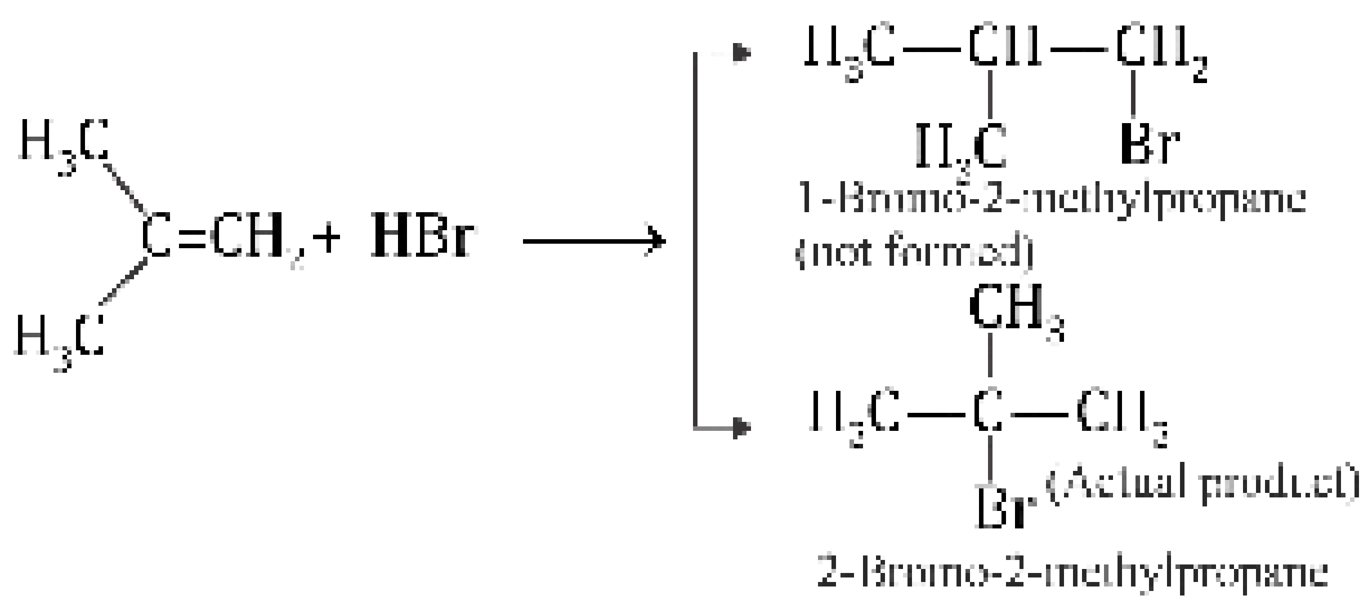
(Carbocation)

The carbocation then reacts with the halide ion.



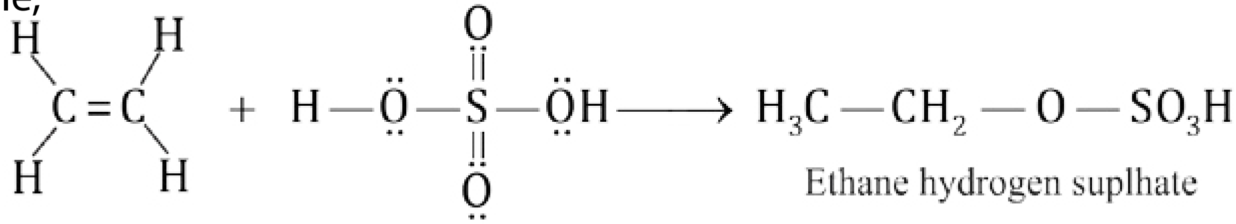
The addition of hydrogen halide over an unsymmetrical alkene is governed by Markownikov's Rule. The rule states that; in the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, constituting the double bond, which has least number of hydrogen atoms.





3. Addition of Sulphuric Acid

When alkenes are treated with cold concentrated sulphuric acid, they are dissolved because they react by addition to form alkyl hydrogen sulphate. For example,

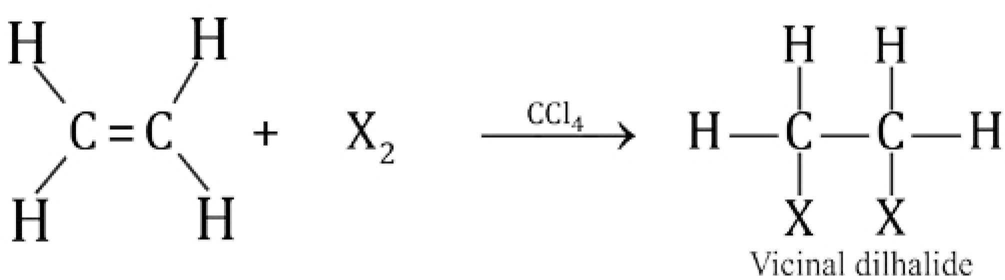


These alkylhydrogen sulphates on boiling with water decompose to give corresponding alcohols. The overall reaction involves the addition of water to an alkene and it is, therefore, called hydration reaction.

$$H_3C—CH_2—O—SO_3H + H_2O \xrightarrow{100^o C} H_3C—CH_2—OH + H_2SO_4$$

4. Addition of Halogens

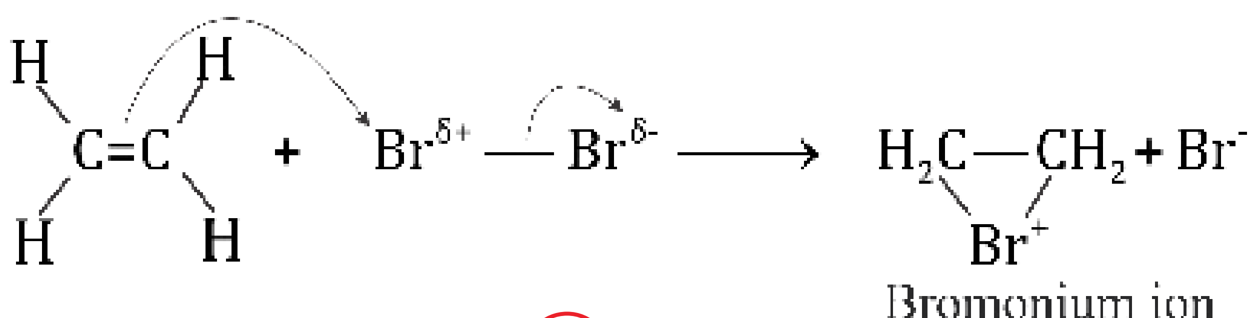
The alkenes on treatment with halogen in an inert solvent like carbon tetrachloride at room temperature give vicinal dihalides or 1,2 dihalogenated products. For example,



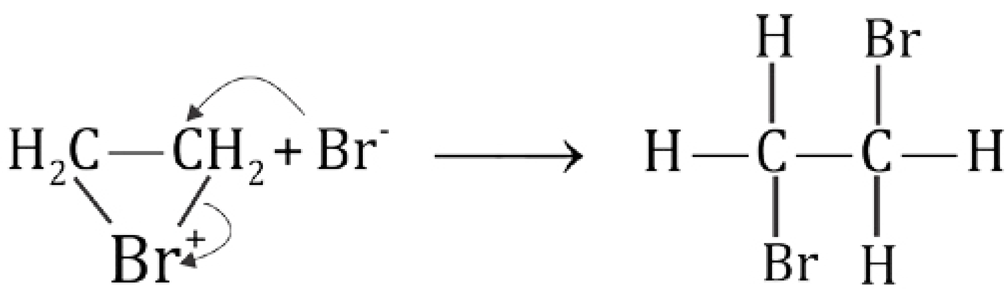
Br_2 and Cl_2 are effective electrophilic reagents. Fluorine is too reactive to control the reaction. Iodine does not react.

Mechanism:

a. A bromine molecule becomes polarized as it approaches the alkene. This polarized bromine molecule transfers a positive bromine atom to the alkene resulting in the formation of a bromonium ion.



b. The nucleophilic bromide ion then attacks on the carbon of the bromonium ion to form vic. dibromide and the colour of bromine is discharged. A trans product is formed.



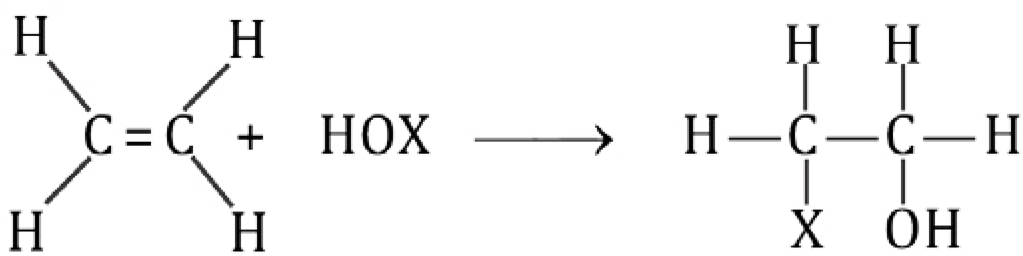
Bromonium ion 1, 2-Dibromoethane

This test is used for the detection of a double bond.

5. Addition of Hypohalous acid (HOX)

If the halogenation of an alkene is carried out in an aqueous solution, haloalcohol is formed called a Halohydrin. In this reaction, molecules of the solvent become reactants too.

$$X_2 + H_2O \longrightarrow HOX + HX$$

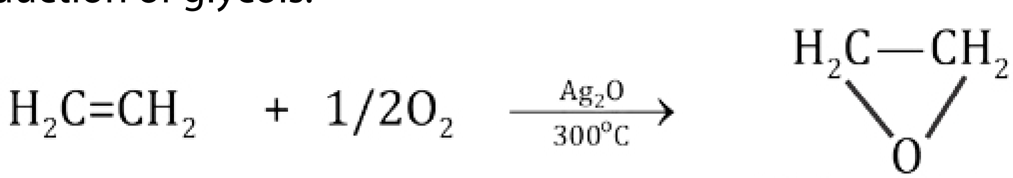


$X_2 = Cl_2$ or Br_2 Halohydrin

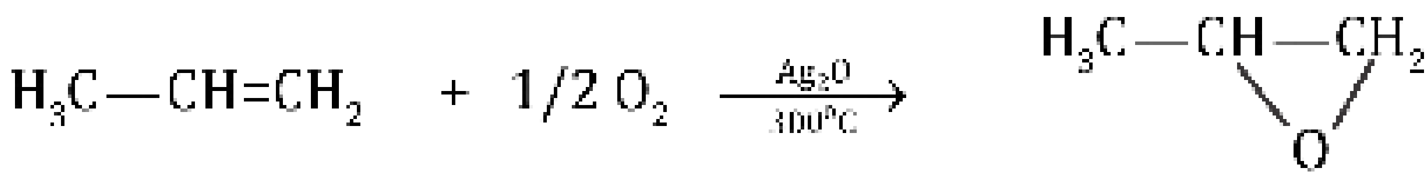
B. OXIDATION REACTIONS

1. Addition of Oxygen

Alkenes when mixed with oxygen or air and passed over a silver oxide catalyst at high temperature and pressure, add an atom of oxygen to form epoxides. Epoxides serve as the starting substances for the industrial production of glycols.



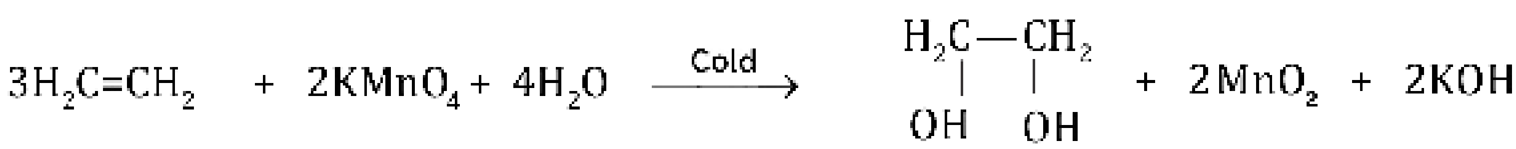
Ethylene oxide or Ethylene epoxide



Propylene oxide

2. Hydroxylation

When alkenes are treated with mild oxidizing reagents like dilute (1%) alkaline $KMn0_4$ solution (Baeyer's Reagent) at low temperature, hydroxylation of duoubie bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of $KMnO_4$ solution is discharged during the reaction. It is also a test for the presence of unsaturation in the molecules. For example,



Ethylene glycol

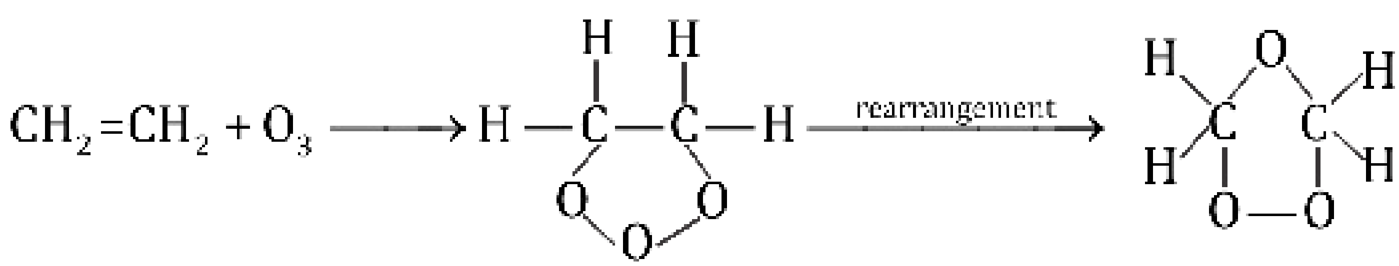
3. Combustion

Alkenes burn in air with luminous flame and produce CO_2 and H_2O vapours. Ethene forms a highly explosive mixture with air or oxygen.

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O + heat$$

4. Ozonolysis

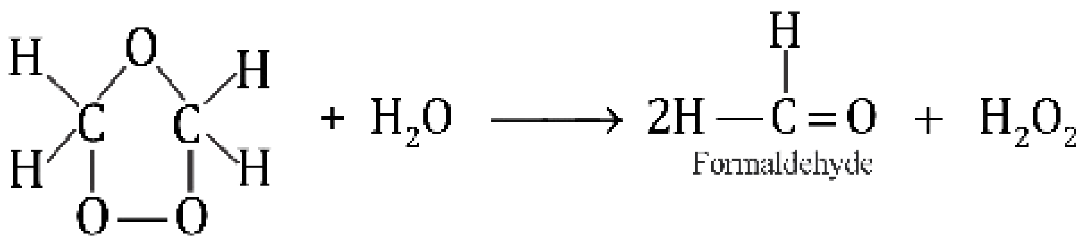
Ozone (O_3) is a highly reactive allotropic form of oxygen. It reacts vigorously with alkenes to form unstable molozonide. It rearranges spontaneously to form an ozonide.



Molozonide unstable

Ozonide

Ozonides are unstable compounds and are reduced directly by treatment with zinc and H_2O. The reduction produces carbonyl compounds (aldehydes or ketones).



$$H_2O_2 + Zn \longrightarrow ZnO + H_2O$$

Ozonolysis is used to locate the position of double bond in an alkene.

C. Polymerization

In this ‘process small organic molecules (monomers) combine together to form larger molecules known as Polymers.Ethene at 400°C and 100 atm pressure, polymerize to polythene or polyethylene.

$$n\ CH_2{=}CH_2 \xrightarrow[\substack{100\text{ atm pressure} \\ \text{traces of } O_2 (0.1\%)}]{400^{\circ}C} \left[CH_2 - CH_2 \right]_n$$

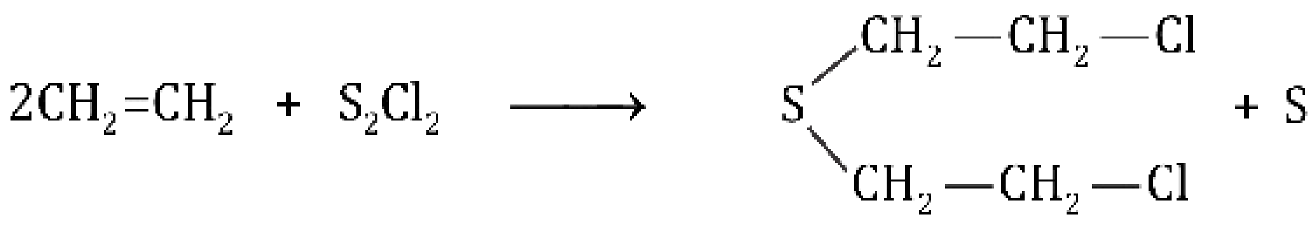
Polyethylene

A good quality polythene is obtained, when ethene is polymerized in the presence of aluminium triethyl $Al(C_2H_5)_3$ and titanium tetrachloride catalysts ($TiCl_4$).

8.4.5 Uses of Ethene:

Ethene is used:

1. for the manufacture of polythene, a plastic material used for making toys, cables, bags, boxes, etc.
2. for artificial ripening of the fruits.
3. as a general anaesthetic.
4. for preparing ‘Mustard gas’ a chemical used in World War I. The name comes from its mustard like odour. It is not a gas, but a high boiling liquid that is dispersed as a mist of tiny droplets. It is a powerful vesicant i.e., causes blisters.



2,2-Dichloro ethyl sulphide (Mustard gas)

5. as a starting material for a large number of chemicals of industrial use such as glycols (antifreeze), ethyl halide, ethyl alcohol, etc.

8.5 ALKYNES

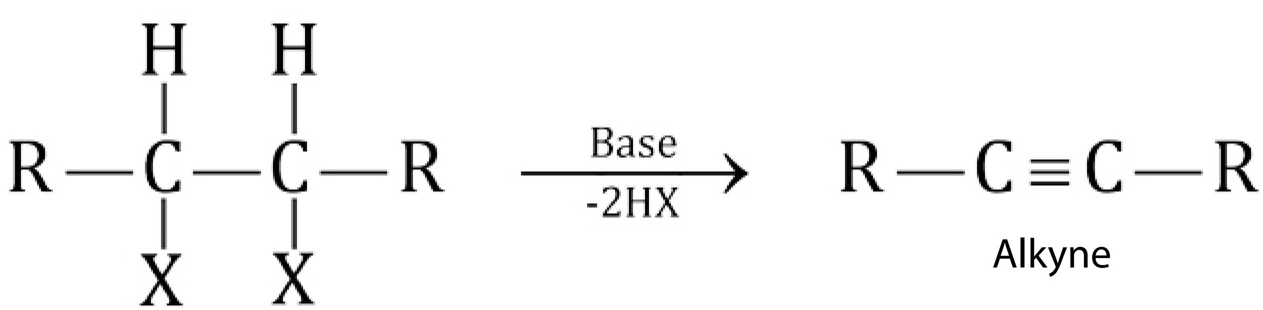
Unsaturated hydrocarbons which contain a triple bond are called Alkynes. They have the general molecular formula C_nH_{2n-2} and contain two hydrogen atoms less than the corresponding alkenes.

The first member of the Alkyne series has the formula C_2H_2 and is known as Ethyne or Acetylene.

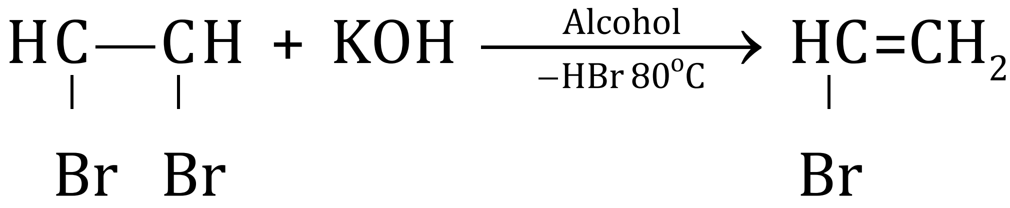
8.5.1 General Methods of Preparation

1. Dehydrohalogenation of Vicinal Dihalides

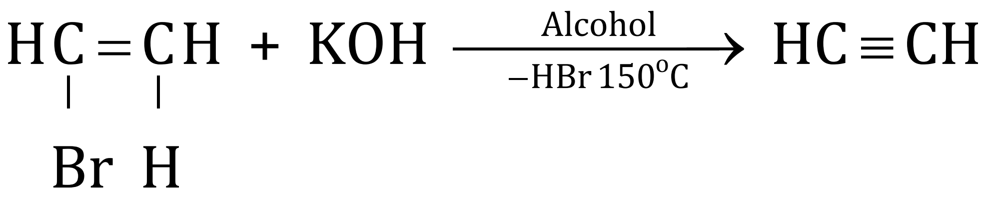
Vicinal dihalide on treatment with a strong base eliminates two molecules of hydrogen halides from two adjacent carbons to give an alkyne.



1,2-Dihalide



1,2-Dibromoethane Vinyl bromide



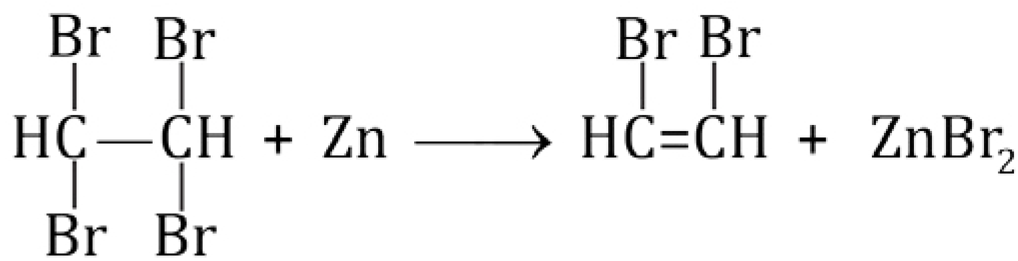
Ethyne

The second molecule of hydrogen halide is removed with great difficulty and requires drastic conditions.

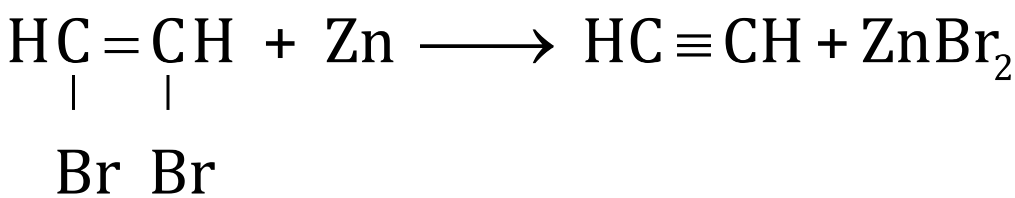
2. DehalogenationofTetrahalides

Tetra haloalkanes on treatment with active metals like Zn, Mg, etc. form alkynes.

(i)

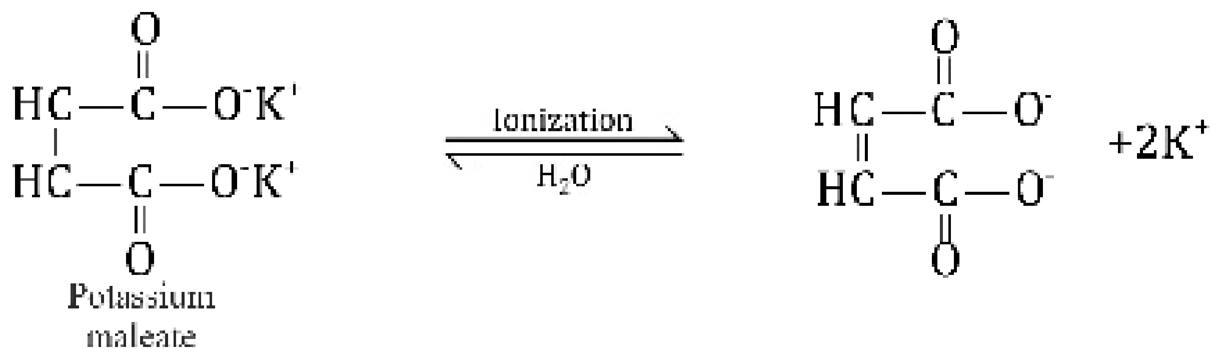


(ii)

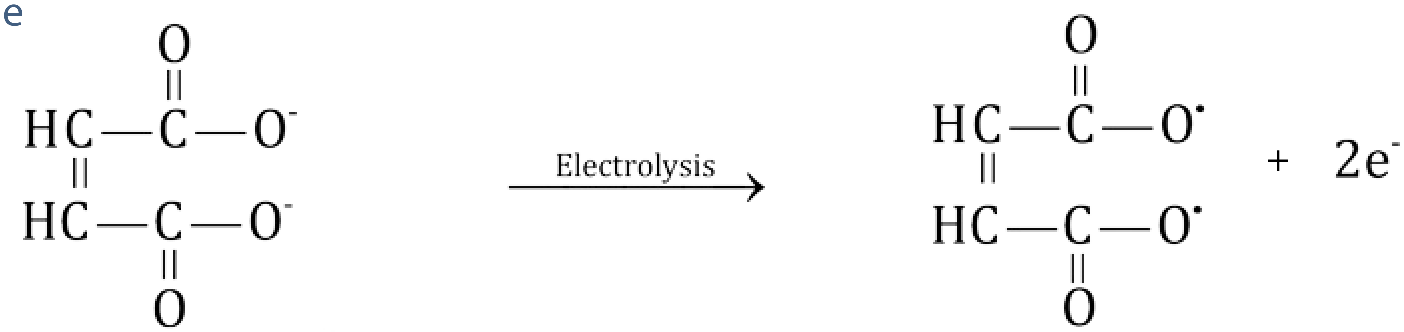


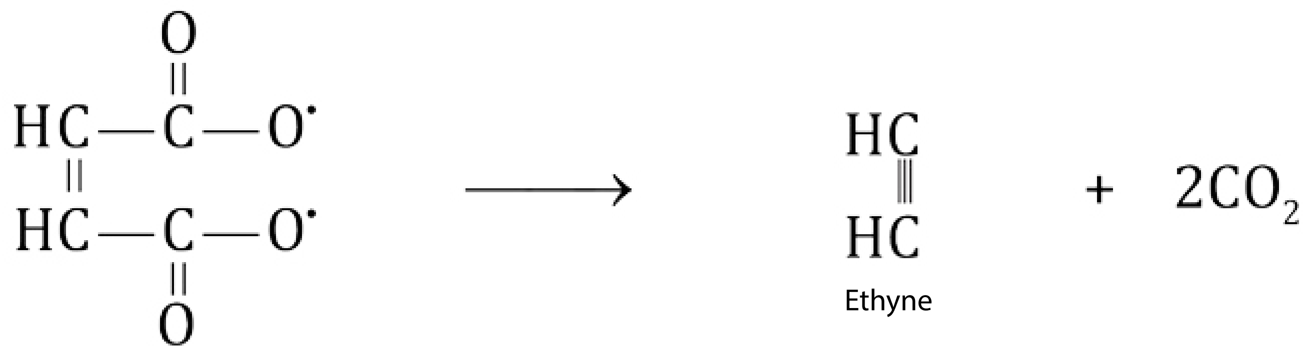
3. Electrolysis of Salts of Unsaturated Dicarboxylic Acids

Kolbe's electrolytic method involves electrolysis of aqueous solution of Na or K salts of unsaturated dicarboxylic acids.



At Anode





At Cathode

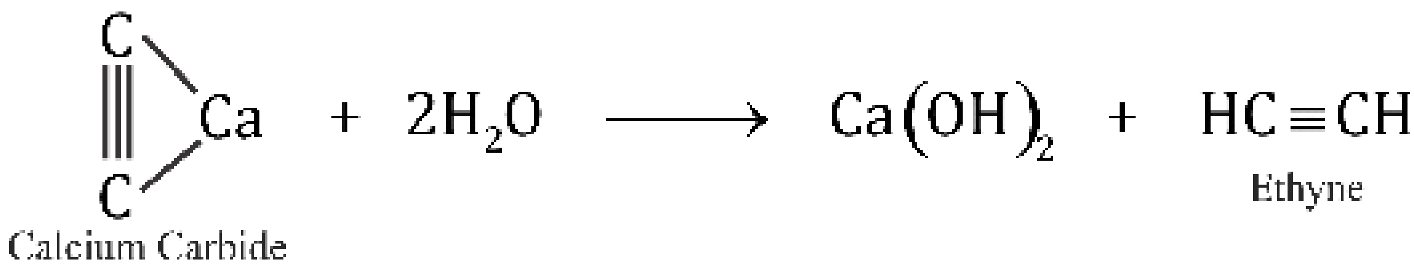
$$2H_2O + 2e^- \longrightarrow 2OH^-$$

$$2K^+ + 2OH^- \longrightarrow 2KOH$$

Industrial Preparation of Ethyne

On industrial scale ethyne is prepared by the reaction of calcium carbide (CaC_2) with water Calcium carbide is prepared by heating lime (CaO) and coke (C) at a very high temperature in an electric furnace.

$$CaO + 3C \xrightarrow{2000^{o}C} CaC_2 + CO$$



8.5.2 Physical Characteristics

1. They are colourless, odourless, except acetylene which has a garlic like odour,
2. The first three members are gases (ethyne, propyne, butyne) at room temperature, The next eight members (C_5 - C_{12}) are liquids and higher members are solids.

3 The melting points, boiling points and densities increase gradually with the increase in molecular masses.
4 They are nonpolar and dissolve readily in solvents like ether, benzene and carbon tetrachloride.

8.5.3 Reactivity of Alkynes

In alkynes, the carbon atoms are held together by a triple bond, a σ-bond and two π-bonds. The electron density between the carbon atoms is very high which draws atoms very close to each other. Electrons in a triple bond are, therefore, less exposed and thus less reactive towards electrophilic reagents.

8.5.4 Reactions

A. Addition Reactions:

Alkynes undergo addition reactions like alkenes but add two molecules of the reagent instead of one.

1. Addition of Hydrogen:

Alkynes react with hydrogen gas in the presence of a suitable catalysts like finely divided Ni, Pt, or Pd. Initially alkenes are formed which then take up another molecule of hydrogen to form an alkane.

$$HC\equiv CH + H_2 \xrightarrow[\text{heat}]{\text{Ni}} H_2C{=}CH_2$$

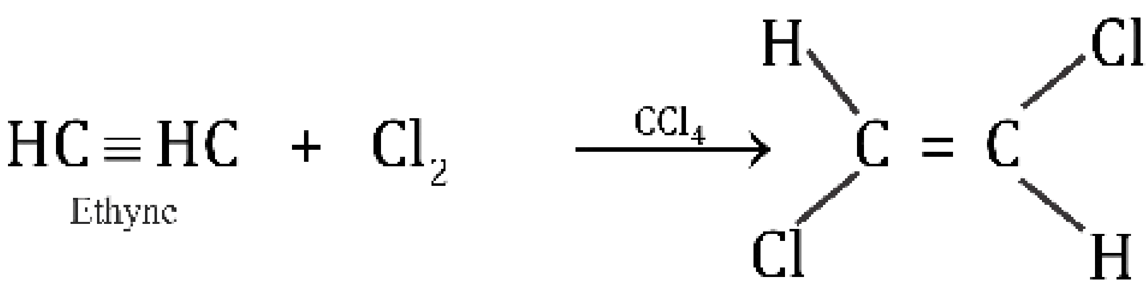
Ethyne Ethene

$$CH_2{=}CH_2 + H_2 \xrightarrow[\text{heat}]{\text{Ni}} H_3C{-}CH_3$$

Ethene Ethene

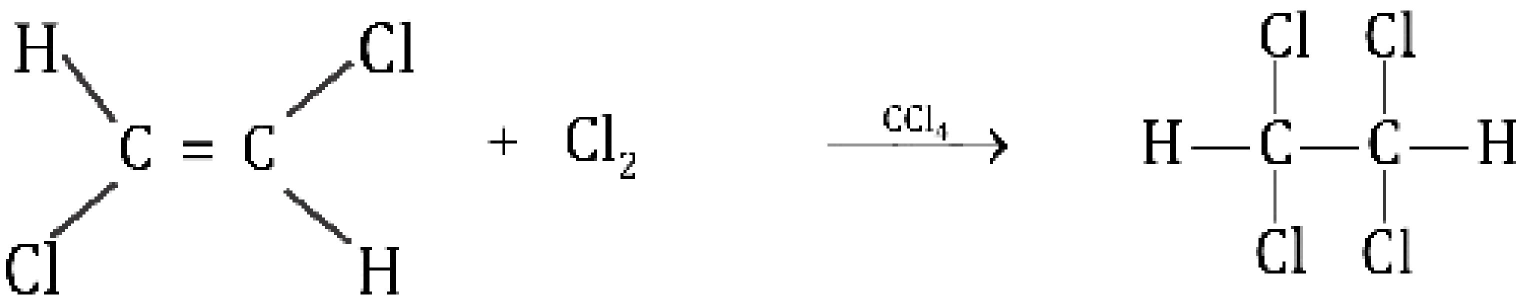
2. Addition of Halogens:

One or two molecules of halogens can be added to alkynes giving dihalides and tetra halides respectively.Chlorine and bromine add readily while iodine reacts rather slowly.



Ethyne

1,2 Dichloroethane

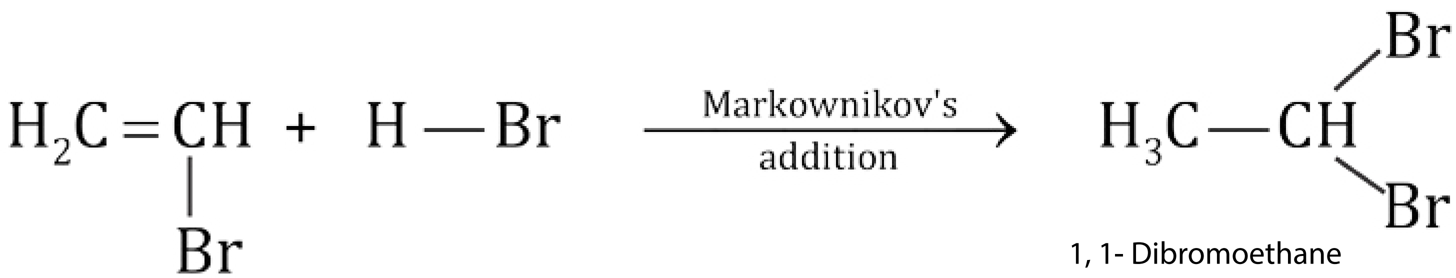


1,1,2,2=Tetracholorethane

3. Addition of Halogen Acids:

Alkynes react with hydrogen chloride and hydrogen bromide to form dihaloalkanes. The reaction occurs in accordance with Markownikov's rule.

$$\underset{\text{Ethyne}}{HC\equiv CH} + H-Br \longrightarrow \underset{\text{Vinyl bromide}}{H_2C=\underset{\substack{|\\ Br}}{CH}}$$



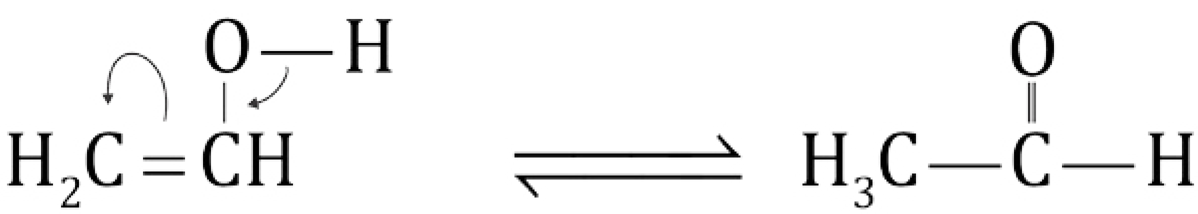
1, 1- Dibromoethane

4. Addition of Water:

Water adds to alkynes in the presence of mercuric sulphate dissolved in sulphuric acid at 75°C. The reaction is important industrially. For example,

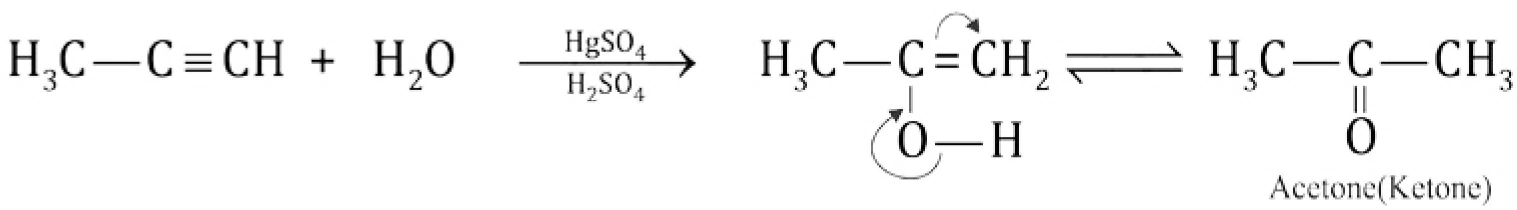
$$HC\equiv CH + H^{ä+}-OH^{ä-} \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{Vinyl alcohol}}{H_2C=CH-O-H}$$

Vinyl alcohol is an unstable enol. The enol has the hydroxy group attached to a doubly bonded carbon atom and isomerises to acetaldehyde.



Acetaldehyde

All other alkynes give ketones.



5. Addition of Ammonia and Hydrogen Cyanide:

NH_3 and HCN react with ethyne in the presence of suitable catalysts, to give nitriles.

$$HC\equiv CH + NH_3 \xrightarrow[300^{\circ}C]{Al_2O_3} H_3C-C\equiv N + H_2$$

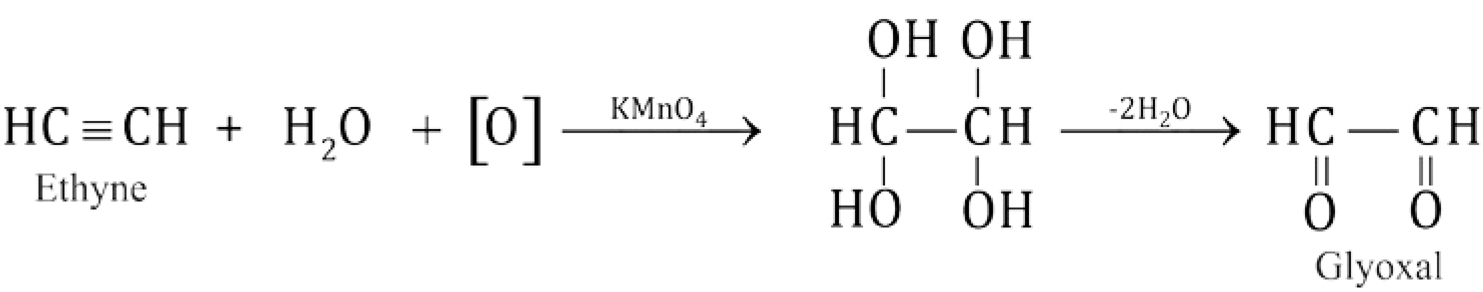
Methyl Nitrile

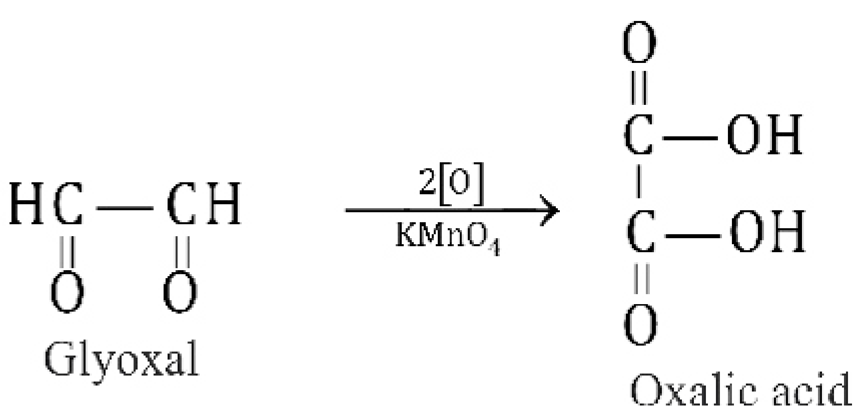
$$HC\equiv CH + HCN \xrightarrow[\Delta]{Cu_2Cl_2/NH_4Cl} CH_2{=}CH-CN$$

Acrylonitrile

B. Oxidation Reactions

1. Ethyne on oxidation with strong alkaline KMnO, gives glyoxal.





2. Combustion:

Alkynes when burnt in air or oxygen produce heat and evolves CO_2 and H_2O. The reaction is highly exothermic for acetylene and the resulting oxyacetylene flame is used for welding and cutting of metals.

$$2HC\equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + \text{heat}$$

C. Polymerization

Alkynes polymerize to give linear or cyclic compounds depending upon the temperature and catalyst used. However, these polymers are different from the polymers of the alkenes as they are usually low molecular weight polymers.

1. Conversion of Acetylene to Divinyl Acetylene

When acetylene is passed through an acidic solution of cuprous chloride and ammonium chloride and then allowed to stand for several hours at room temperature, vinyl acetylene and divinyl acetylene are obtained.

$$HC\equiv CH + HC\equiv CH \xrightarrow{Cu_2Cl_2,NH_4Cl} H_2C=CH-C\equiv CH$$

Vinyl acetylene
(1- Buten-3-yne

$$H_2C=CH-C\equiv CH+HC\equiv CH \xrightarrow{Cu_2Cl_2,NH_4Cl} H_2C=CH-C\equiv C-CH=CH_2$$

Divinyl acetylene
(l,5-Hexdiene-3-yne)

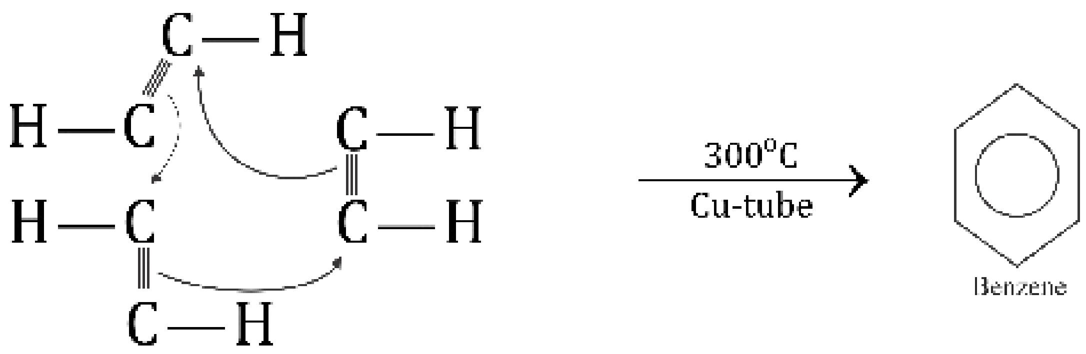
If HCl is added to vinyl acetylene, chloroprene is obtained which readily polymerize to neoprene, used as synthetic rubber.

$$\underset{\text{Vinyl acetylene}}{H_2C=CH-C\equiv CH}+(\text{conc.})HCl \xrightarrow{Cu_2Cl_2,NH_4Cl} \underset{\text{Chloroprene}}{H_2C=CH-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2}$$

$$\text{Chloroprene} \xrightarrow{\text{Polymerization}} \text{Neoprene (synthetic rubber)}$$

2. Conversion of Acetylene to Benzene

When acetylene is passed through a copper tube at 300°C, it polymerizes to benzene.



D. Acidic Nature of Alkynes

In ethyne and other terminal alkynes like propyne, the hydrogen atom is bonded to the carbon atom with sp-s overlap. An 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 atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.

$$H-C\equiv C^{\text{ä}-}-H^{\text{ä}+}$$

1. When 1-alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium .alkynides or acetylides are obtained.

$$R-C\equiv CH + NaNH_2 \xrightarrow{\text{liq } NH_3} R-C\equiv C^-Na^+ + NH_3$$

$$HC\equiv CH + 2Na \longrightarrow Na^+C^-\equiv C^-Na^+ + H_2$$

Sodium acetylide

Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature. Acetylides of copper and silver are obtained by passing acetylene in the ammoniacal solution of cuprous chloride and silver nitrate respectively.

$$HC \equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\substack{\text{Dicopperacetylide} \\ \text{(Reddish brown ppt.)}}}{CuC \equiv CCu} + 2NH_4Cl + 2H_2O$$

$$HC \equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\substack{\text{Disilver acetylide} \\ \text{(white ppt.)}}}{AgC \equiv CAg} + 2NH_4NO_3 + 2H_2O$$

Silver and copper acetylides react with acids to regenerate alkynes.

$$AgC \equiv CAg + H_2SO_4(dil.) \longrightarrow HC \equiv CH + Ag_2SO_4$$

$$AgC \equiv CAg + 2HNO_3(dil.) \longrightarrow HC \equiv CH + 2AgNO_3$$

These alkynides are used for the preparation, purification, separation, and identification of alkynes.

8.5.5 Uses of Ethyne

Ethyne is used:

1. in oxyacetylene torch which is in turn used for welding and cutting metals.
2. for the preparation of alcohols, acetic acid and acetaldehyde.
3. for the manufacture of polymers like PVC, polyvinyl acetate, polyvinyl ethers, orlon and neoprene rubber.
4. to prepare acetylene tetrachloride a solvent for varnishes, resins, and rubber.
5. for ripening of fruits.

8.5.6 Comparison of Reactivities of Alkanes, Alkenes and Alkynes

The general decreasing reactivity order of alkanes, alkenes and alkynes is as follows:

Alkenes > Alkynes > Alkanes

It has already been explained that a π-bond in alkenes is not only weak but its electrons are more exposed to an attack by an electrophilic reagent. Both these facts make the alkenes a very reactive class of compounds.

Alkynes although contain two π-bonds are less reactive than alkenes towards electrophilic reagents. This is because the bond distance between the two triple bonded carbon atoms is very short and hence the π -electrons are not available to be attacked by electrophilic reagents.Alkynes are, however, more reactive than alkenes towards nucleophilic reagents.

KEYPOINTS

1. Hydrocarbons are made up of carbon and hydrogen only. Saturated hydrocarbons are called alkanes. They do not contain functional groups.
2. Alkanes react with halogens by a free radical mechanism to give haloalkanes. Then mechanism consists of three steps, initiation, propagation and termination.
3. Alkenes are unsaturated hydrocarbons with at least one C=C. The double bond is composed of a σ and a π bond. Carbon atoms in alkenes are sp^2 hybridized.
4. Alkenes are very reactive compounds. They undergo electrophilic reactions very easily.
5. Addition of unsymmetrical reagent to an unsymmetrical alkene takes place in accordance with the Markownikov's rule.
6. Alkenes can be very easily oxidized with cold $KMnO_4$ solution, O_2 or ozone. With ozone both the bonds between carbon atoms are cleaved.
7. Hydrocarbons containing a triple bond are known as alkynes or acetylenes.
8. Alkynes undergo addition reactions and two molecules of a reagent are added in it.
9. Ethyne and other terminal alkynes contain a weakly acidic hydrogen and they react with ammoniacal cuprous chloride and ammoniacal silver nitrate to give acetylides
10. The decreasing reactivity order of alkanes, alkenes and alkynes are as follows:

$$\text{Alkenes} > \text{Alkynes} > \text{Alkanes}$$

EXERCISE

Q.1. Fill in the blanks.

1. Ozone reacts with ethene to form____________ .
2. Lindlar' s catalyst is used for____________ of alkynes.
3. Divinyl acetylene is a _______________ acetylene.
4. Vicinal dihalides have two halogens on__________carbon atoms.
5. Ethyne is acidic in character because of___________ hybridization.
6. Halohydrins are formed due to addition of___________ in ethene.
7. Ethylene glycol is produced when___________ reacts with cold alkaline $KMnO_4$ solution.
8. Mustard gas is a high boiling ______________ .
9. Ethyne has______________ like odour.
10. Ethyne is obtained by the reaction of_________ with calcium carbide.

Q.2. Indicate True or False.

1. Addition of HX to unsymmetriacal alkanes takes place according to Markownikov's rule.
2. Methane reacts with bromine water and its colour is discharged.
3. Mustard gas is a blistering agent.
4. Methane is also called marsh gas.
5. Ethyne is a saturated compound.
6. Baeyer's reagent is used to locate a double bond in an alkene.
7. Alkanes usually undergo substitution reactions.
8. Benzene is a polymer of ethene.
9. Acrylonitrile can be obtained from ethyne.
10. Ethyne is more reactive towards electrophilic reagents than ethene.

Q. 3. Multiple choice questions. Encircle the correct answer.

i) Preparation of vegetable ghee involves

(a) Halogenation (b) Hydrogenation

(c) Hydroxylation (d) Dehydrogenation

ii) Formula of chloroform is:

(a) CH_3Cl (b) CCl_4 (c) CH_2Cl_2 (d) $CHCl_3$

iii) The presence of a double bond in a compound is the sign of

(a) Saturation (b) Unsaturation (c) Substitution (d) None

iv) Vinyl acetylene combines with HCl to form

(a) Polyacetylene (b) Benzene

(c) Chloroprene (d) Divinyl acetylene

v) The addition of unsymmetrical reagent to an unsymmetrical alkene is in accordance with the rule

(a) Hund's rule (b) Markownikov's rule

(c) Pauli's Exclusion Principle (d) Aufbau Principle

vi) Synthetic rubber is made by polymerization of

(a) Chloroform (b) Acetylene

(c) Divinylacetylene (d) Chloroprene

vii) β-β'- dichloroethyl sulphide is commonly known as

(a) Mustard gas (b) Laughing gas

(b) Phosgene gas (d) Bio-gas

ix) When methane reacts with Cl_2 in the presence of diffused sunlight the products obtained are:

(a) Chloroform only (b) Carbon tetrachloride only

(c) Chloromethane and dichloromethane (d) Mixture of a, b, c

x) Which one of the following gases is used for artificial ripening of fruits.

(a) Ethene (b) Ethyne (c) Methane (d) Propane

Q. 4. Write the structural formula for each of the following compounds

,

i) 2-Methylpropane. ii) Neopentane.
iii) 3-Ethylpentane. iv) 4-Ethyl-3,4-dimethylheptane.
v) 2,2,3,4-Tetramethylpentane vi) 4-iso-Propylheptane.
vii) 2,2-Dimethylbutane. viii) 2,2-Dimethylpropane.

Q. 5. Write down names of the following compounds according to IUPAC-system.

(i) $H_3C-CH_2-\underset{\displaystyle |\atop \displaystyle H_2C-CH_3}{CH}-CH_2CH_3$

(ii) $(CH_3)_3C-CH_2-C(CH_3)_3$

(iii) $H_3C-\underset{\displaystyle |\atop \displaystyle CH_3}{CH}-CH_2-CH(CH_3)_2$ (the terminal CH carries two CH_3 groups)

(iv) $(CH_3)_2CH-\underset{\displaystyle |\atop \displaystyle CH_3}{CH}-CH(CH_3)_2$

(v) $CH_3CH_2C(CH_3)_2CH(CH_2CH_3)CH_3$

(vi) $(CH_3CH_2)_3CH$

(vii) $CH_3C(CH_3)_2(CH_2)_2CH_3$

(viii) $(C_6H_5)_3CH$

Q. 6. What are the rules for naming alkanes? Explain with suitable examples.

Q. 7. (a) Write down the structural formulas for all the isomeric hexanes and name them according to IUPAC system

(b) The following names are incorrect. Give the correct IUPAC names,

i) 4-Methylpentane ii) 3,5,5-Trimethylhexane
iii) 2-Methyl-3-Ethylbutane

Q.8. (a) Explain why alkanes are less reactive than alkenes? What is the effect of branching on the melting point of alkanes ?

(b) Three different alkanes yield 2-methylbutane when they are hydrogenated in the presence of a metal catalyst. Give their structures and write equations for the reactions involved.

Q.9. (a) Out line the methods available for the preparation of alkanes.

(b) How will you bring about the following conversions?

i) Methane to ethane. ii) Ethane to methane,

iii) Acetic acid to ethane. iv) Methane to nitromethane.

Q.10. (a) What is meant by octane number? Why does a high octane fuel has a less tendency to knock in an automobile engine?

(b) Explain free radical mechanism for the reaction of chlorine with methane in the presence of sunlight .

Q. 11. (a) Write structural formulas for each of the following compounds.

i) Isobutylene ii) 2,3,4,4-Tetramethyl-2-pentene

iii) 2 ,5-Heptadiene iv) 4,5-Dimethyl-2-hexene

v) Vinylacetylene vi) 1,3-Pentadiene

vii) 1-Butyne viii) 3-n-Propyl-1, 4-pentadiene

ix) Vinyl bromide x) But-1 -en.3 -yne

xi) 4-Methyl-2-pentyne xii) Isopentane

(b) Name the following compounds by IUPAC system.

(i) $H_3C—CH=CH(CH_2)_2CH_3$

(ii) $(CH_3)_2C=CH_2$

(iii) $CH_3—CH_2—CH_2—C(CH(CH_3)_2)=CH_2$

$$\begin{array}{l} CH_3—CH_2—CH_2—\overset{}{C}=CH_2 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad CH(CH_3)_2 \end{array}$$

(iv) $CH_2=CH—CH=CH_2$

(v)

$$\begin{array}{l} CH_2=C—CH_2CH_2CH_3 \\ \qquad\quad | \\ \qquad\ C_2H_5 \end{array}$$

(vi) $CH\equiv C—CH_3$

(vii) $CH_3—C\equiv C—CH_3$

(viii) $CH_2=CH—C\equiv C—CH=CH_2$

(ix) $CH\equiv C—CH=CH—C\equiv CH$

(x) $CH_2=CH—C\equiv CH$

Q. 12. (a) Describe different methods for the preparation of alkenes. How would you establish that ethylene contains a double bond?

(b) Give structure formulas of the alkenes expected to form by the dehydrohalogenation of the following compounds with a strong base:

i) 1 -Chloropentane ii) 2-C hloro-3-methy lbutane

iii) l-Chloro-2,2-dimethyl propane.

Q. 13. (a) Write down chemical equations for the preparation of propene from the following compounds.

i) $CH_3 — CH_2 — CH_2 — OH$ ii) $CH_3 — C = CH$

iii) iso-Propyl chloride

(b) Write skeleton formula showing only the arrangement of carbon atoms for all the possible alkenes of the molecular formula C_5H_{10}.

Q. 14. (a) How may ethene be converted into ethyl alcohol?

(b) Starting from ethene, outline the reactions for the preparation of following compounds.

i) 1,2-Dibromoethane ii) Ethyne iii) Ethane

iv) Ethylene glycol

(c) How will you bring about the following conversions:

i) 1-Butene to 1-Butyne ii) 1-Propanol to $CH_3—CH—CH_2Cl$

Q. 15. Show by means of chemical equations how the following cycle of changes may be affected.

$$\text{Ethane} \longrightarrow \text{Ethene} \longrightarrow \text{Ethyne} \longrightarrow \text{Ethane}$$

Q. 16. Write down structural formulas for the products that are formed when 1-butene will react with the following reagents:

i) H_2, Pt ii) Br_2 in CCl_4
iii) Cold dil. $KMnO_4$\OH iv) HBr
v) O_2 in the presence of Ag vi) HOCl
vii) dil. H_2SO_4

Q. 17. In the following reactions, identify each lettered product.

i) $$\text{Ethyl alcohol} \xrightarrow{\text{conc.}H_2SO_4} A \xrightarrow{Br_2} B \xrightarrow[\text{KOH}]{\text{alcoholic}} C$$

ii) $$\text{Propene} \xrightarrow{Br_2} D \xrightarrow[\text{KOH}]{\text{alcoholic}} E \xrightarrow{\text{HCN}} F$$

Q.18. After an ozonolysis experiment, the only product obtained was acetaldehyde CH_3CHO. Can you guess the structural formula of this compound.

Q. 19. (a) The addition of sulphuric acid to an alkene obeys Markownikov's rule. Predict the structures of the alcohols obtained by the addition of the acid to the following compounds.
i) Propene ii) 1-Butene iii) 2-Butene
(b) Predict the most likely product of the addition of hydrogen chloride to 2-methyl-2-butene. Explain the formation of this product.

Q. 20. Why are some hydrocarbons called saturated and others unsaturated? What type of reactions are characteristics of them?

Q.21. (a) Describe methods for the preparation of Ethyne.
(b) How does ethyne react with:
i) Hydrogen ii) Halogen acid
iii) Alkaline $KMnO_4$ iv) 10% H_2SO_4 in the presence of $HgSO_4$.
v) Ammonical cuprous chloride
(c) Mention some important uses of methane, ethene and ethyne.

Q.22 . Describe how you could distinguish ethane, ethene and ethyne from one another by means of chemical reactions.

Q.23. (a) How will you synthesize the following compounds starting from ethyne.

i) Acetaldehyde ii) Benzene
iii) Chloroprene iv) Glyoxal
v) Oxalicacid vi) Acrylonitrile
vii) Ethane viii) Methyl nitrile
(b) Write a note on the acidity of ethyne.

Q. 24. (a) Compare the reactivity of ethane, ethene and ethyne.
(b) Compare the physical properties ot alkanes, alkenes and alkynes.

Q. 25. How does propyne react with the following reagents.
(a) $AgNO_3/NH_4OH$
(b) Cu_2Cl_2/NH_4OH
(c) $H_2O/H_2SO_4/HgSO_4$

Q. 26. A compound has a molecular formula C_4H_6, when it is treated with excess hydrogen in the presence of Ni-catalyst, a new compound C_4H_{10} is formed.When C_4H_6 is treated with ammoniacal silver nitrate a white precipitate is formed. What is the structural formula of the given compound.

Q.21. (a) Identify A and B.

$$CH_3CH_2CH_2OH \xrightarrow{PCl_5} A \xrightarrow{Na/Ether} B$$

(b) Give the general mechanism of electrophilic addition reactions of alkenes.

CHAPTER

9

AROMATIC HYDROCARBONS

In This Chapter You Will Learn

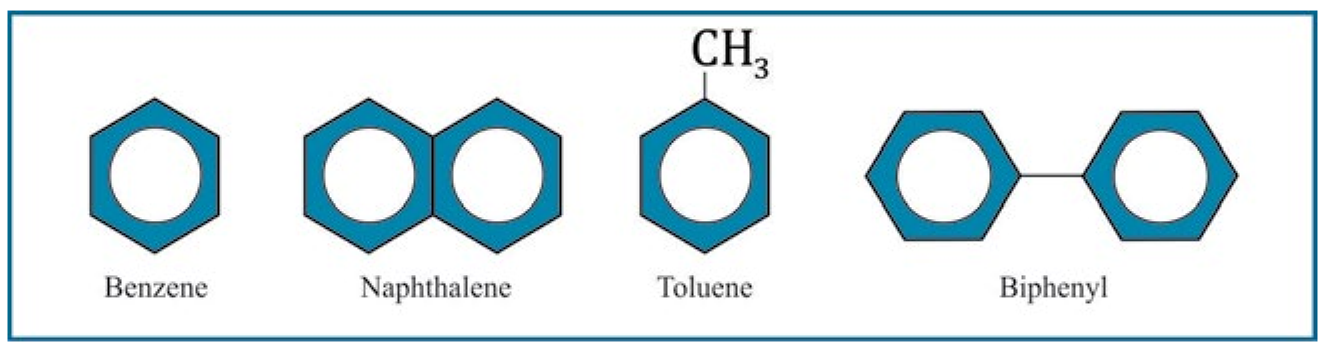
1. To name simple aromatic hydrocarbons, and their derivatives.
2. The Kekule and resonance approaches to explain the structure and stability of benzene.
3. About the preparation of benzene.
4. About the electrophilic substitution, oxidation and addition reactions of benzene.
5. About the isomerism which arises when a second substituent enters the ring.
6. How does the presence of a group alters the reactivity of benzene ring towards electrophilic substitution reactions.
7. The comparison of reactivities of alkanes, alkenes and benzene.

9.1 INTRODUCTION

The term aromatic was derived from the Greek word 'aroma' meaning "fragrant" and was used in Organic Chemistry for a special class of compounds. These compounds have a low hydrogen to carbon ratio in their molecular formula and have a characteristic odour. However, it was soon realized that many aromatic compounds are odourless whereas many others are fragrant though they are not aromatic.

Further, when aromatic compounds of higher molecular mass were subjected to various methods of degradation, they often produced benzene or derivatives of benzene. It was observed that almost all the aromatic compounds have a six carbon unit in their molecules like benzene. Hence, benzene was recognized as the simplest and the parent member of this class of compounds.

So aromatic hydrocarbons include benzene and all those compounds that are structurally related to benzene.



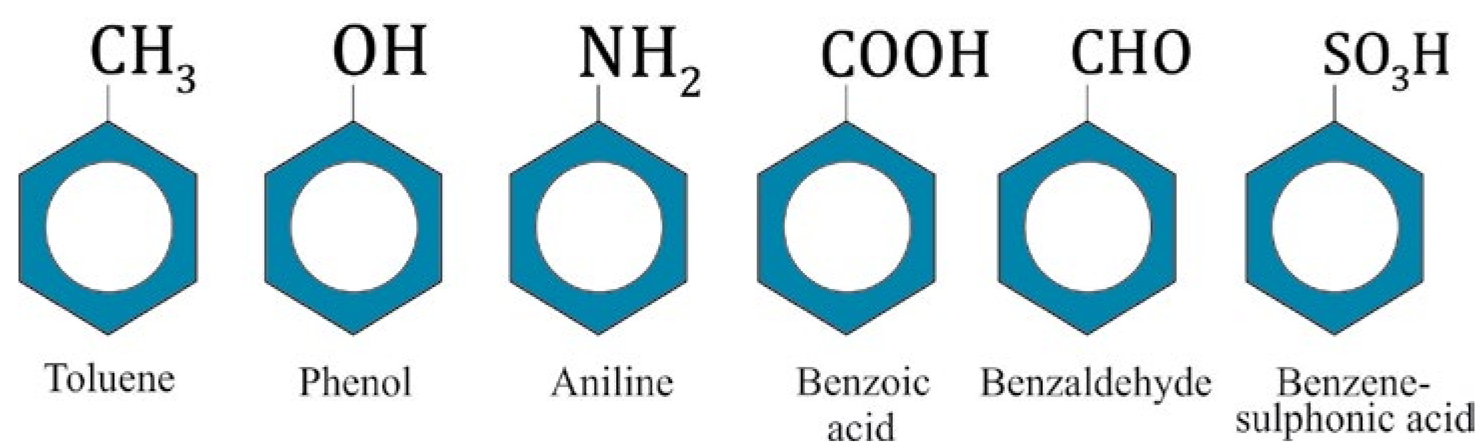
Animation 9.1 : Polycyclic aromatic hydrocarbn
Source & Credit : Qchitool

It appears from the definition of aromatic hydrocarbons that any study of this class of compounds must begin with the study of benzene. Benzene has characteristic structural features. It has a regular planar hexagonal structure. On the basis of the number of benzene rings aromatic hydrocarbons can be categorized into following classes.

a. Monocyclic Aromatic Hydrocarbons and their derivatives
b. Polycyclic Aromatic Hydrocarbons

a. Monocyclic Aromatic Hydrocarbons and their Derivatives

Aromatic hydrocarbons containing one benzene ring in their molecules are called Monocyclic Aromatic Hydrocarbons, e.g. benzene and its derivatives.



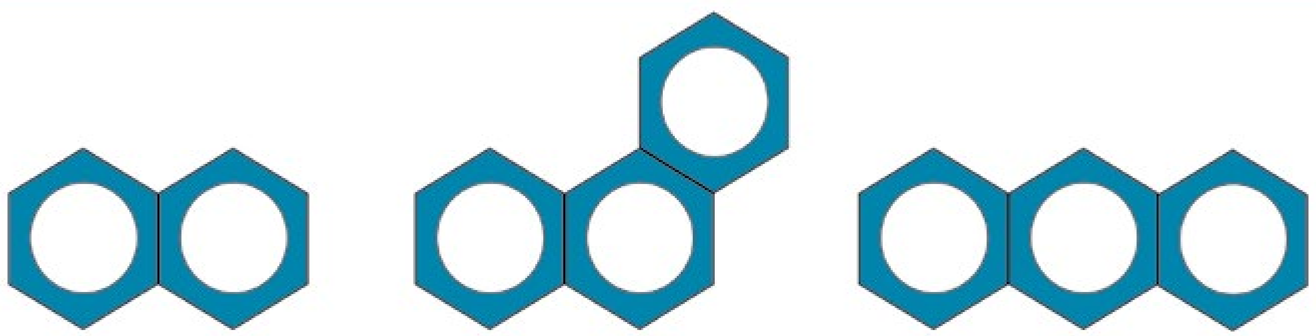
b. Polycyclic Aromatic Hydrocarbons

Aromatic hydrocarbons containing two or more benzene rings in their molecules are called Polycyclic Aromatic Hydrocarbons. They may be divided into two main classes.

(i) Those in which benzene rings are isolated, e.g. bi phenyl,diphenylmethane, etc.

Biphenyl Diphenylmethane

(ii) Those in which the benzene rings are fused together at ortho positions so that the adjacent rings have a common carbon to carbon bonds, e.g. naphthalene, phenanthrene and anthracene



Naphthalene Phenanthrene Anthracene

Animation 9.2 : Larger cyclic aromatic hydrocarbons
Source & Credit : sandia

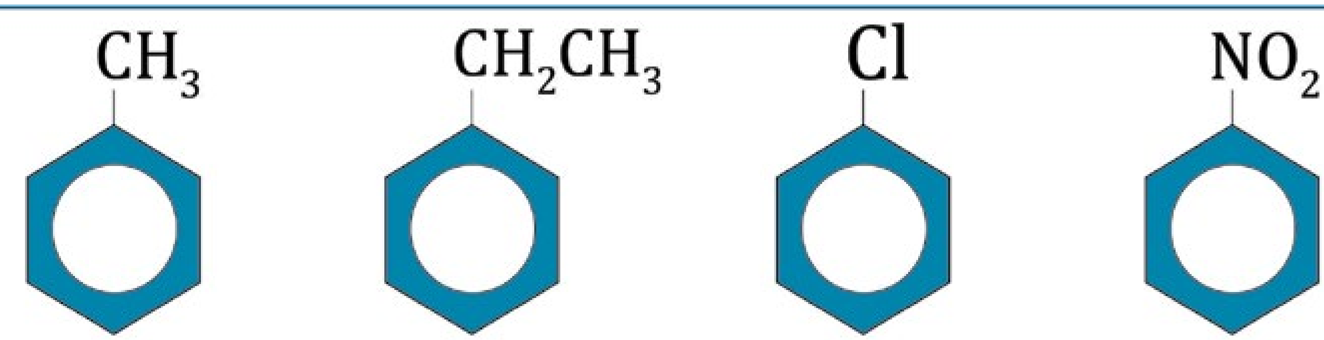
9.2 NOMENCLATURE

(Monocyclic Aromatic Hydrocarbons and their Derivatives)

The nomenclature of the aromatic hydrocarbons is much more complex than that of aliphatic hydrocarbons. The system used for naming benzene and its derivatives generally depends on the number of substituents on the benzene ring.

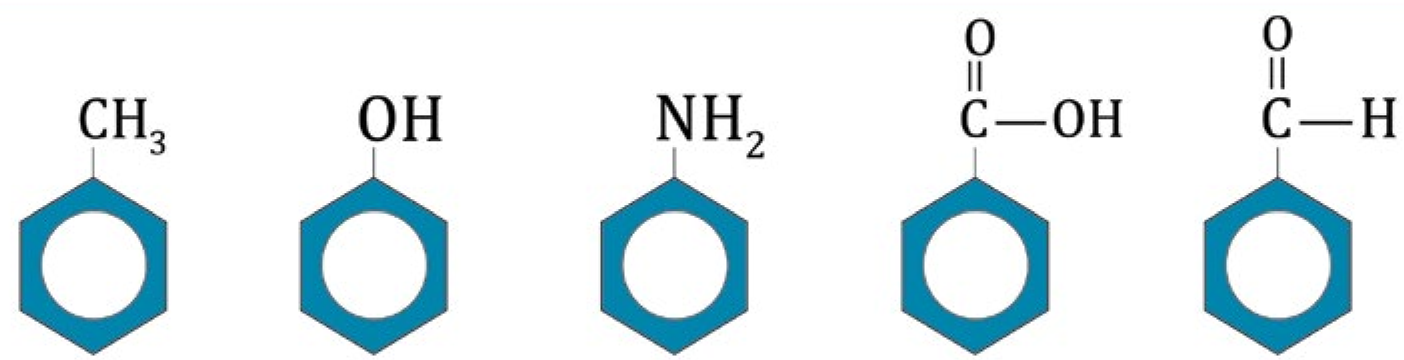
Some important rules of naming are given below.

1. Mono-substituted benzene derivatives are named by prefixing benzene with the name of the substituent. The whole name is written as one word, e.g.



Methylbenzene Ethylbenzene Chlorobenzene Nitrobenzene

2. There are certain monosubstituted benzene derivatives which are given the special names, like methylbenzene as toluene, hydroxybenzene as phenol etc.

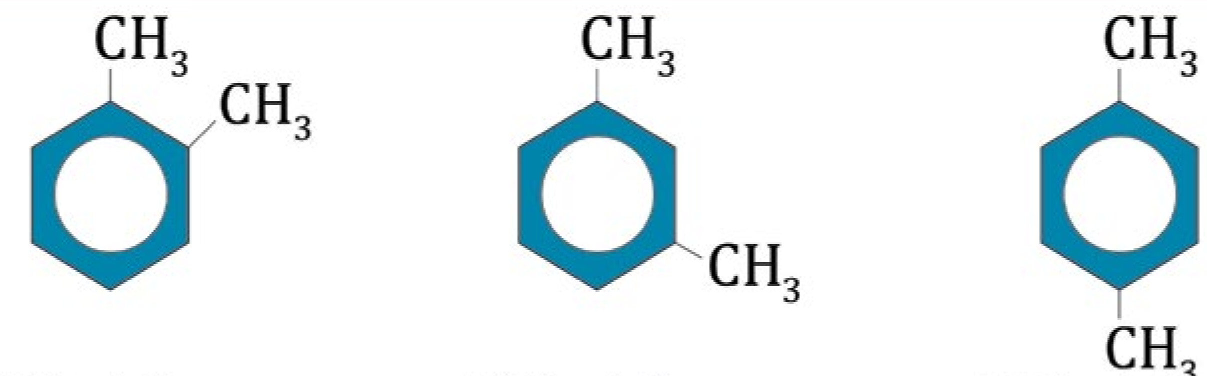


Toluene Phenol Aniline Benzoic acid Benzaldehyde

All the six positions in benzene are exactly equivalent so there is only one monosubsituted benzene.

When a hydrogen atom is removed from benzene, we get a phenyl group symbolized by C_6H_5- or Ph-. Substituted phenyl groups are called aryl groups.

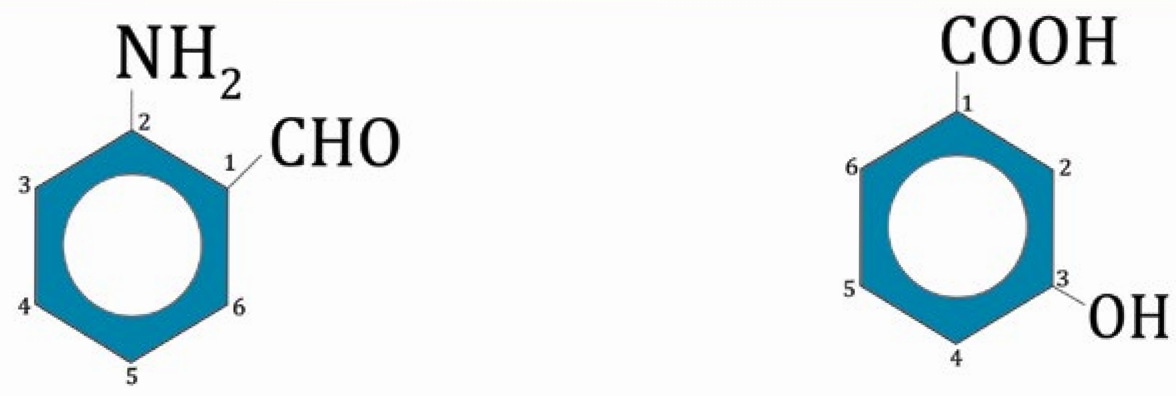
3. The second substituent in benzene would give rise to three isomeric products designated as ortho (1,2), meta(1,3) and para(1,4),e.g.



1,2 Dimethylbenzene (o-xylene) 1,3 Dimethylbenzene (m-xylene) 1,4 Dimethylbenzene (p-xylene)

4. If two or more substituents are different, then the substituent that is treated as a high priority group, is given the number 1 position in the benzene ring. Other groups are numbered by counting from position 1 in the manner which gives them the lowest number.

Animation 9.3 : Monocyclic ring breathing mode in Toluene
Source & Credit : Kemi



2-Aminobenzaldehyde 3-Hydroxybenzoic acid

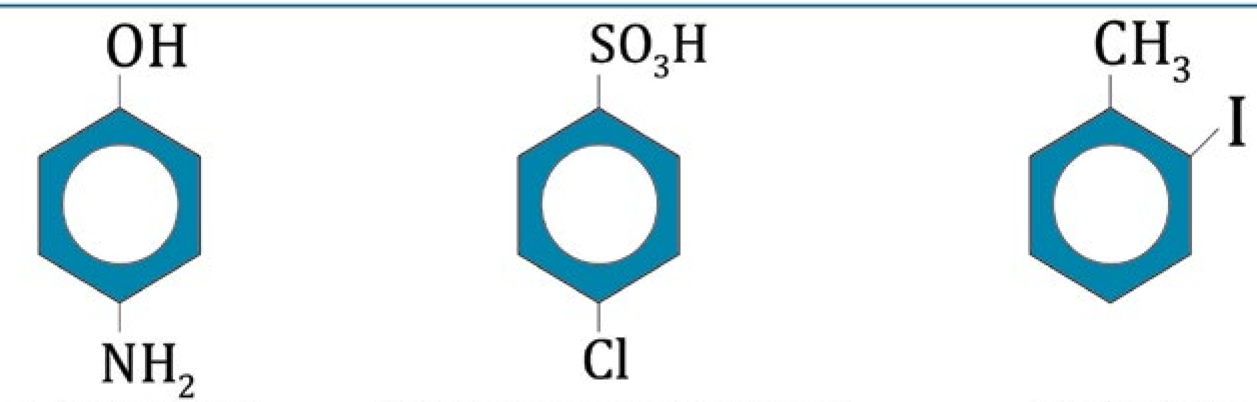
The order of priority of the groups (left to right):

— COOH, — CN, — CHO, — $COCH_3$, — OH, — NH, — OR, — R.

5. If the two substituents are different and they are not present in priority order list, they are named in alphabetical order. The last named substituent will be at position 1, e.g.,

3-Chloroiodobenzene 2-Bromonitrobenzene

6. If there is a substituent on the ring which gives a special name to the molecule, then special name is used as parent name to the molecule, e.g.



4-Aminophenol 4-Chlorobenzenesulphonic acid 2-Iodotoluene

9.3 BENZENE

Benzene was discovered by Michael Faraday in 1825 in the gas produced by the destructive distillation of vegetable oil and twenty years later it was also found in coal-tar by Hoffmann.

9.3.1 Structure of Benzene

Molecular Formula

1. The empirical formula of benzene is determined by the elemental analysis.
2. Its molecular mass determined by the vapour density method is 78.108. This is six times the empirical formula mass (CH = 12 + 1 = 13). Therefore, the molecular formula of benzene is C_6H_6.
3. The molecular formula of benzene indicates that it is highly unsaturated compound.

9.3.2 Straight Chain Structures Ruled Out:

i) Two of the possible straight chain formulas suggested for benzene are :

$HC \equiv C—CH_2—CH_2—C \equiv CH$ (1,5-Hexadiyne).

$H_2C{=}CH—C \equiv C—CH{=}CH_2$ (l,5-Hexadiene-3-yne).

A compound having a structure as above should behave like an alkene or alkyne, both are oxidized by alkaline $KMnO_4$ solution. On the contrary, benzene is stable to $KMnO_4$ solution i.e. it does not decolorize $KMnO_4$ solution. Benzene gives addition reactions with hydrogen and halogens, which indicate the presence of three double bonds.

But benzene also gives substitution reactions with conc. HNO_3 and conc. H_2SO_4 which indicate that benzene has a saturated structure.

ii) Considering a straight chain structure for benzene and further assuming that each carbon carries one H-atom, it should be capable of forming three monosubstitution products.

But benzene yields only one monosubstituent product.

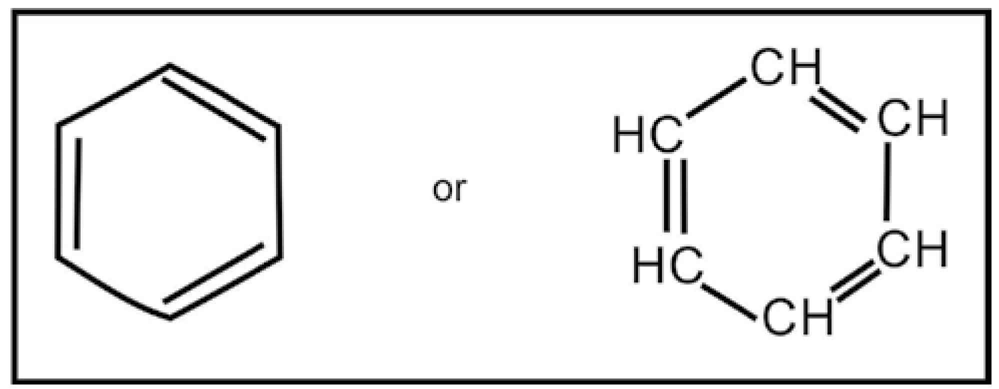
iii) The molecular formula of benzene C_6H_6 does not correspond to any of the open chain hydrocarbons, such as alkane $C_nH_{2n+2}(C_6H_{14})$, alkene $C_nH_{2n}(C_6H_{12})$ or alkyne C_nH_{2n-2} (C_6H_{10}).

It means benzene does not belong to open chain hydrocarbon and therefore possibility of a straight chain structure is ruled out.

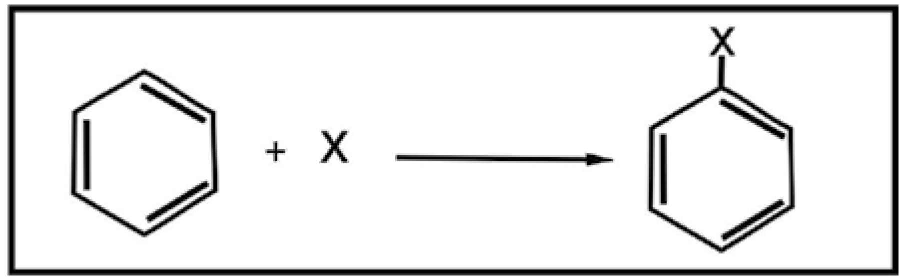
9.3.3 Kekule's Structure

The structure of benzene continued to be a serious problem for chemists for about 40 years. A German chemist, Kekule at last solved the problem in 1865. Kekule proposed a cyclic regular hexagonal structure for benzene, which contains three double bonds alternating with three single bonds.

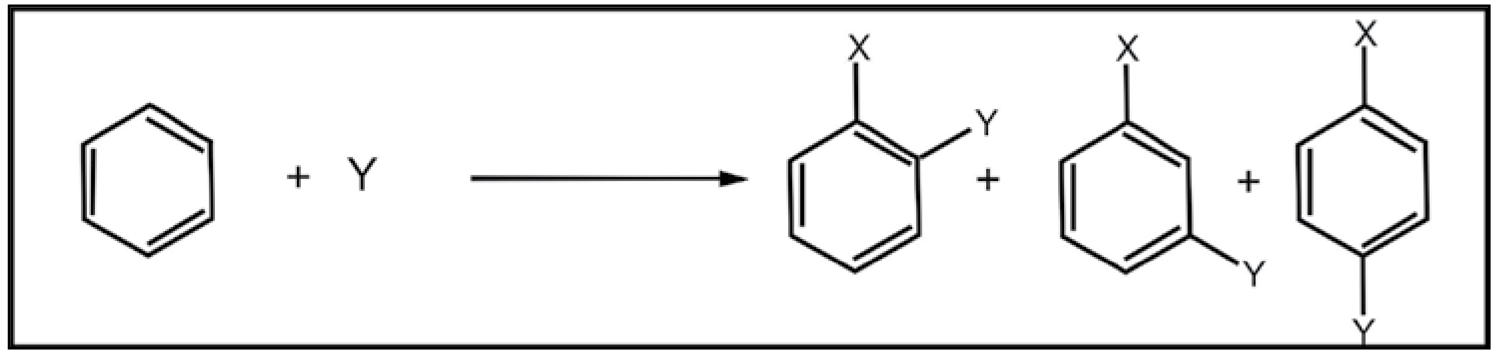
He supported his theory by the following arguments.



(i) Benzene gives only one monosubstituted product.



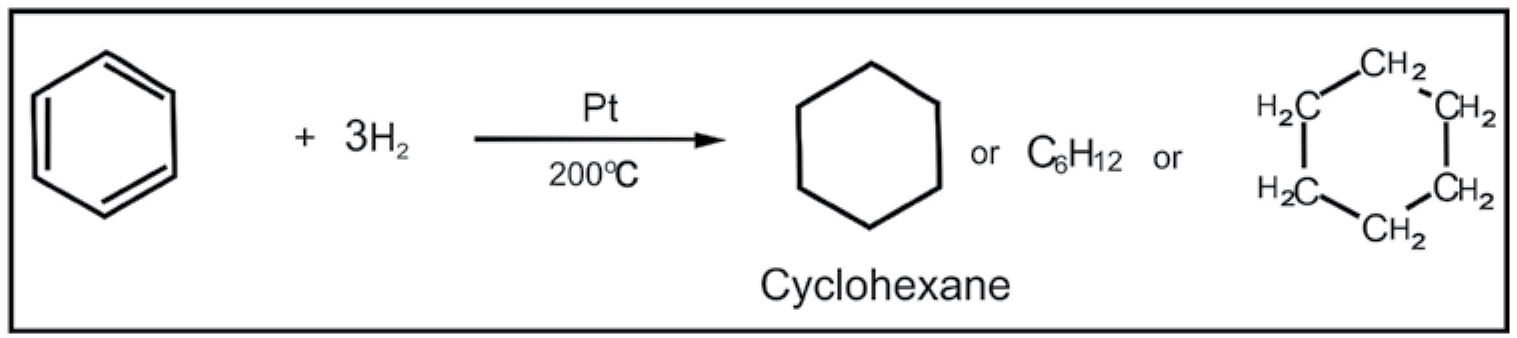
(ii) Benzene gives only three disubstituted products.



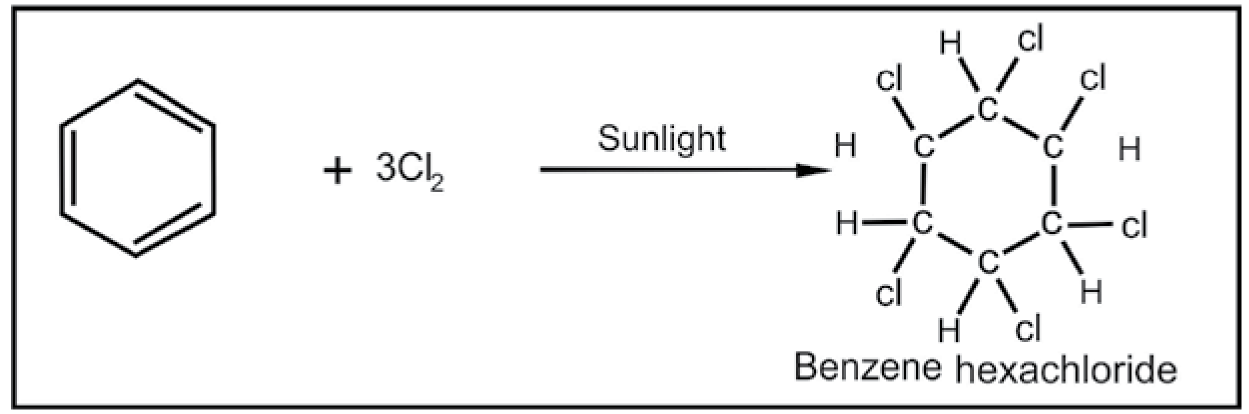
These points confirm the regular hexagonal structure for benzene in which all the carbon atoms are occupying identical positions in the molecule. Therefore, benzene forms only one toluene, one phenol and one nitro benzene.

(iii) Benzene adds three hydrogen molecules in the presence of a catalyst.

Animation 9.4 : Phenol and Alcohol
Source & Credit : footdoc



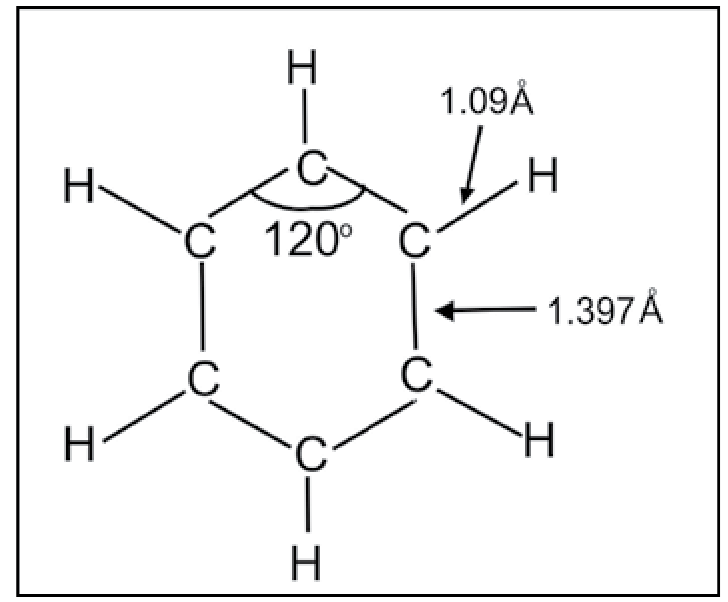
iv) Benzene adds three molecules of chlorine in the presence of sunlight.



These two reactions confirm the presence of three double bonds alternating with three single bonds.

9.3.4 X-Ray Studies of Benzene Structure

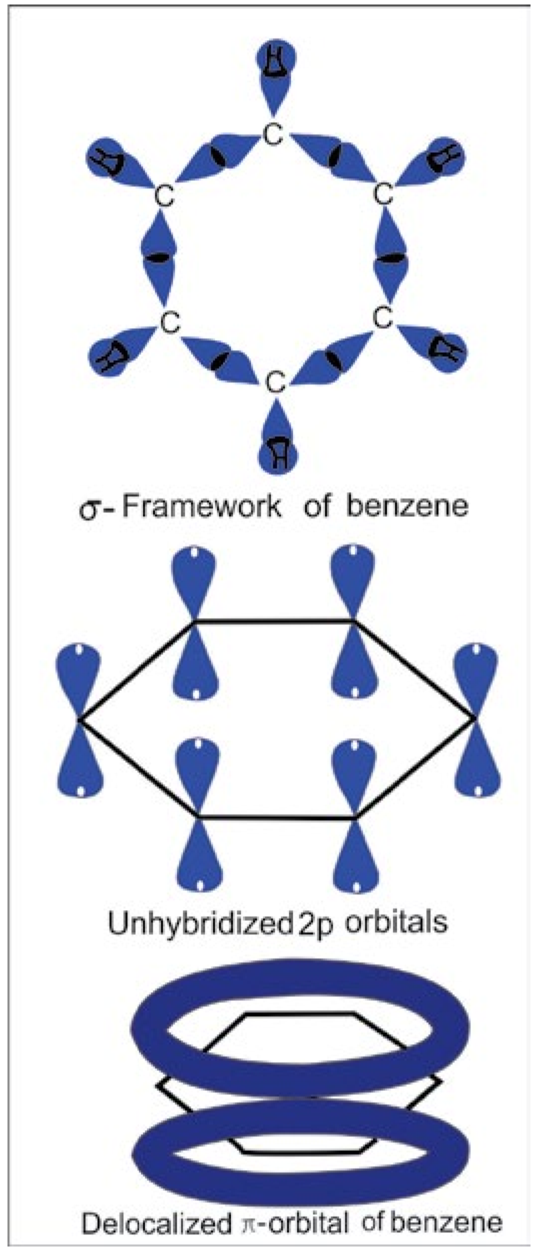
The X-ray studies of benzene have confirmed the hexagonal structure for it. These studies have also revealed that all the carbon and hydrogen atoms are in the same plane. All the angles are of 120°. All C - C and C -H bond lengths are 1.397Å and 1.09 Å, respectively.



Objections to Kekule's Formula

Kekule's formula with three double bonds demands a high degree of unsaturation from benzene while usually it exhibits a saturated character. Thus benzene yields substitution products readily and forms addition products reluctantly. Benzene is also a very stable compound. All these properties of benzene can be easily explained using the modem theories about its structure.

9.3.5 Modern Concepts About the Structure of Benzene Atomic Orbital Treatment of Benzene



The hexagonal frame-work of benzene can be conveniently explained using hybridization approach. According to this, each carbon in benzene is sp^2 hybridized. The three sp^2 hybrid orbitals on each carbon are utilized to form three σ-bonds, two. with adjacent carbon atoms and one with hydrogen.

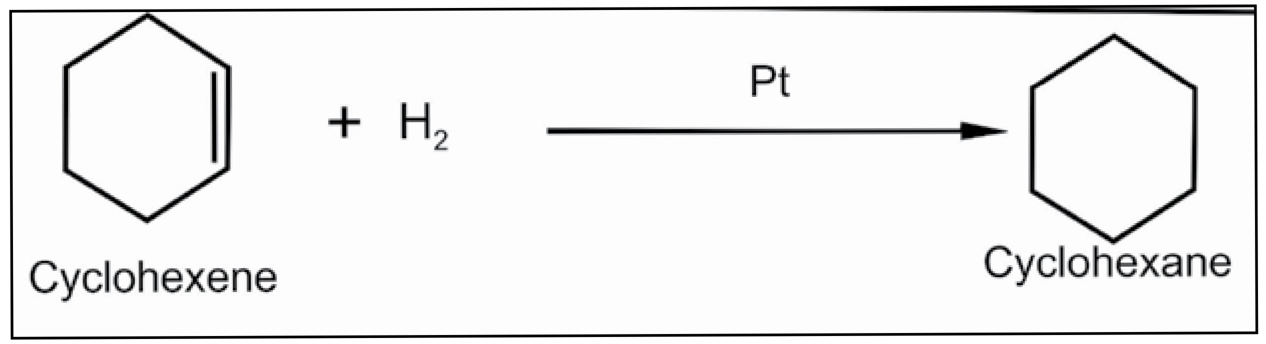
The unhybridized $2p_z$ orbitals remain at right angle to these sp^2 orbitals. Since all the sp^2 orbitals are in the same plane therefore all the carbon and hydrogen atoms are coplanar.

All the angles are of 120° which confirms the regular hexagonal structure of benzene. The unhybridized $2p_z$ orbitals partially overlap to form a continuous sheath of electron cloud, enveloping, above and below, the six carbon-carbon sigma bonds of the ring. Since each $2p_z$ orbital is overlapped by the $2p_z$ orbitals of adjacent carbon atoms, therefore, this overlapping gives, 'diffused' or 'delocalized' electron cloud.

9.3.6 The Stability of Benzene

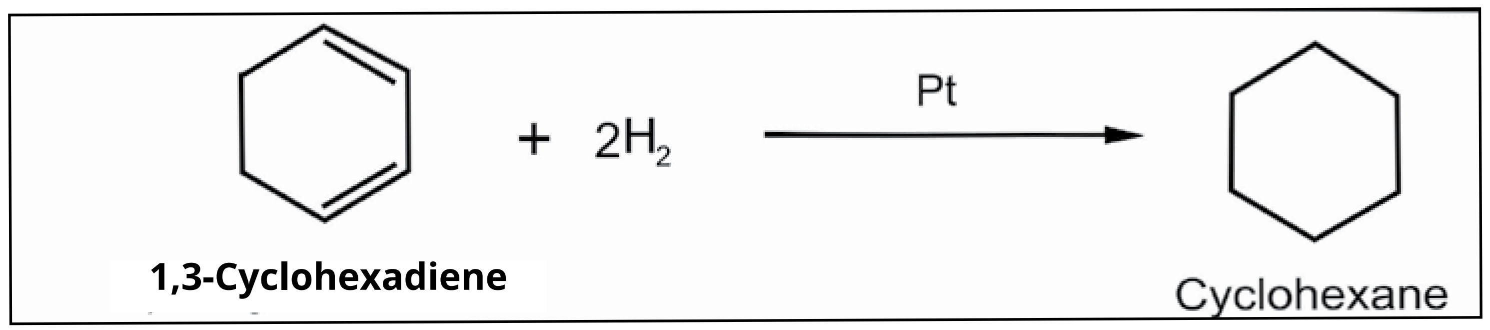
As mentioned earlier benzene is an extraordinary stable molecule. This stability is due to the extensive delocalization of electron cloud. The extent of stability of benzene can be measured by comparing it with hypothetical compound, 1,3,5- cyclohexatriene. This can be done by estimating their heats of hydrogenation.

Cyclohexene, a six membered ring containing one double bond, can be easily hydrogenated to give cyclohexane. When the ΔH for this reaction is measured it is found to be -119.5 kJ/mole, very much like that of any similarly substituted alkene.



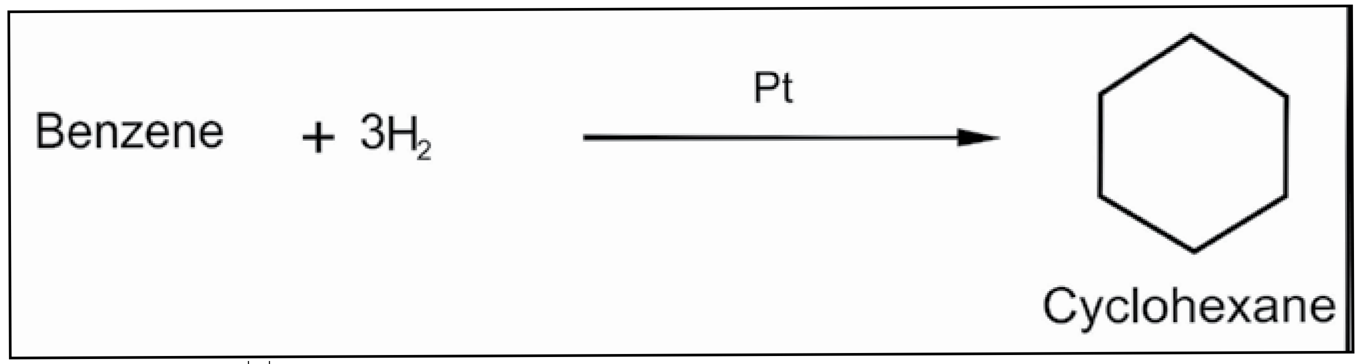
We would expect that hydrogenation of 1,3-cyclohexadiene would liberate roughly twice as much heat and thus have ΔH equal to about -239 kJ/mole. When this experiment is done, the result is ΔH = -231.5 kJ/mole. This result is quite close to what we calculated, and the difference can be explained by taking into account the fact that compounds containing conjugated double bonds are usually somewhat more stable than those containing isolated double bonds.

Animation 9.5 : Kekulé benzene
Source & Credit : Ch.imperial



Calculated ΔH = 2(-119.5) = -239 kJ/mole
Observed ΔH = -231.5 kJ/mole

If we extend this kind of thinking, and if benzene is simply 1,3,5-cyclohexatriene, we would predict that benzene would liberate approximately -358.5 kJ/mole (3 x -119.5) when it is hydrogenated. When the experiment is actually done the result is surprisingly different. The reaction is exothermic but only by -208 kJ/mole.



Calculated ΔH = (3 x -119.5) =-358.5 kJ/mole
Observed ΔH = -208 kJ/mole
Difference = 150.5 kJ/mole

When the results are represented by the following figure, it becomes clear that benzene is much more stable than we calculated it to be.

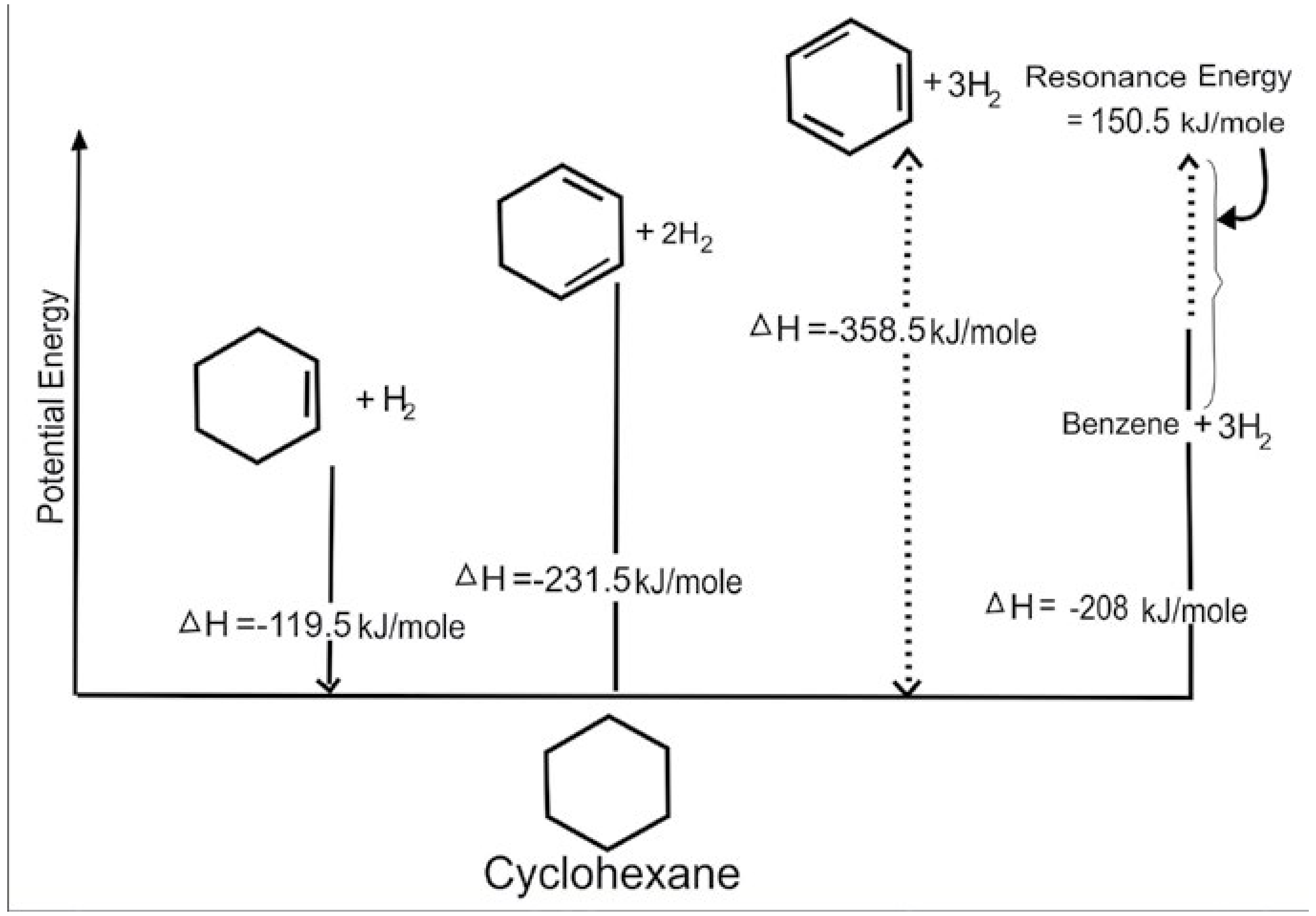


Fig.9.1 Relative stabilities of Cyclohexene,1,3- Cyclohexadiene, 1,3,5-Cyclohexatriene (hypothetical) and benzene.

Animation 9.6 : Benzene derivative
Source & Credit : Cod.edu

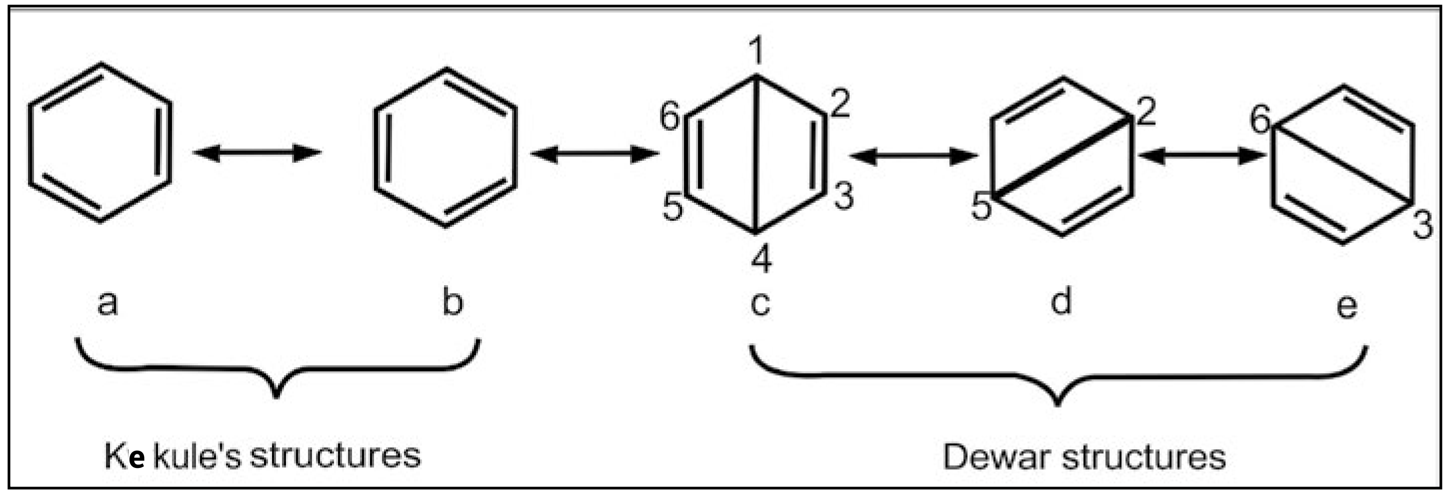
Animation 9.7 : Bonding in a molecule of benzene from a molecular orbital point
Source & Credit : lite.msu.edu

Indeed, benzene is more stable than the hypothetical 1,3,5-cyclohexatriene by 150.5 kJ/mole. This difference between amount of heat actually released and that calculated on the basis of the Kekule's structure is now called the 'Resonance energy' of the compound. It means benzene shows the phenomenon of resonance which makes it more stable than others. In benzene electrons are delocalized making it a very stable molecule.

9.3.7 The Resonance Method

Resonance

"The possibility of different pairing schemes of valence electrons of atoms is called resonance" and the different structures thus arranged are called "Resonance structures". The resonance is represented by a double headed arrow ($\leftrightarrow$) e.g. the following different pairing schemes of the fourth valence (the p-electrons) of carbon atoms are possible in benzene.



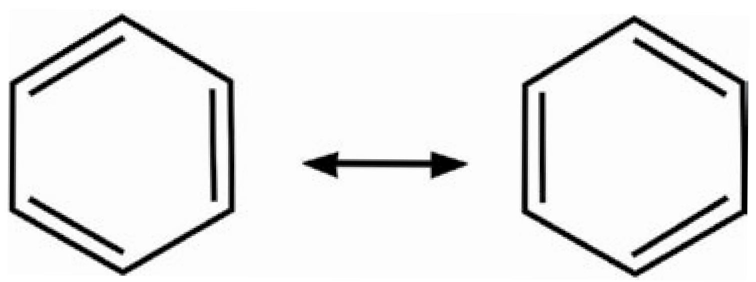
(a), (b) were proposed by Kekule and c, d, e, were proposed by Dewar. The stability of a molecule increases with increase in the number of its resonance structures. Thus molecule of benzene is chemically quite stable.

In Dewar structure the carbon atoms at opposite positions 1-4, 2-5 and 3-6 are at larger distances than those in the adjacent positions 1-2,2-3,3-4,4-5,5-6 and 6 -1. Therefore the bondings between C_1-C_4, C_2-C_5 and C_3-C_6 are not favourable energetically.

Hence the Dewar structures for benzene have minor contribution towards the actual structure of benzene.

Infact, the structure of benzene is a resonance hybrid of all the five structures (a), (b), (c), (d) and (e) in which the Kekule's structure (a) and (b) have the larger contribution. Therefore, benzene molecule can be represented by either of the two Kekule's structure.

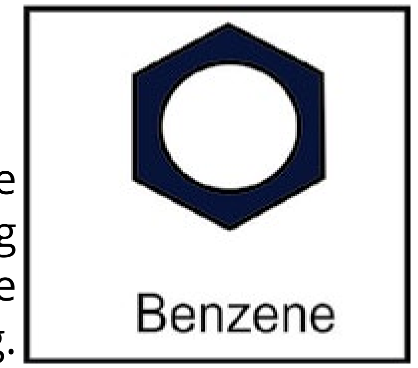
The three alternate single and double bonds in the Kekule's structures are called conjugate bonds or resonating bonds.



Since the structure of benzene is a resonance hybrid, therefore all the C-C bond lengths are equal but different from those in alkanes, alkenes and alkynes.

In alkanes the C-C bond length is 1.54Å.
In alkenes the C = C bond length is 1.34Å.
In alkynes the C ≡ C bond length is 1.20Å.
In benzene the C-C bond length is 1.397Å.

The C - C bond length in benzene is intermediate between those in alkanes and alkenes. The resonating single and double bonds in benzene can better be represented as a complete circle inside the ring.

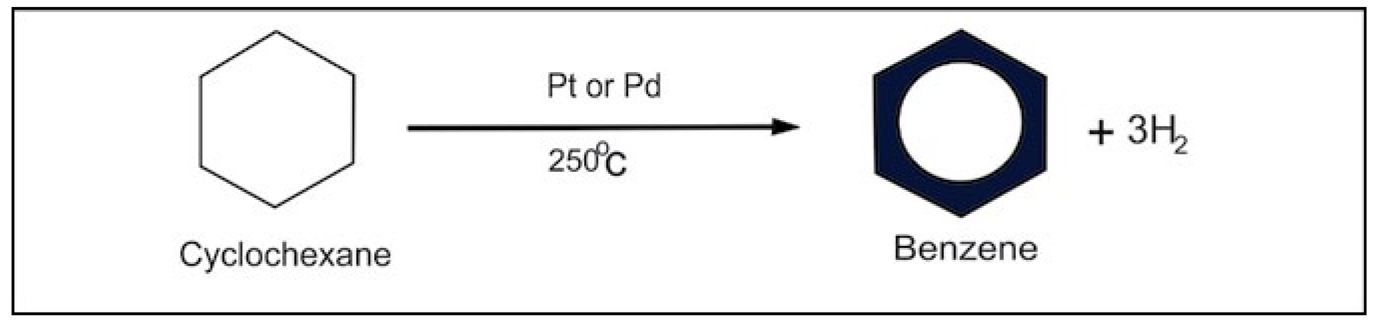


9.4 PREPARATION OF BENZENE

Benzene and other aromatic hydrocarbons are readily obtained in large quantities from coal and petroleum. Benzene and some other hydrocarbons can also be obtained from petroleum by special cracking methods. Some of the methods generally used for the preparation of benzene are as follows.

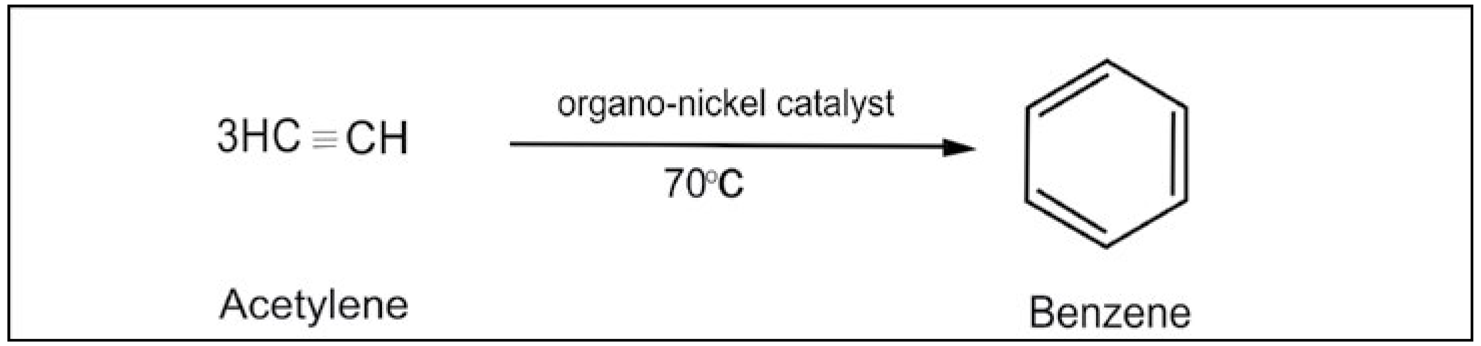
1. Dehydrogenation of Cyclohexane

When cyclohexane or its derivative is dehydrogenated we get benzene or a substituted benzene. The reaction is carried out by the use of a catalyst at elevated temperature.



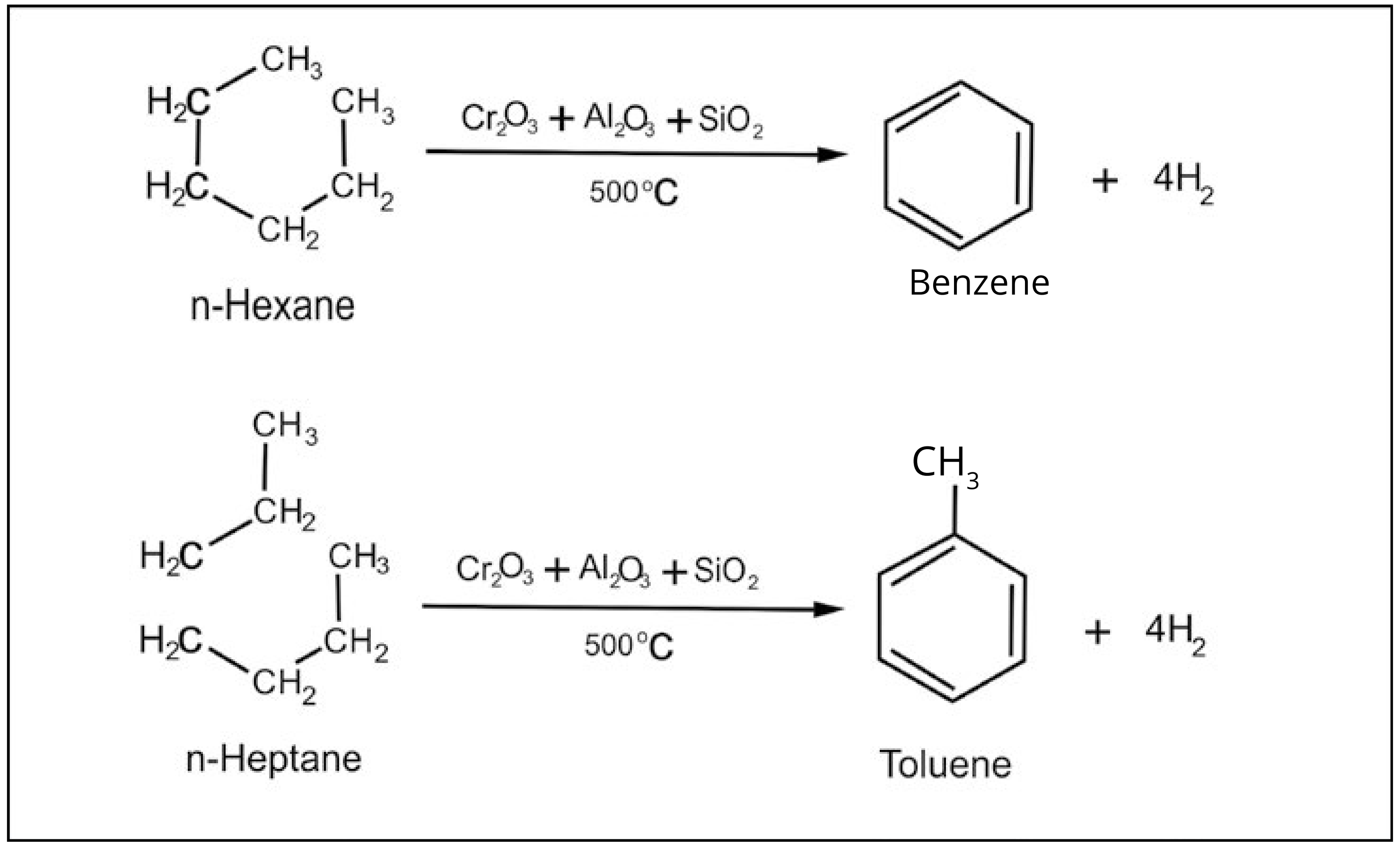
2. From Acetylene:

Benzene is formed by passing acetylene under pressure over an organo-nickel catalyst at 70°C.



3. FromAlkanes

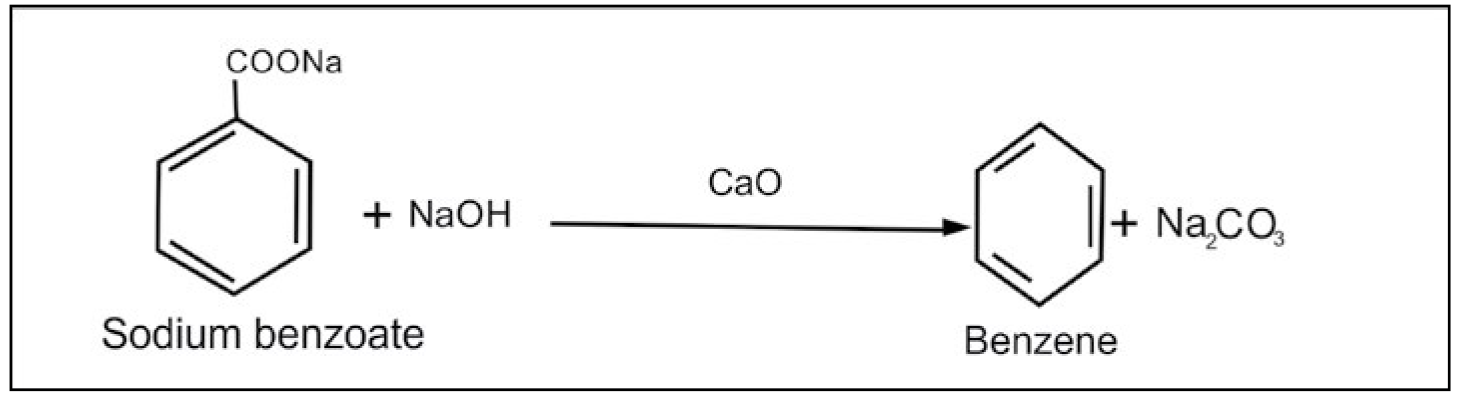
Benzene and toluene are also prepared by passing the vapours of n-haxane or n-heptane over a mixture of catalysts Cr_2O_3 + Al_2O_3 + SiO_2 at 500°C.



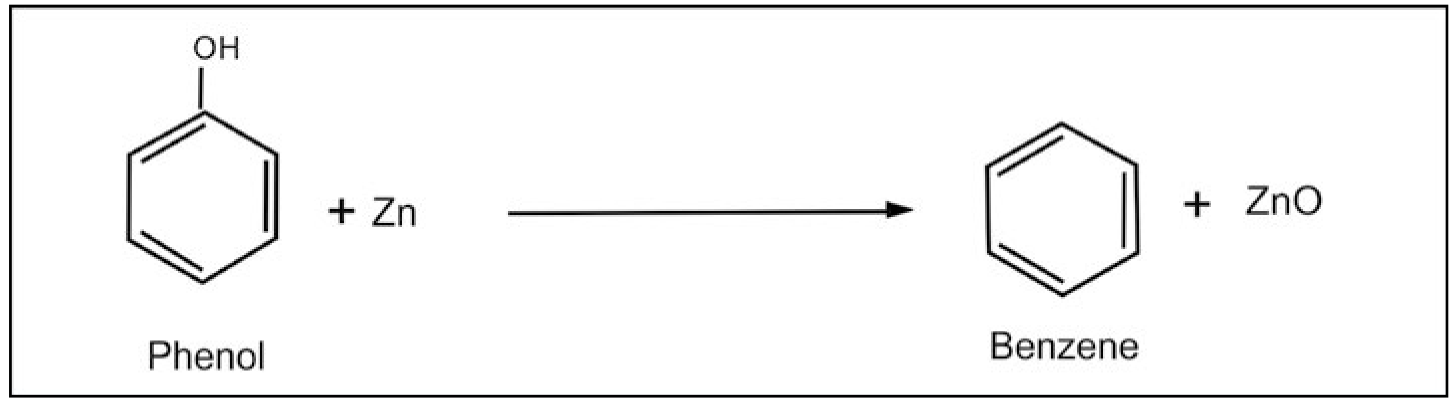
4. Preparation in the Laboratory

Benzene can be prepared in the laboratory by any one of the following methods.

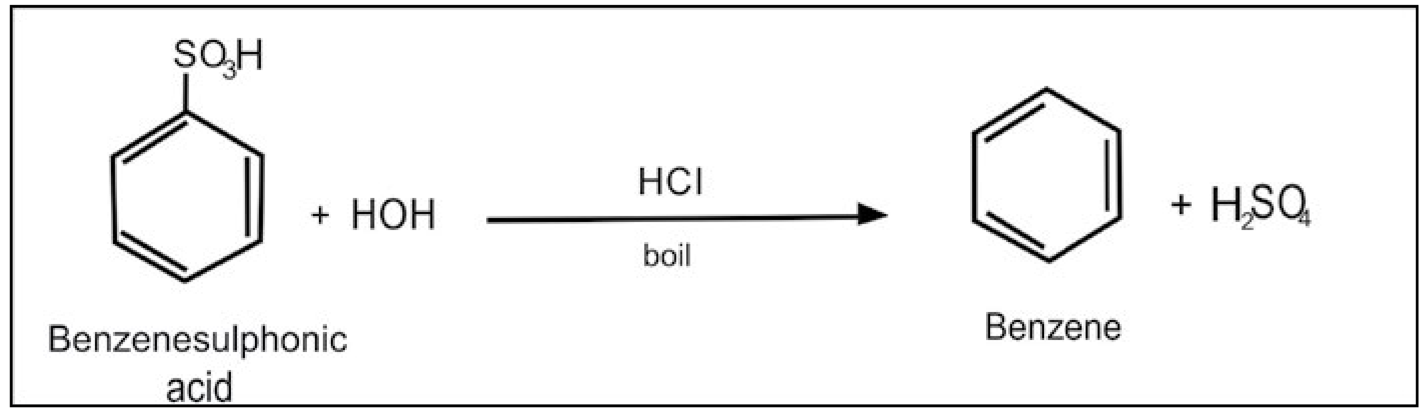
i. By heating sodium salt of benzoic acid with soda lime.



ii. By distilling phenol with zinc dust.

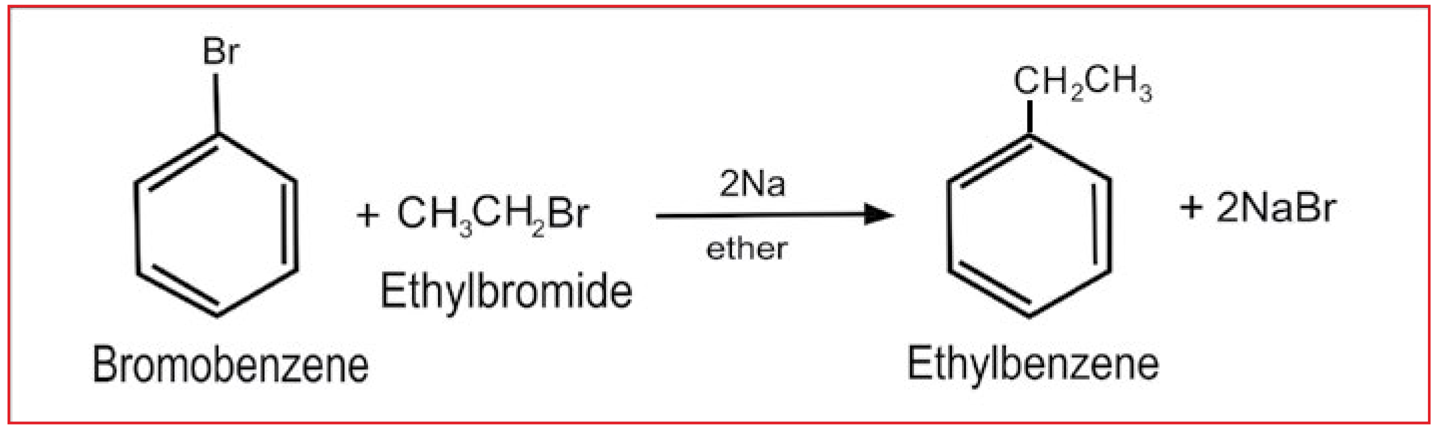


iii. By the hydrolysis of benzenesulphonic acid with superheated steam or by boiling with dil. HCl.



5. Wurtz-Fittig Reaction

The Wurtz reaction for the synthesis of alkanes was extended by Fittig in 1864 to the synthesis of alkyl aromatic hydrocarbons.



Animation 9.8 : Alkenes due to resonance
Source & Credit : Chemistry.boisestate.edu

9.5 REACTIONS OF BENZENE

9.5.1 General Pattern of Reactivity of Benzene Towards Electrophiles

The highly stable, delocalized electrons of benzene ring are not readily available for the nucleophillic attack like the electrons of alkenes.

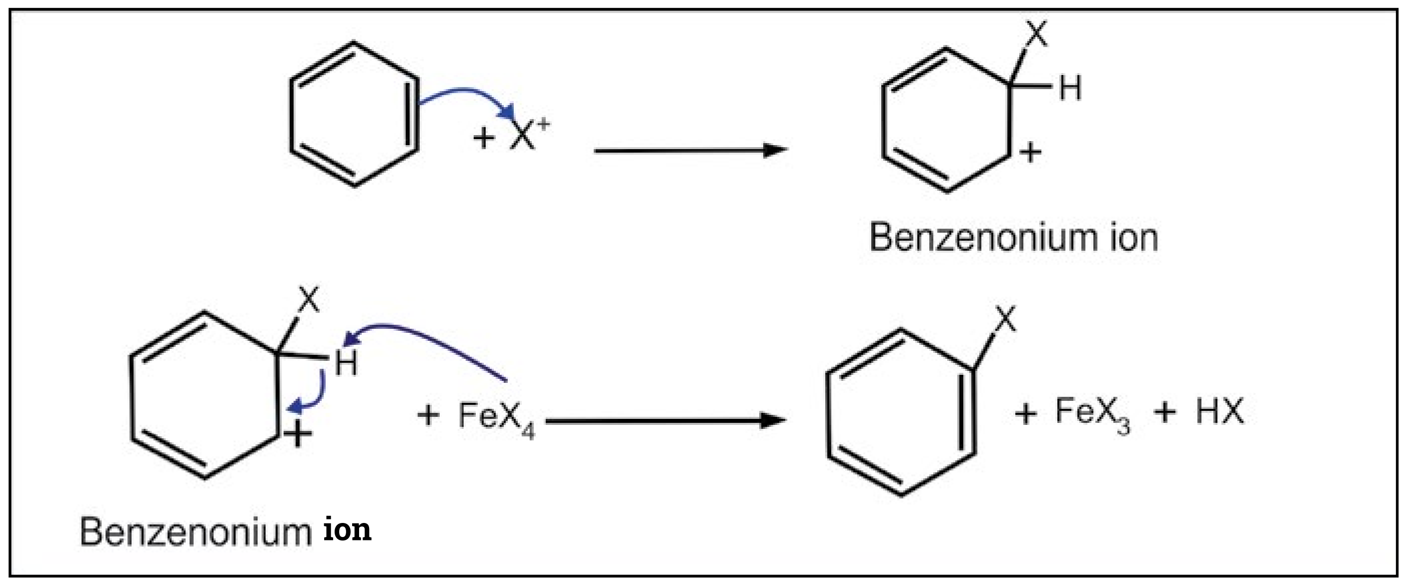
Therefore, the electrons of benzene ring do not assist in the attack of weak electrophiles. It means that more powerful electrophiles are required to penetrate and break the continuous sheath of electron cloud in benzene, e.g., substitution of halogen in benzene requires iron or corresponding ferric halide as a catalyst. Infact iron too is first converted into FeX_3 which further reacts with halogen molecule to produce a powerful electrophile.

$$2Fe + 3X_2 \rightarrow 2FeX_3$$

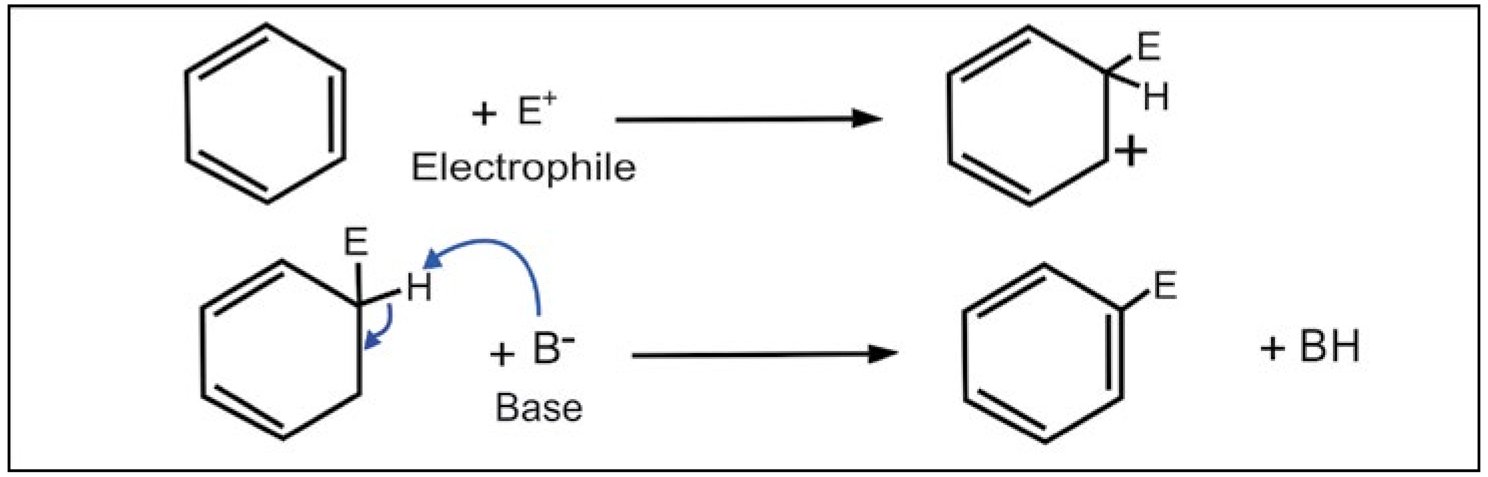
$$FeX_3 + X_2 \rightarrow FeX^-_4 + X^+$$

Tetra haloferrate ion (III) — Halogenonium ion

The halogenonium ion X^+ thus produced attacks as a powerful electrophile on the electrons of benzene ring.



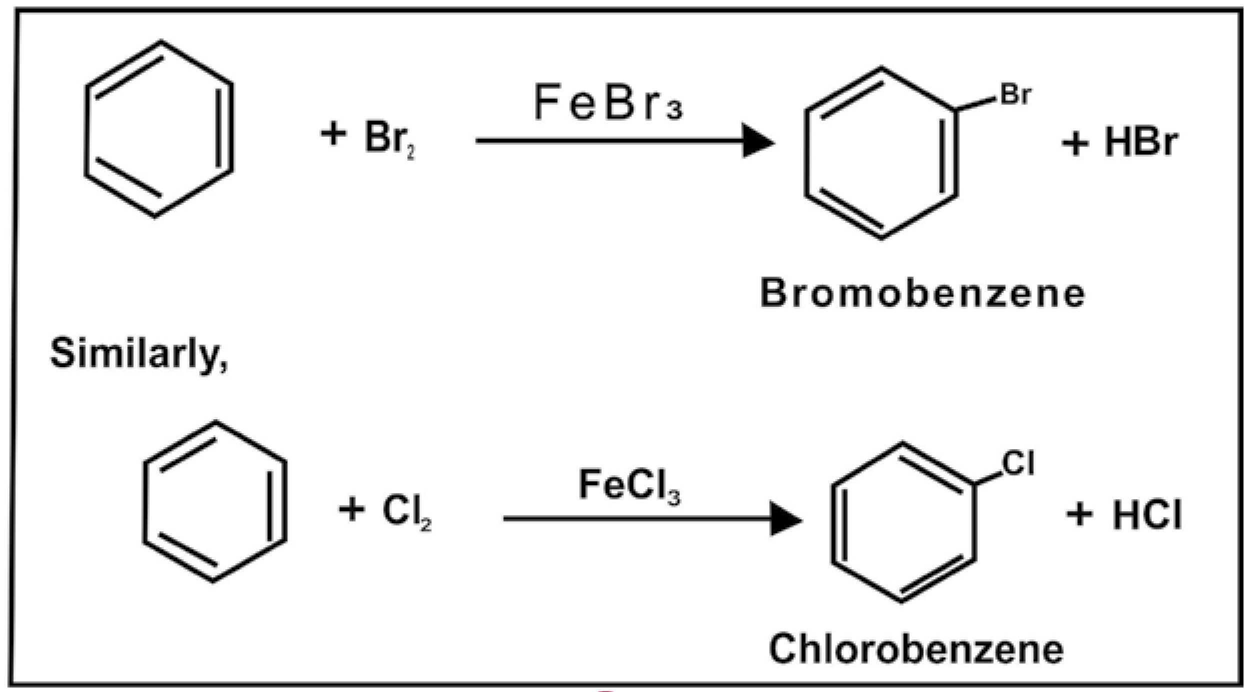
The addition product is not favourable because in its formation the characteristic stability of benzene is lost. The only possible product is the substitution product in which the stability of benzene is retained. Therefore, the general pattern of the chemical reactivity of benzene towards electrophiles can be shown as follows.



9.5.2 Electrophilic Substitution Reactions

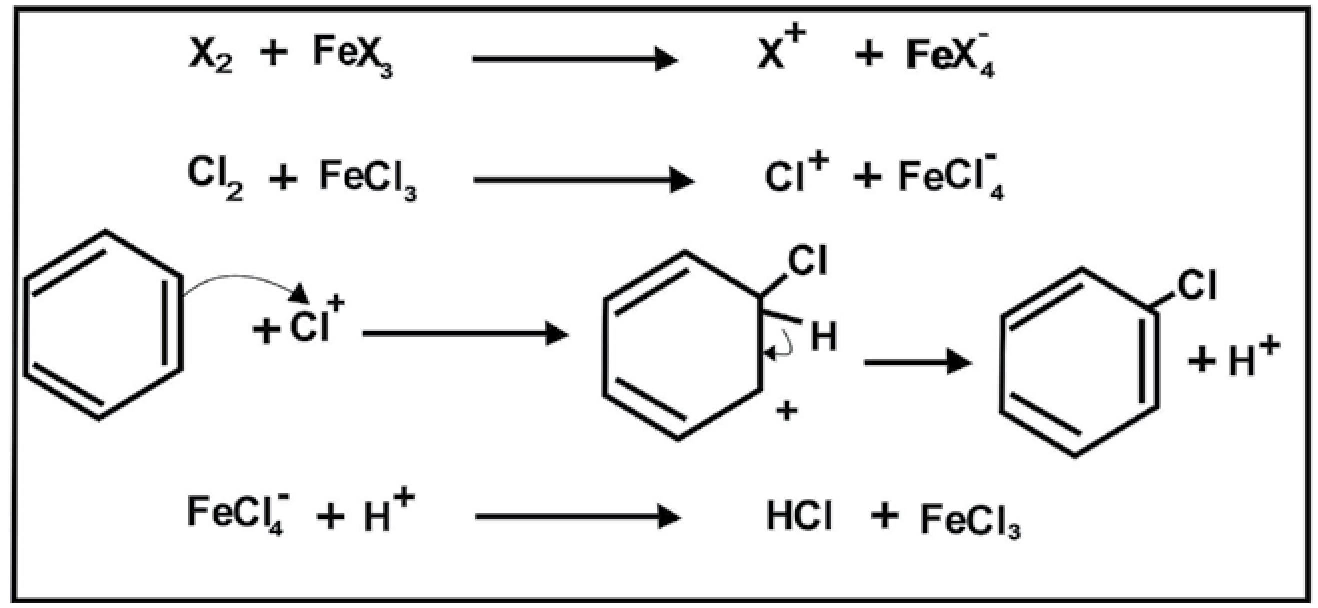
1. Halogenation

The introduction of halogen group in benzene ring is called "Halogenation" Benzene reacts with halogen in the presence of a catalyst like $FeBr_3$, $AlCl_3$, etc. Chlorination and bromination are normal reactions but fluorination is too vigorous to control. Iodination gives poor yield.

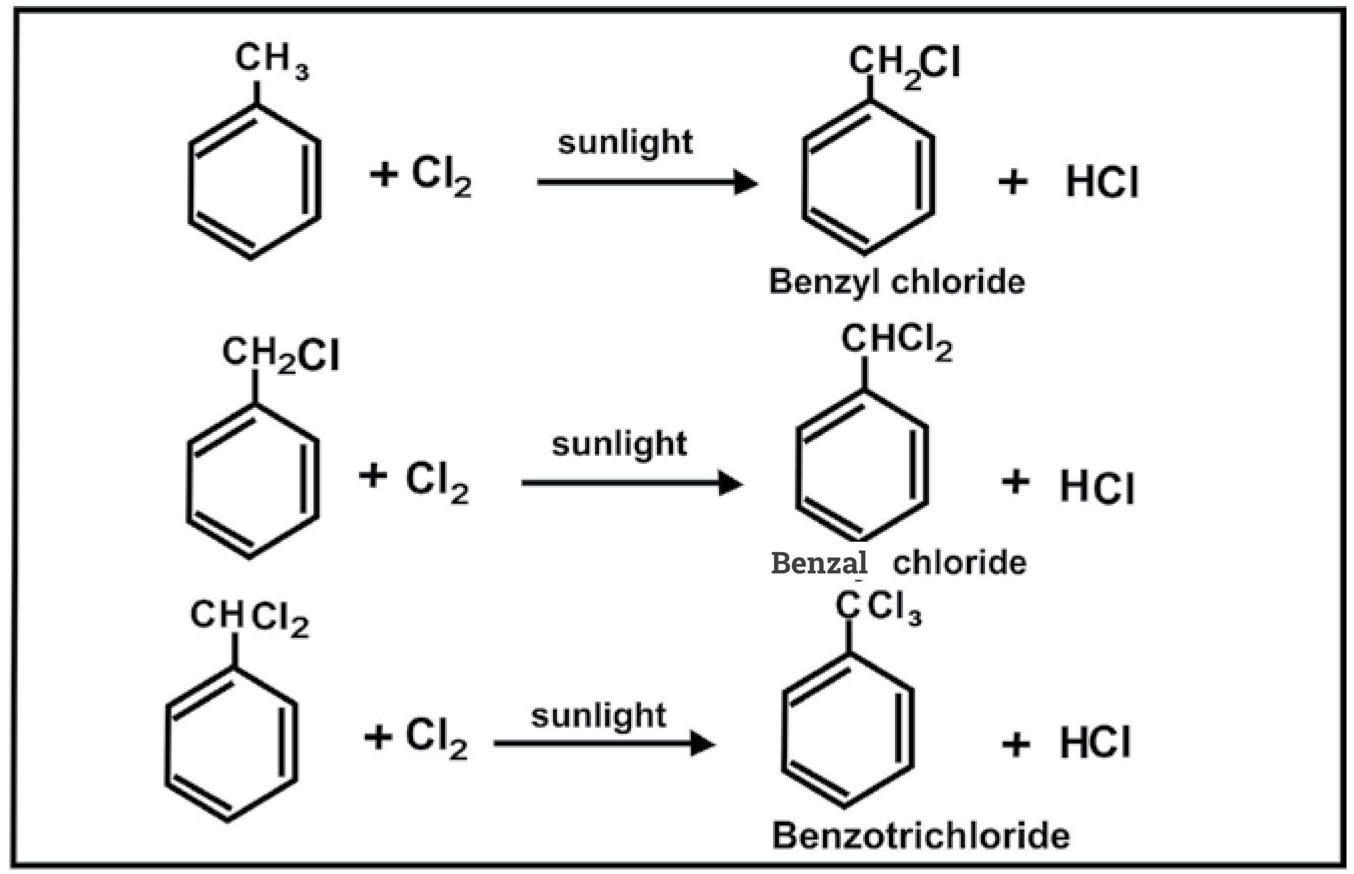


Mechanism:

The actual halogenating agent is X^+ (i.e. Cl^+ or Br^+) is formed by the following mechanism.

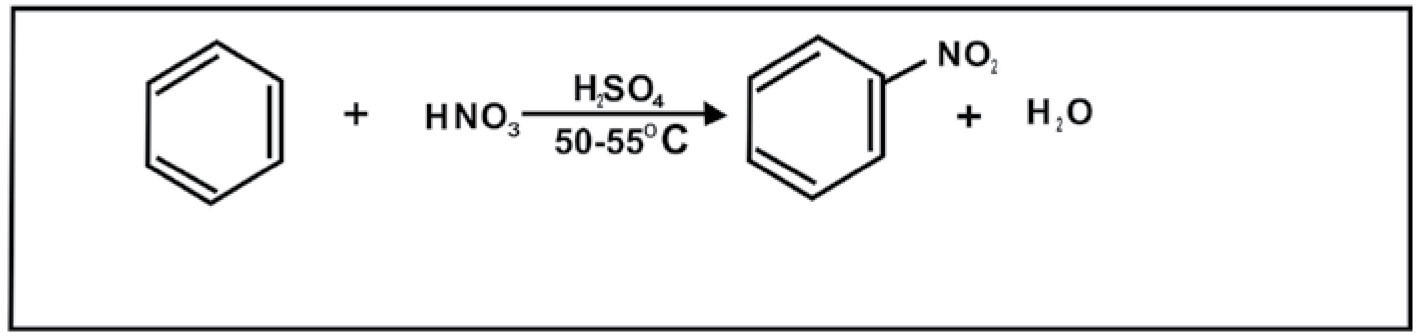


When alkyl benzenes are treated with chlorine or bromine in the presence of sunlight, only the alkyl groups are substituted.



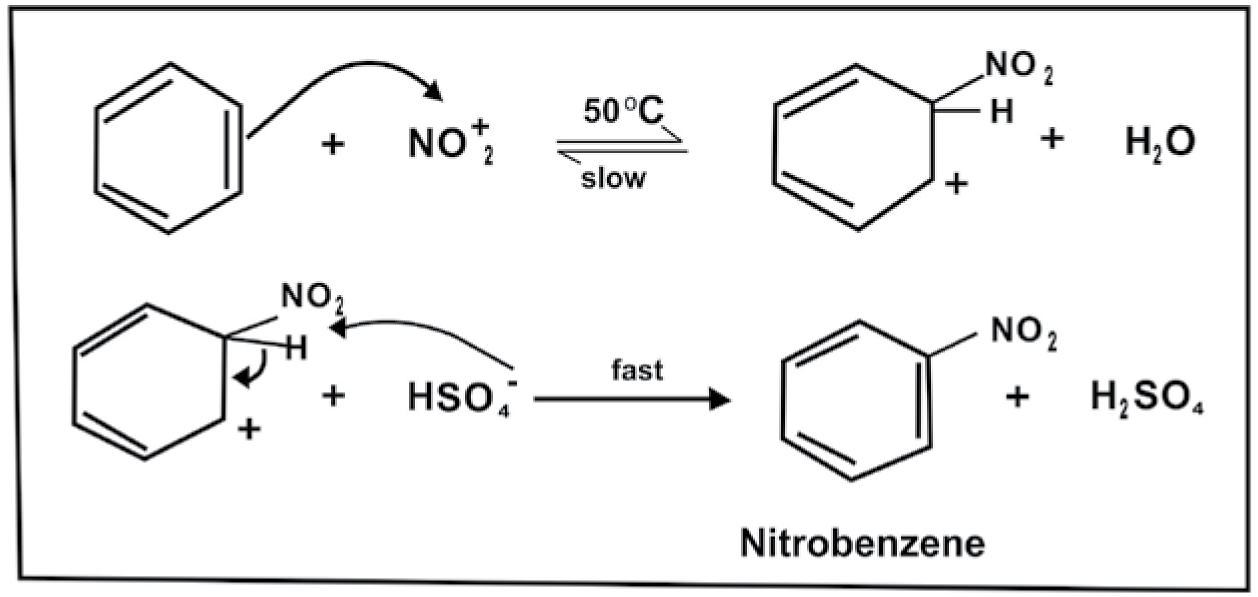
2. Nitration

The introduction of NO_2 group in benzene ring is called "Nitration". The nitration of benzene takes place when it is heated with a 1:1 mixture of con. HNO_3 and con.H_2SO_4 at 50- 55°C. Sulphuric acid reacts with nitric acid to generate nitronium ion, (NO_2^+).



Mechanism:

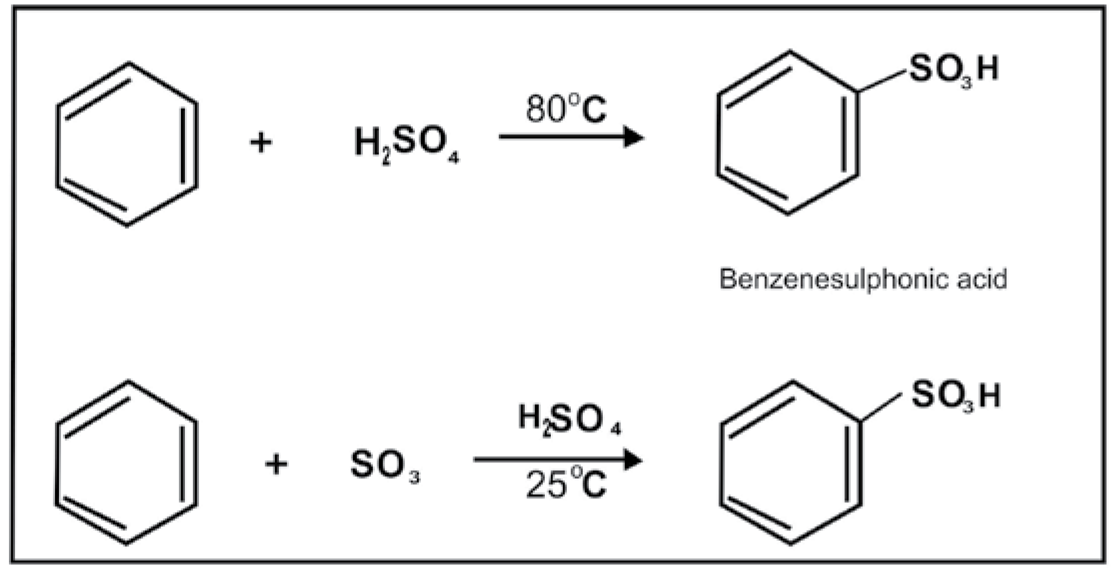
$$HNO_2 + H_2SO_4 \xrightarrow{50-55^0C} NO_2^+ + HSO_4^- + H_2O$$



Animation 9.9 : Nitration of benzene mechanism
Source & Credit : Sustainability.sellafieldsites

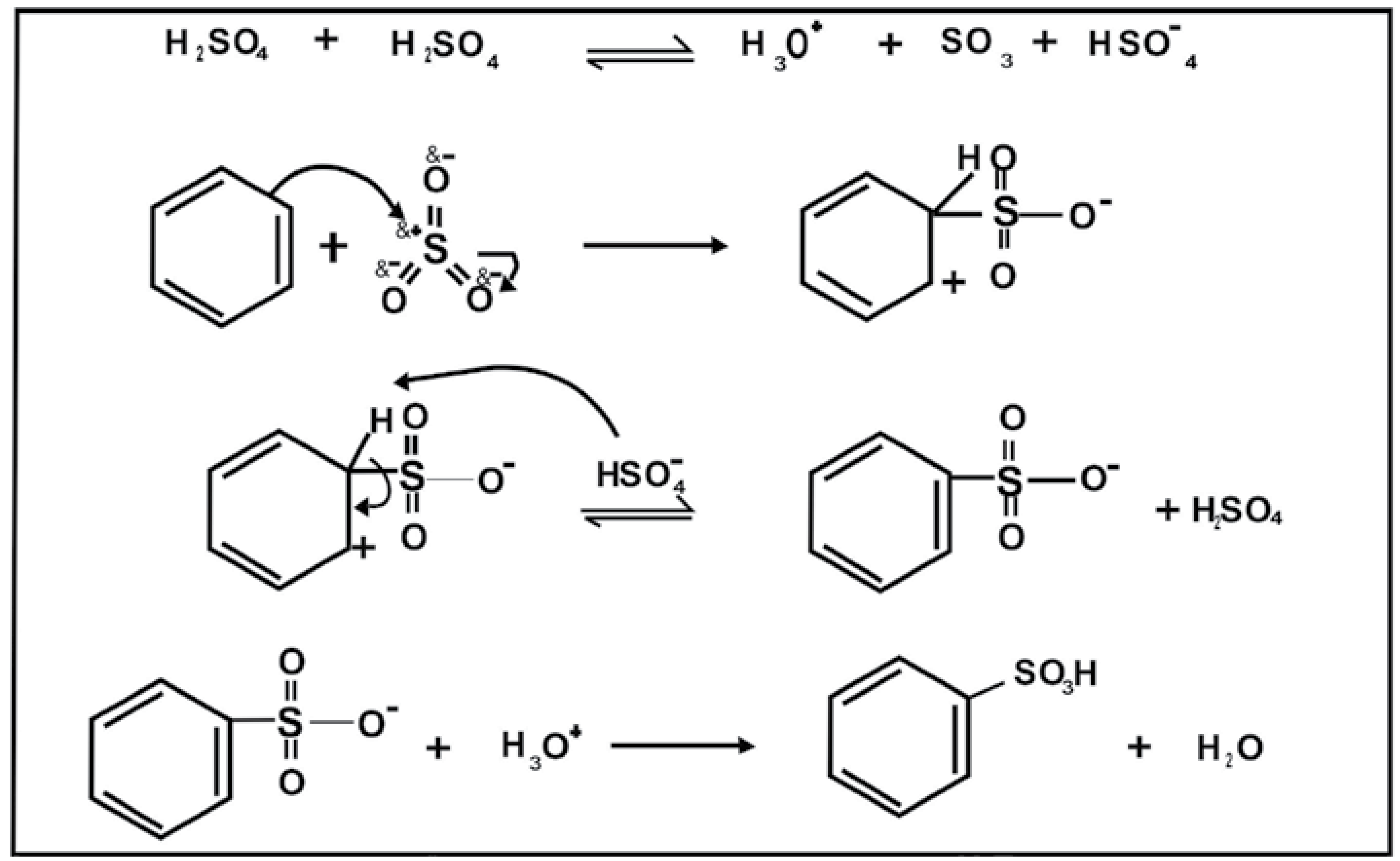
3. Sulphonation

The introduction of sulphonic acid group in benzene ring is called Sulphonation. When benzene is heated with fuming H_2SO_4 or conc. H_2SO_4 it yields benzene sulphonic acid.



Mechanism:

When sulphuric acid alone is used, the actual electrophile in this reaction is SO_3.

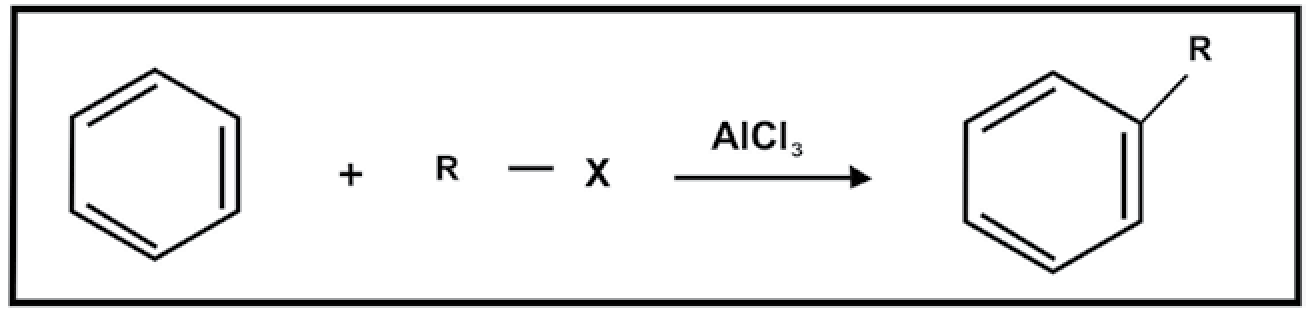


3. Friedel-Crafts Reactions

The alkylation and acylation of benzene are called friedel-Crafts reactions.

a) Alkylation

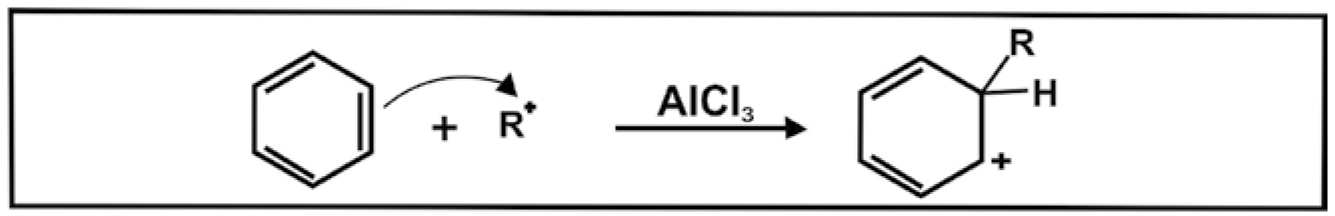
The introduction of an alkyl group in the benzene ring in the presence of an alkyl halide and a catalyst $AlCl_3$ is called Friedel-Crafts alkylation or Alkylation.

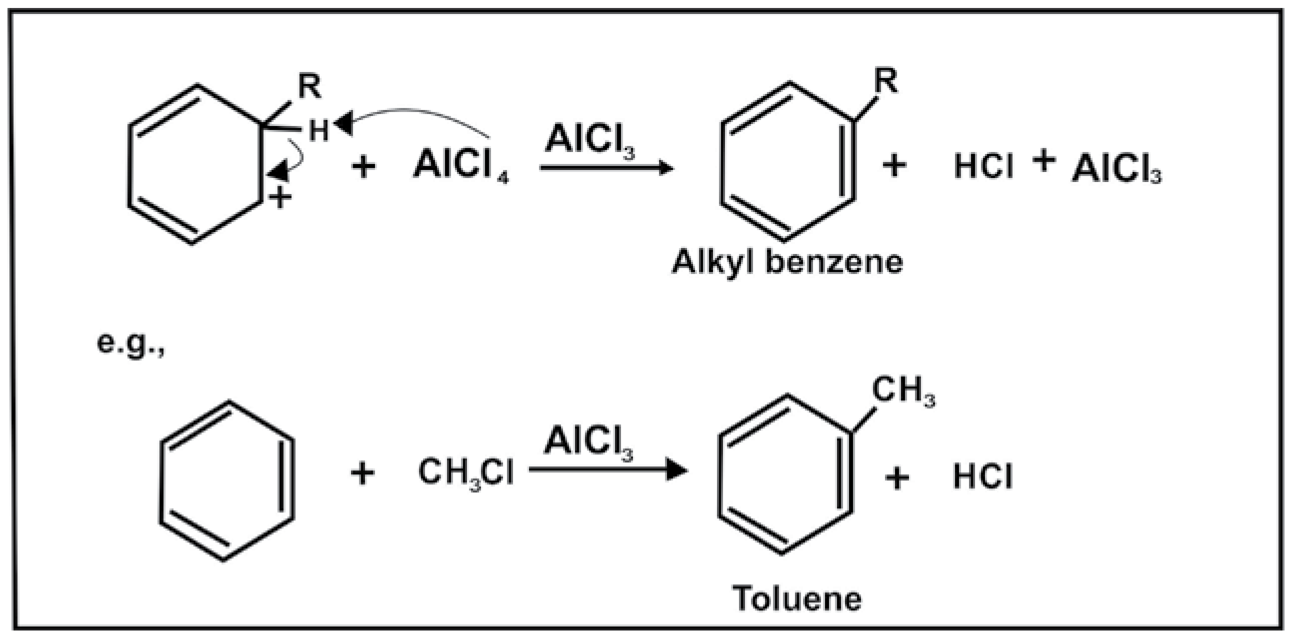


Mechanism:

$$R—Cl + AlCl_3 \rightarrow AlCl^-_4 + R^+$$

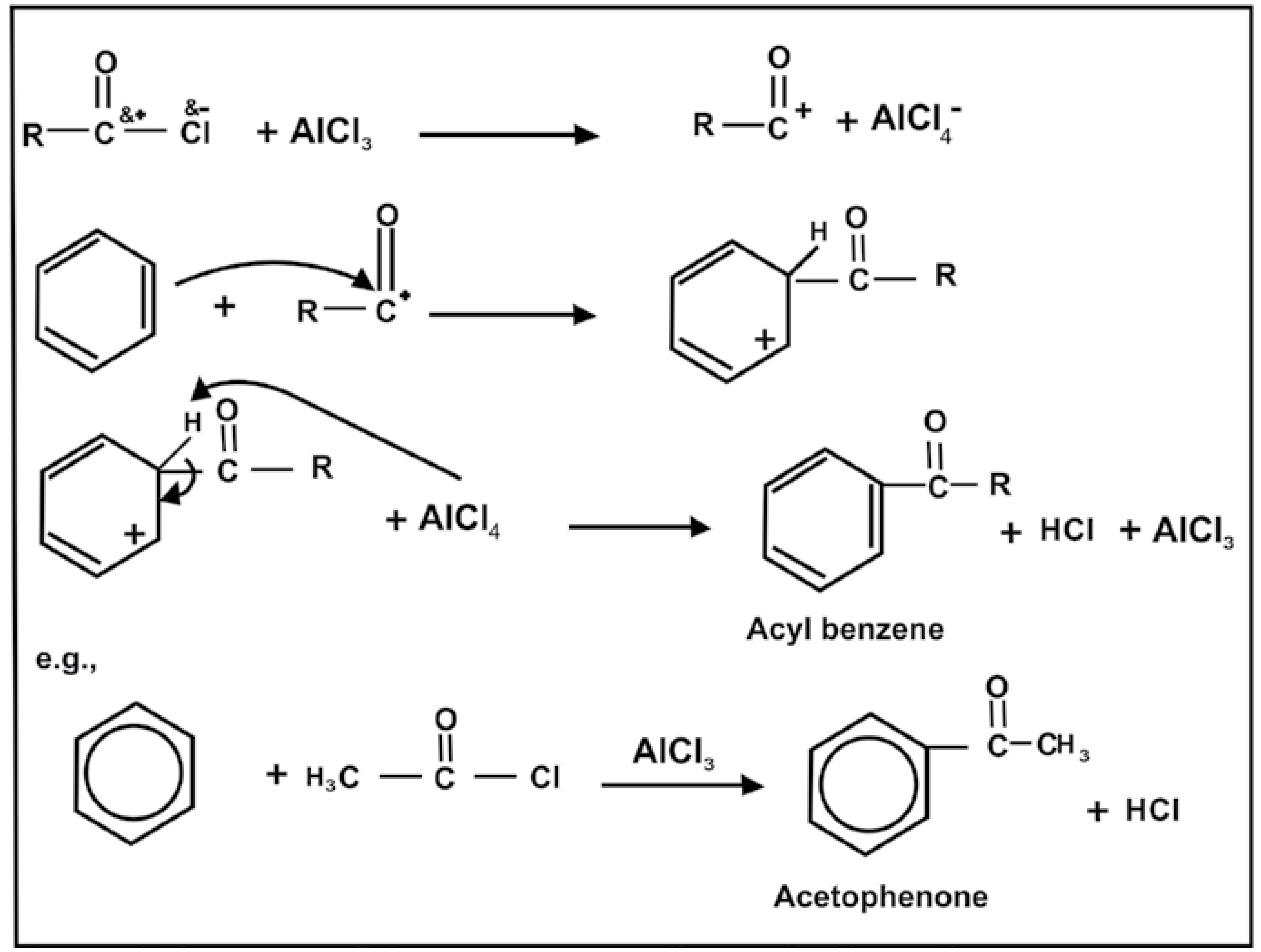
Carbocation





b) Acylation:

The introduction of an acyl group R-C(=O) in the benzene ring in the presence of an acyl halide and a catalyst $AlCl_3$ is called Friedel Crafts Acylation or Acylation.



Animation 9.10 : Friedel crafts reaction

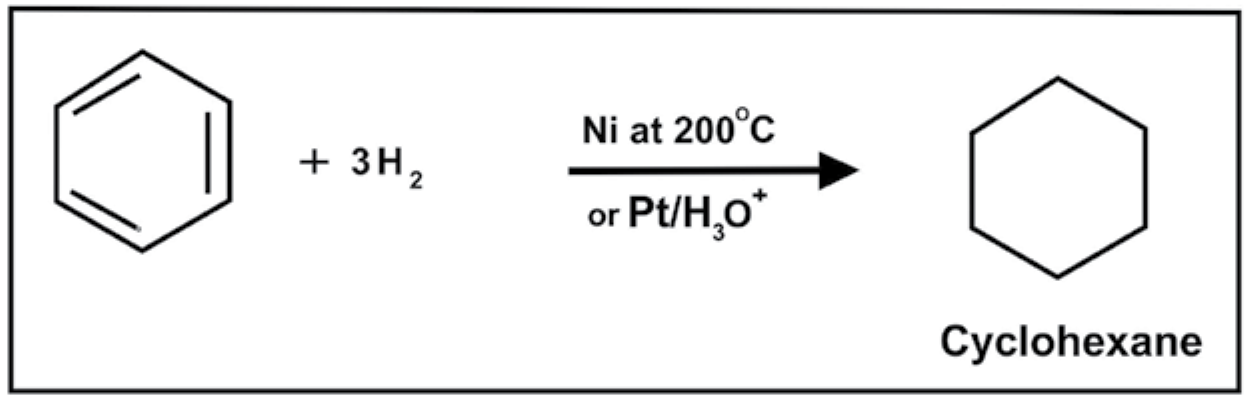
Source & Credit : Friedelcraft.chez.com

9.5.3 Reactions in which Benzene Ring is Involved

1. Addition Reactions

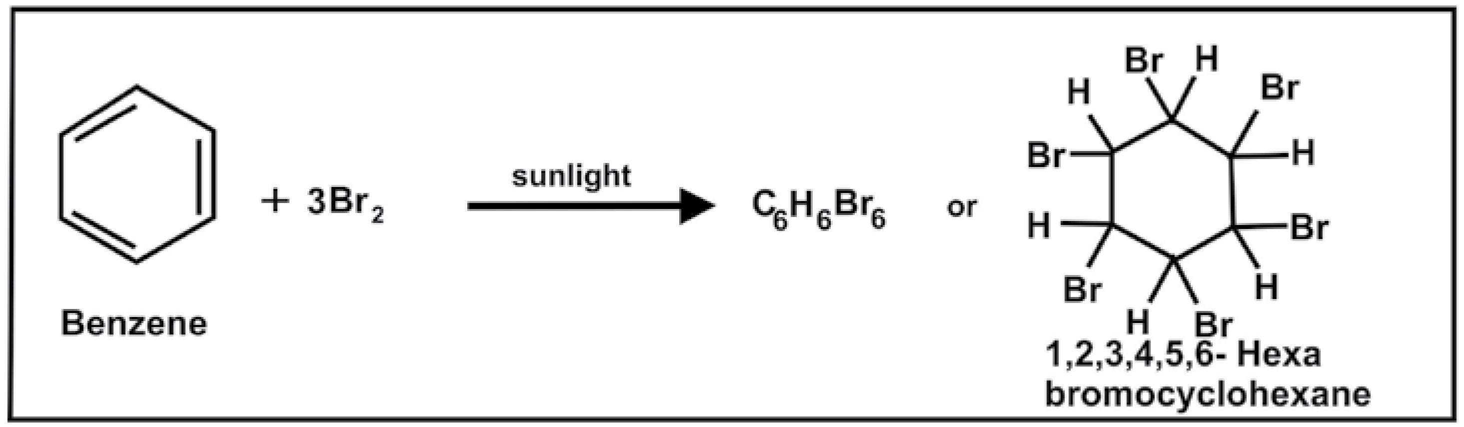
(a) Reduction:

Benzene is reduced to cyclohexane on heating at high temperature with hydrogen in the presence of Pt in an acidic solvent (acetic acid) or Ni at 200°C as a catalyst.



(b) Halogenation

Benzene reacts with chlorine and bromine in the presence of sunlight to give addition products, hexachlorobenzene or hexabromobenzene. Fluorination is too vigorous while iodination is slow.



(c) Combustion

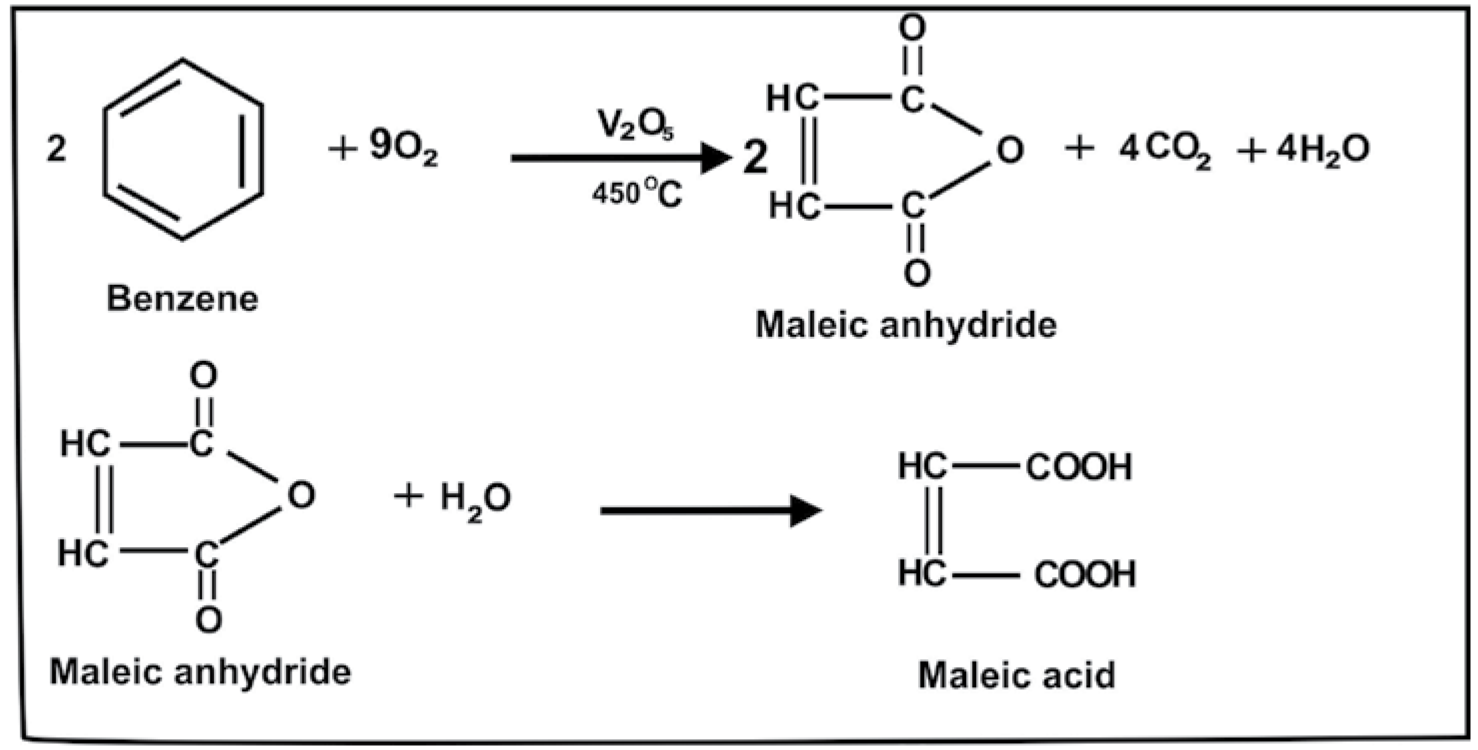
When benzene is burnt in free supply of air, it is completely oxidized to CO_2 and H_2O.

$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$$

(d) Oxidation

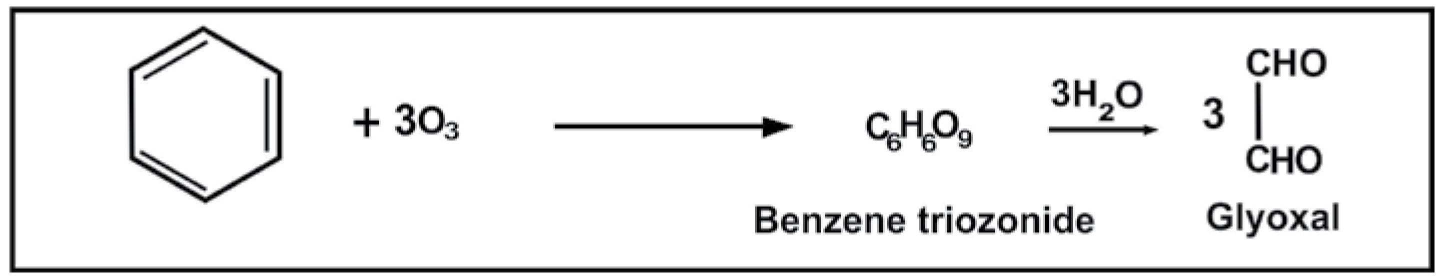
i) Catalytic Oxidation

Benzene is not oxidized by $KMnO_4$ or $K_2Cr_2O_7$ at room temperature. The ring is destroyed when benzene is strongly heated with air in the presence of V_2O_5 as a catalyst.



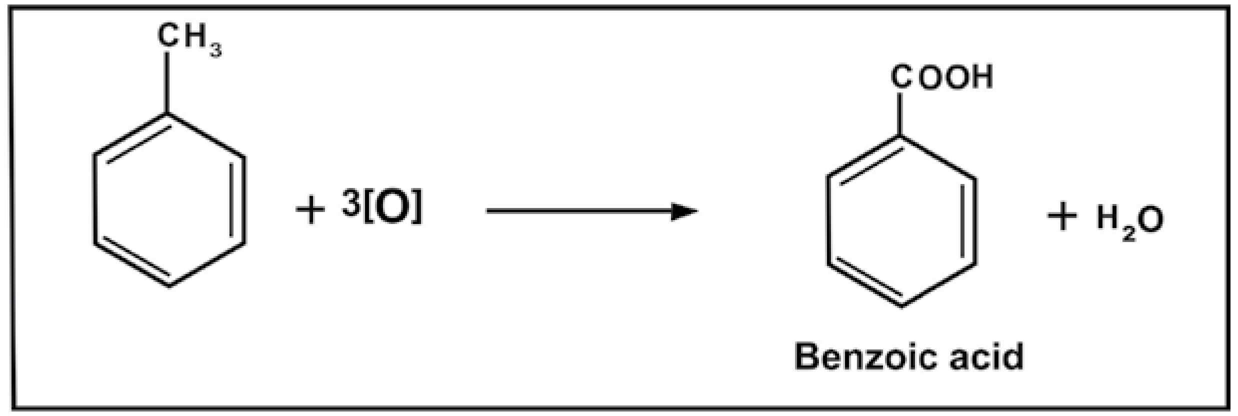
ii) Ozonolysis

Benzene reacts with ozone and gives glyoxal through benzene triozonide.

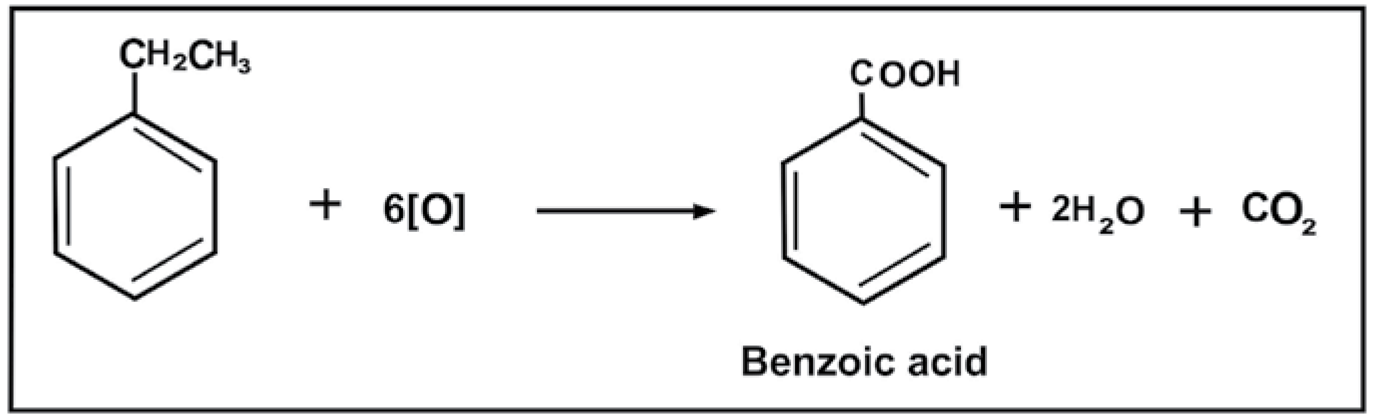


Side Chain Oxidation

Alkyl benzenes are readily oxidized by acidified $KMnO_4$ or $K_2Cr_2O_7$. In these reactions, the alkyl groups are oxidized keeping the benzene ring intact.

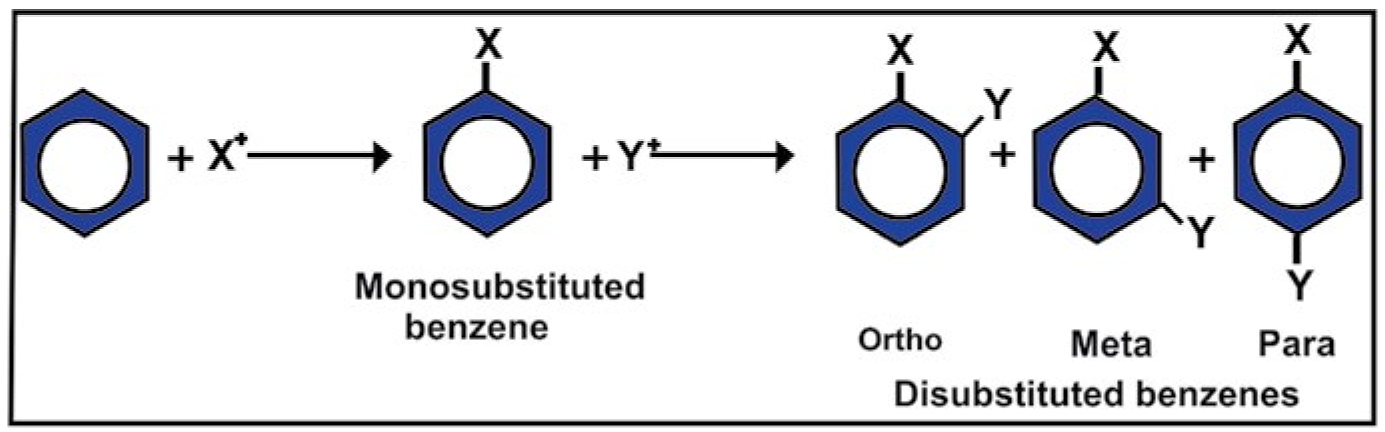


Whatever the length of an alkyl group may be it gives only one carboxyl group. Moreover the colour of $KMnO_4$ is discharged. Therefore this reaction is used as a test for alkyibenzenes.



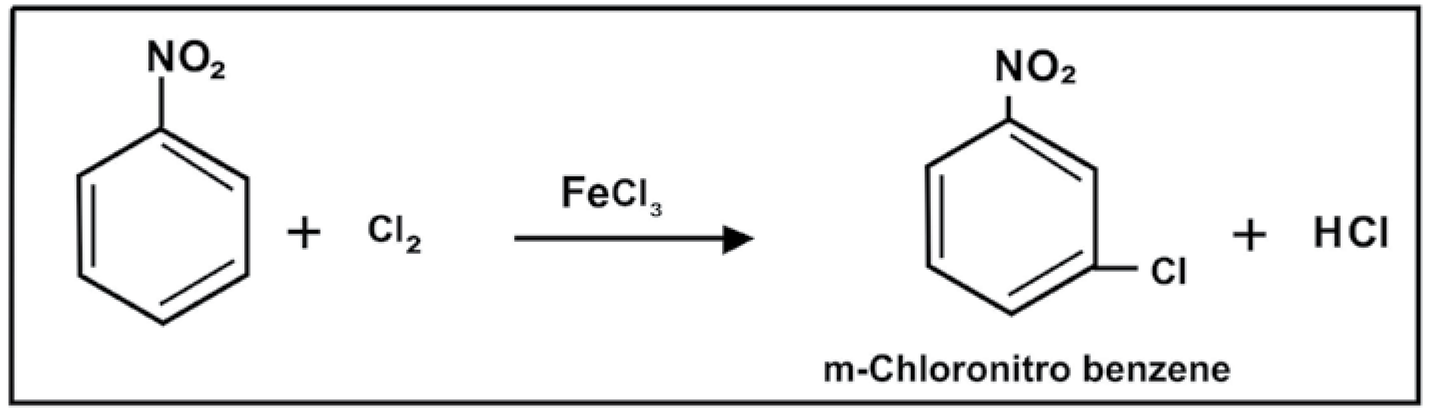
9.5.4 Orientation in Electrophilic Substitution reactions

When an electrophilic substitution reaction takes place on benzene ring, we get only one monosubstituted benzene because all the six positions in the ring are equivalent. However, the introduction of a second group into the ring may give three isomeric disubstituted products, ortho, meta and para.

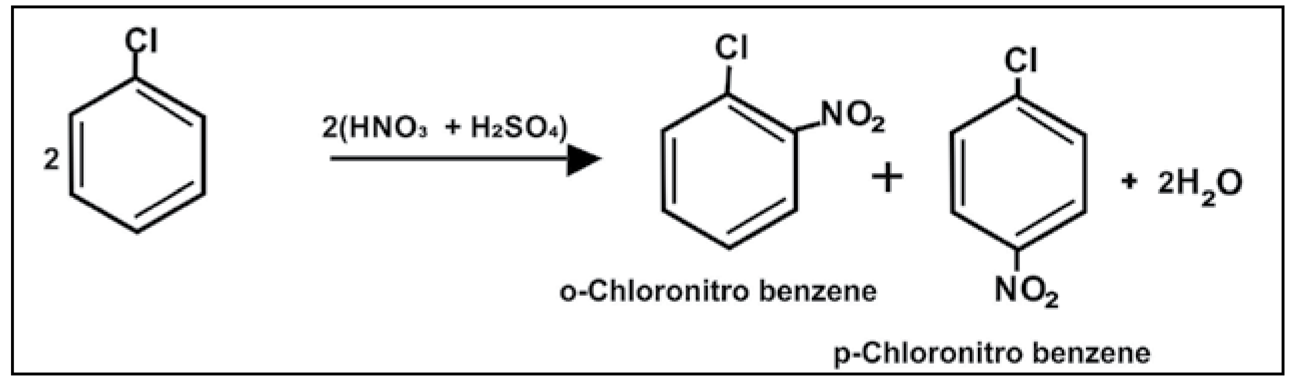


On chance basis 40% ortho, 40% meta and 20% para disubstituted products are expected.

But the actual disubstitution of benzene does not follow this principle of chance, e.g. m - Chloronitro benzene is the main product of the following halogenation reaction.



On the other hand a mixture of o- Chloronitrobenzene and p-Chloronrtrobenzene is obtained from the nitration of chlorobenzene.



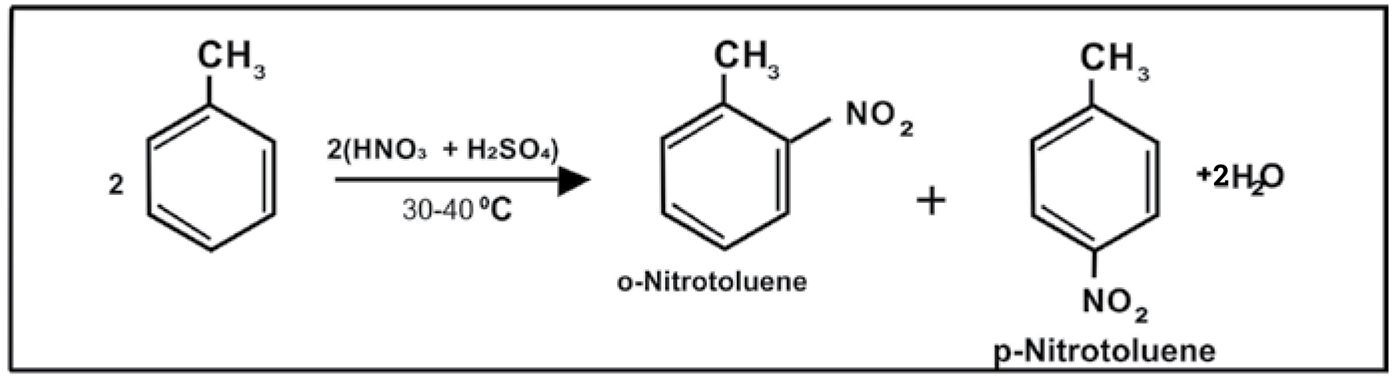
It means that the group present in the mono-substituted benzene ring has the directive effect and thus determines the position or orientation for the new incoming groups. Therefore, there are two types of groups:

1. ortho- and para- directing groups
2. meta- directing groups

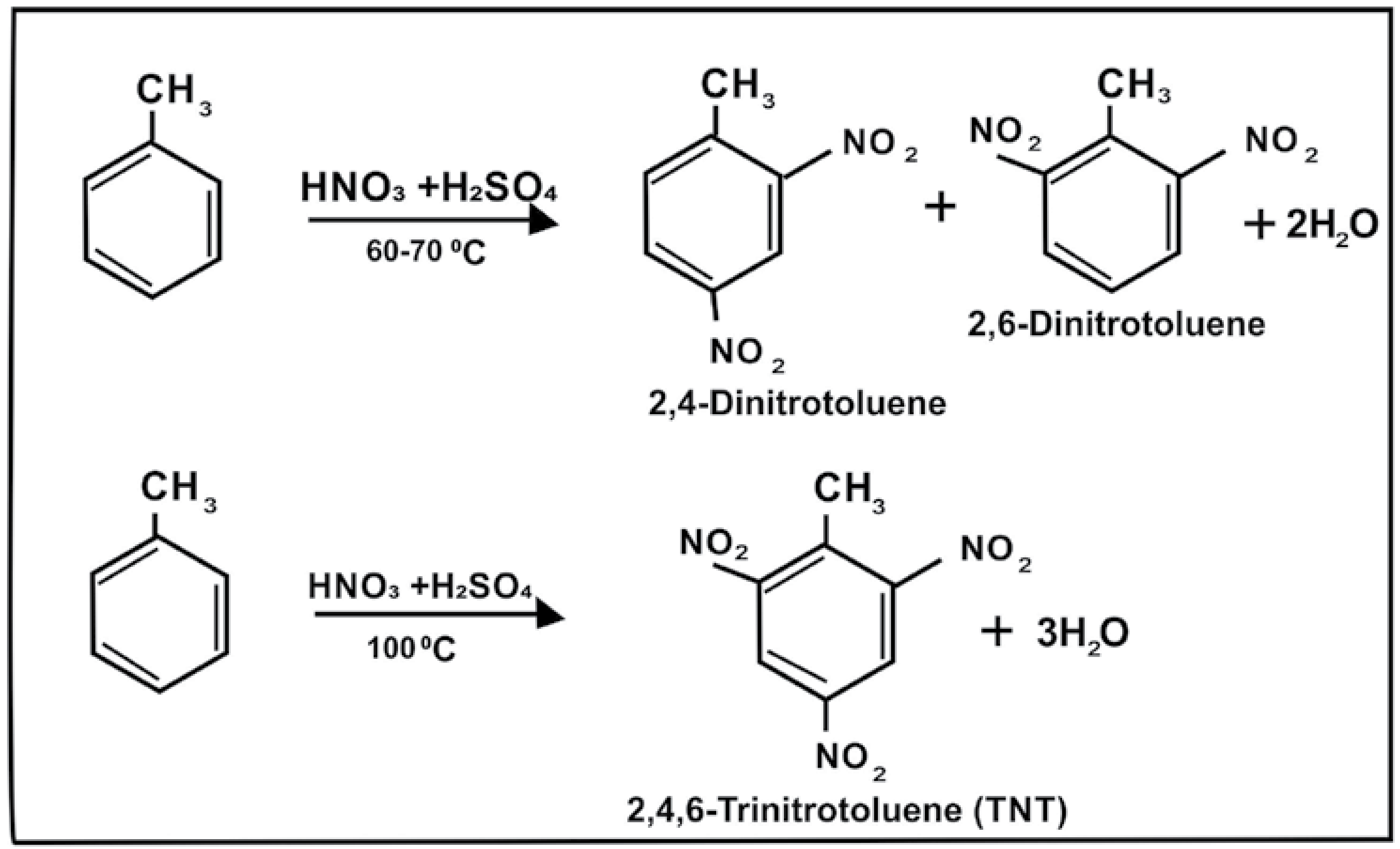
1. ortho and para Directing Groups

These groups release electrons to the benzene ring, thereby facilitating the availability of electrons to the electrophiles at ortho and para positions.

This results in the increased chemical reactivity of benzene ring towards electrophilies. The benzene ring can offer more than one positions (ortho and para) to the new incoming groups. These groups are called ortho and para directing groups, e.g.



The electron releasing effect of methyl group is significant and it makes the ring a good nucleophile. Due to this increased reacivity, more nitro groups can enter the ring.



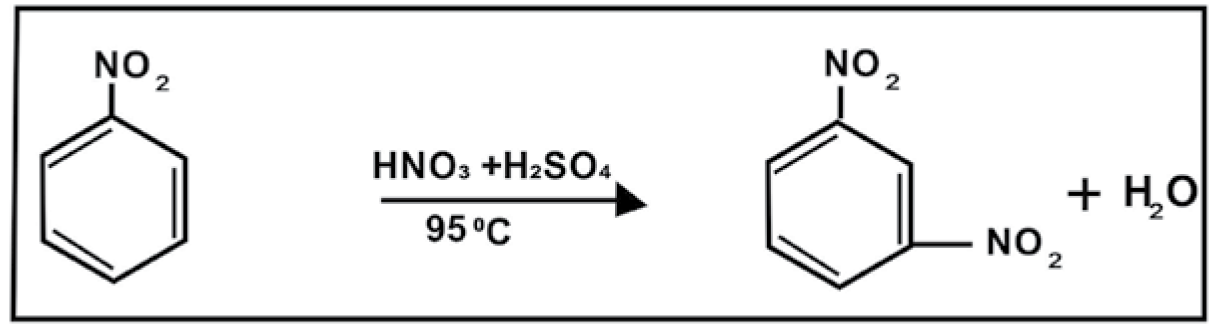
Other examples of ortho and para directing groups are:-

$$-N(CH_3)_2, -NH_2, -OH, -OCH_3, -Cl, -Br, -I$$

2. meta -Directin g Groups

These groups withdraw the electrons of the benzene ring towards themselves, thereby reducing their availability to the electrophiles.

This results in the decreased chemical reactivity of benzene. Moreover, due to the electron withdrawing effect of such substituents, the ortho and para positions are rendered more electron deficient than the meta position. Thus the incoming electrophile will prefer to attack on meta position rather than ortho and para positions. These groups are called meta-directing groups, e.g.



The substitution of third nitro group is not possible, other examples of meta directing groups are:

$$-N^+R_3, \quad -C\equiv N, \quad -COOH, \quad -CHO, \quad -COR$$

9.6 COMPARISON OF REACTIVITIES OF ALKANES,ALKENES AND BENZENE

We have studied that alkanes are unreactive class of compounds and their unreactivity is due to their non-polar nature and the inertness of σ-bond. However, they undergo substitution reactions relatively easily and these reactions involve free radicals.

Alkenes, on the other hand, are very reactive class of compounds and their reactivity is due to the inherent weakness of the π-bond and the availability of π electrons for the electrophilic reagents.

They undergo electrophilic addition reactions easily. Being relatively unstable, alkenes undergo polymerization reactions and they are also readily oxidized.

Benzene is unique in its behaviour. It is highly unsaturated compound and at the same time it is very stable molecule. The stability of benzene, as described earlier, is due to the extensive delocalization of π-electrons. It resembles alkenes when it gives addition reactions. The substitution of benzene, however, does not involve free radicals. These are electrophilic substitution reactions and involve electrophiles.

Its addition reactions require more drastic conditions than those for alkenes. Benzene does not undergo polymerization and it is also resistant to oxidation.

KEYPOINTS

1. Aromatic hydrocarbons include benzene and all those compounds that are structurally related to benzene.
2. Aromatic hydrocarbons containing one benzene ring in their molecules are called monocyclic aromatic hydrocarbons.
3. Aromatic hydrocarbons containing two or more benzene rings in their molecules are called polycyclic aromatic hydrocarbons.
4. Benzene was discovered by Michael Faraday in 1825.
5. The electrons in benzene are loosely held and the ring acts as a source of electrons. Hence benzene is readily attacked by electrophiles in the presence of a catalyst.
6. Since electrophilic substitutions reaction lead to resonance stabilized benzene derivatives so substitutions are the main reactions of benzene.
7. Resonance energy of benzene is 150.5 kJ/mole.
8. Structure of benzene is the resonance hybrid of two Kekule's structures and three Dewar's structures.
9. Groups like NH_2, NHR, - OR, - SH, - OCOR, - X, - OH, etc. which increase the electron density in the nucleus and facilitate further electrophilic substitutions are known as ortho- and para-directing groups.
10. Groups like CN, - CHO, NH_3, NR_3, CCl_3 which hinder further substitution in the benzene nucleus are known as meta- directing groups.

EXERCISE

Q1. Fill in the blanks.

i) The term aromatic was derived from Greek word__________ meaning ______________.
ii) Aromatic hydrocarbons include benzene and all those compounds which are __________ related to benzene.
iii) ____________is recognized as the simplest member of the class of Aromatic Hydrocarbons.
iv) Benzene has______________structure.
v) These removal of hydrogen atom from aromatic hydrocarbons gives a radical. The radicals are called_________ .
vi) Benzene was discovered by Michael Faraday in______ .
vii) The unhybridized $2p_z$ orbitals in benzene partially overlap to form a __________ of electron cloud.
viii) The introduction of halogen group in benzene ring is called______.
ix) The molecular formula of C_6H_6 indicates that it is highly_________ compound.
x) On oxidation in the presence of V_2O_5 benzene gives_________.

Q.2 Indicate True or False.

i) Benzene is more reactive than alkene and less reactive than alkane.
ii) Benzene has a pentagonal structure.
iii) The C-C bond length in benzene molecule is 1.397 Å.
iv) The state of hybridization of carbon in benzene molecule is sp^3.
v) There are six sigma bonds in benzene molecule.
vi) Halogenonium ion produced in electrophilic substitution reactions is a powerful electrophile.
vii) In electrophilic substitution reactions, addition products are favourable.
viii) Sulphonation is carried out when benzene is heated with conc. HNO_3.
ix) In ozonolysis benzene directly gives glyoxal.
x) Benzene has five resonace contributing structures.

Q.3. Multiple choice questions. Encircle the correct answer.

i) The benzene molecule contains
(a) Three double bonds (b) Two double bonds
(c) One double bond (d) Delocalized π-electron charge

ii) Aromatic hydrocarbons are the derivatives of

(a) normal series of paraffins (b) alkene
(c) benzene (d) cyclohexane

iii) Which of the following acid can be used as a catalyst in Friedel-Crafts reactions?
(a) $AlCl_3$ (b) HNO_3 (c) $BeCl_2$ (d) NaCl

iv) Benzene cannot undergo
(a) substitution reactions (b) addition reactions
(c) oxidation reactions (d) elimination reactions

v) Amongst the following, the compound that can be most readily sulphonated is
(a) toluene (b) benzene (c) nitrobenzene (d) chlorobenzene

vi) During nitration of benzene, the active nitrating agent is
(a) NO_3 (b) NO_2^+ (c) NO_2^- (d) HNO_3

vii) Which compound is the most reactive one:
(a) benzene (b) ethene (c) ethane (d) ethyne

viii) The electrophile in aromatic sulphonation is:
(a) H_2SO_4 (b) HSO_4 (c) SO_3 (d) SO_3^+

ix) Aromatic compounds burn with sooty flame because:
(a) They have high percentage of hydrogen.
(b) They have a ring structure.
(c) They have high percentage of carbon.
(d) They resist reaction with air.

x) The conversion of n-hexane into benzene by heating in the presence of Pt is called:
(a) Isomerization (b) Aromatization
(c) Dealkylation (d) Rearrangement

Q. 4. What are aromatic hydrocarbons? How are they classified?

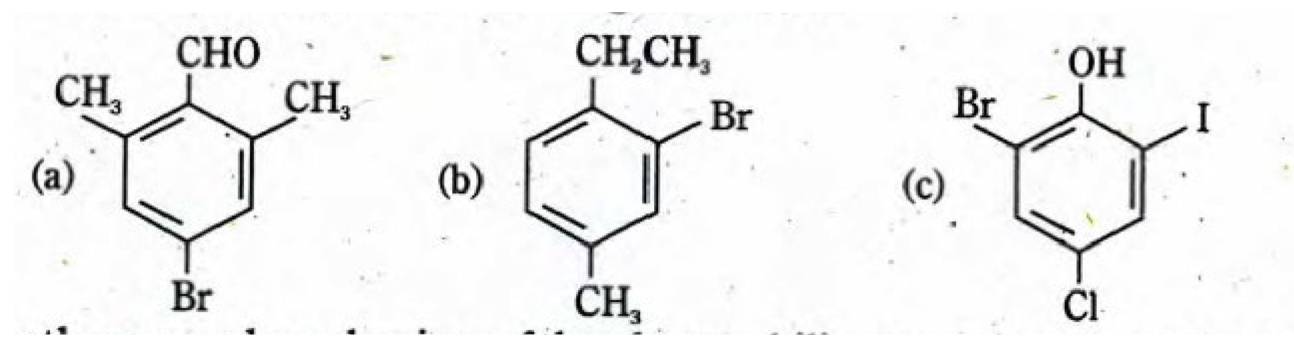
Q. 5. What happens when:
(a) Benzene is heated with conc. H_2SO_4 at 250°C.
(b) Chlorine is passed through benzene in sunlight.
(c) A mixture of benzene vapours and air are passed over heated vanadium pentoxide.
(d) Benzene is burnt in free supply of air.

Q.6. What is meant by the terms:
i) Aromatic ii) Oxidation iii) Sulphonation
iv) Nitration v) Halogenation

Q. 7. (a) Draw structural formulas for the following compounds.
i) m-Chlorobenzoic acid vi) 2,4,6 Trinitrotoluene
ii) p-Hydroxybenzoic acid vii) m-Nitrophenol
iii) o-Bromonitrobenzene viii) p-Dibenzylbenzene
iv) o-Ethyltoluene ix) 2-Amino-5-bromo-3 nitrobenzenesulphonic acid
v) p-Nitroaniline
(b) Give names and the possible isomeric structuresof the following.

i) Xylenes ii) Trimethylbenzene iii) Bromonitrotoluene

Q. 8. Write IUPAC names of the following molecules.



Q. 9. Give the general mechanism of the electrophilic aromatic substitution reactions.

Q. 10. (a) Describe the structure of benzene on the basis of following.
i) Atomic orbital treatment ii) Resonance method
(b) Prove that benzene has a cyclic structure.

Q. 11. Predict the major products of bromination of the following compounds.

(a) Toluene (b) Nitrobenzene (c) Bromobenzene

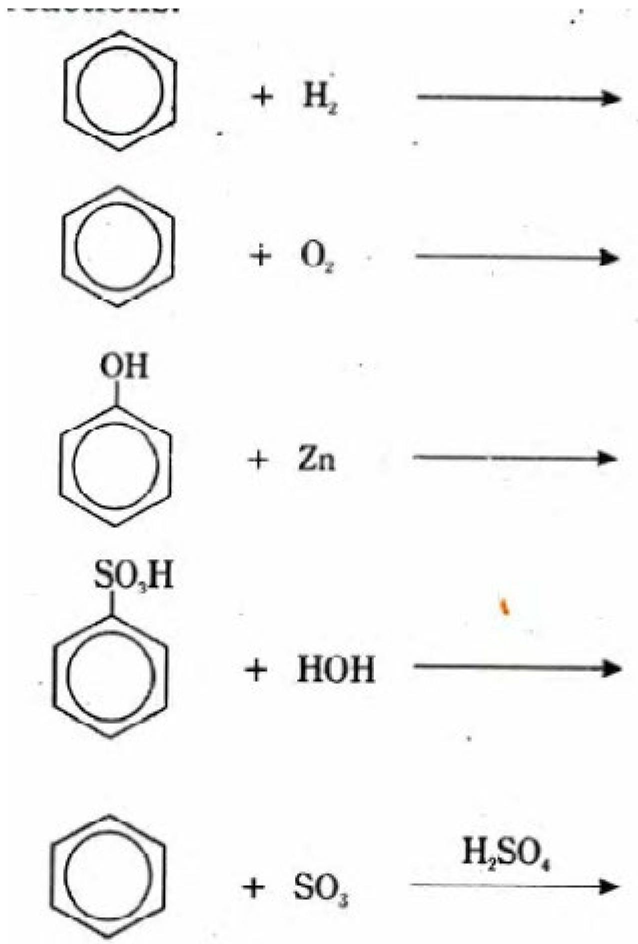
(d) Benzoic acid (e) Benzaldehyde (f) Phenol

Q. 12. How will you prepare the following compounds from benzene in two steps.

(a) m-chloronitrobenzene

(b) p-chloronitrobenzene

Q. 13. Complete the following reactions. Also mention the conditions needed to carry out these reactions.



Q. 14. Detail out three reactions in which benzene behaves as if it is a saturated hydrocarbon and three reactions in which it behaves as if it is unsaturated.

Q. 15. What are Frediel-Crafts reactions. Give mechanism with example of the following reactions.

i) Friedel-Crafts alkylation reactions

ii) Friedel-Crafts acylation reactions.

CHAPTER 10

ALKYL HALIDES

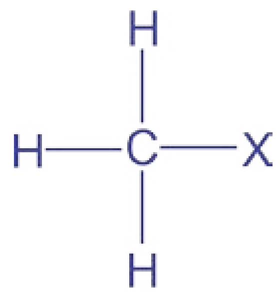
Animation 10.1: Alkyl Halides reaction
Source & Credit: chemwiki

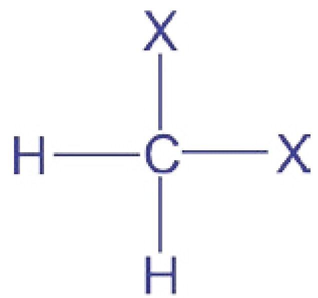
IN THIS CHAPTER YOU WILL LEARN:

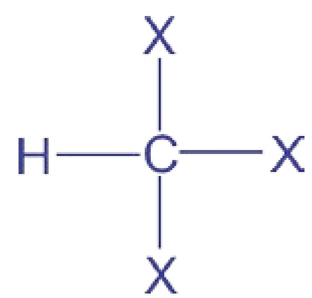
1. How to name an alkyl halide and to classify it into primary, secondary and tertiary alkyl halides.
2. Simple ways of generating alkyl halides.
3. The reason why C-X bond in chemistry is one of the most reactive type.
4. The general mechanistic details of nucleophilic substitution and elimination reactions.
5. The preparation of Grignard's reagent, the reactivity of C-Mg bond and its synthetic applications in organic chemistry.

10.1 INTRODUCTION

Halogen derivatives of alkanes are called haloalkanes. They may be mono, di, tn or poly haloalkanes depending upon the number of halogen atoms present in the molecule.


Monohaloalkane


Dihaloalkanez


Trihaloakane

Among these, monohaloalkanes are also called Alkyl Halides. Their general formula is R -- X , where R may be methyl, ethyl, propyl, etc. and X represents halogen atoms (F, Cl, Br, I). Mono haloalkanes or alkyl halides are further classified into primary, secondary and tertiary alkyl halides depending upon the type of carbon atom bearing the halogen atom.

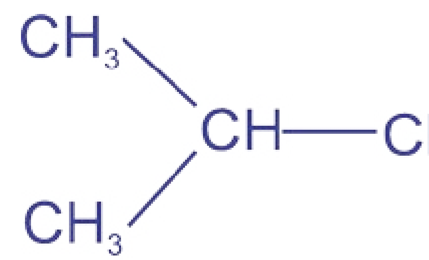
In a primary alkyl halide halogen atom is attached with a carbon which is further attached to one or no carbon atom e.g.,

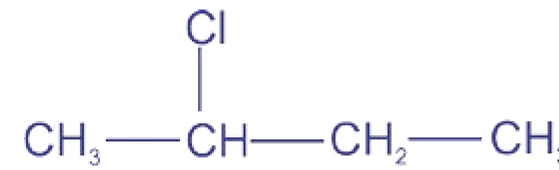
$CH_3 — Cl$ Chloromethane

$CH_3 — CH_2 — Cl$ Chloroethane

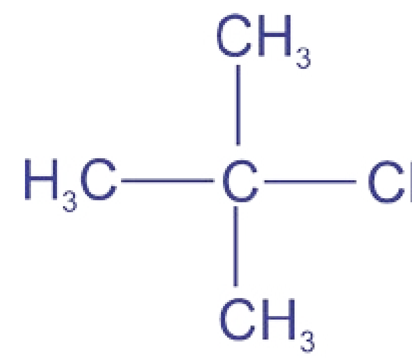
$CH_3 — CH_2 — CH_2 — Cl$ 1-Choropropane

Secondary alkyl halides are those in which halogen atom is attached with a carbon atom which is further attached to two other carbon atoms directly, e.g., secondary carbon atom.


2-Chloropropane


2-Chlorobutane

In tertiary alkyl halides halogen atom is attached to a carbon which is further attached to three carbon atoms directly.


2-Chloro-2-methylpropane

10.2 NOMENCLATURE OF ALKYL HALIDES

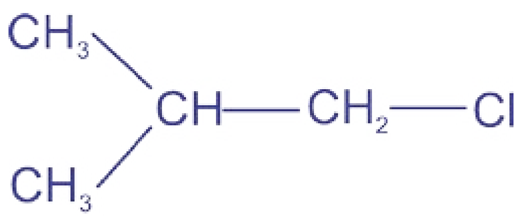
COMMON NAMES

Alkyl halides (monohaloalkanes) are named according to the nature of the alkyl group to which halogen atom is attached. For example,

$CH_3 - Cl$
Methyl chloride

$CH_3 - CH_2 - Br$
Ethyl bromide

$CH_3 - CH_2 - CH_2 - Br$
n-Propyl bromide

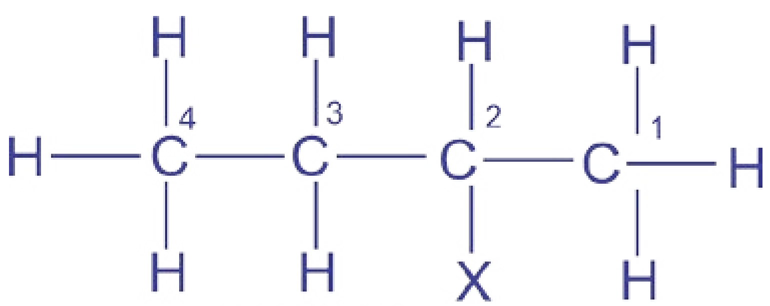

Isobutyl chloride

$CH_3 - CH_2 - CH_2 - CH_2 - Cl$
n-Butylchloride

IUPA C Nomenclature

The systematic names given to alkyl halides follow the underlying rules.

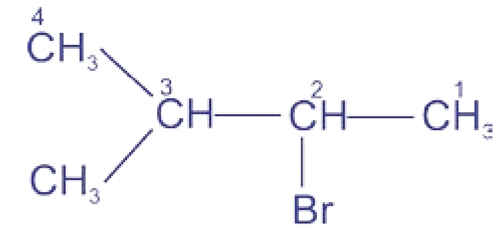
1. Select the longest continuous carbon chain and consider the compound to have been derived from this structure.
2. Number the carbon atoms in the chain so that the carbon atom bearing the functional group (F, Cl, Br, I) gets the lowest possible number, e.g.,

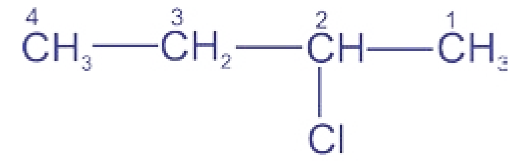

2-Halobutane

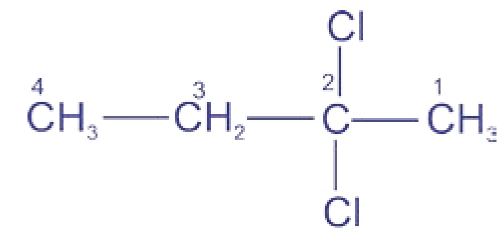
3. If the same alkyl substituent occurs more than once on the chain, the prefix di, tri and so on are used before the name of the alkyl group.
4. The positions of the substituents are indicated by the appropriate numbers separated by commas. If the same substituent occurs twice or more on the same carbon atom the number is repeated.

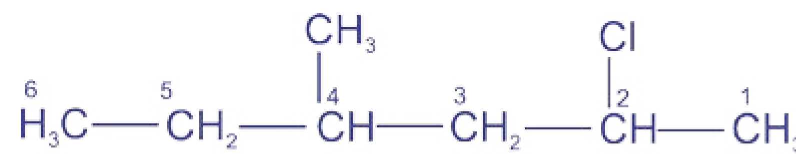
Examples which follow the above mentioned rules:

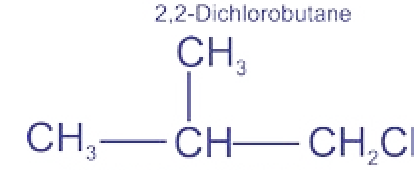

1-Chloropropane

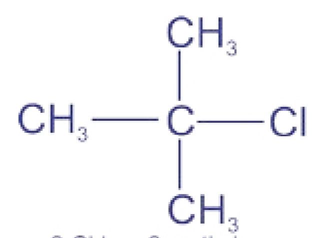

2-Bromo-3-methylbutane

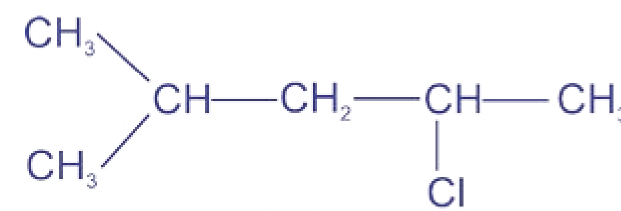

2-Chlorobutane

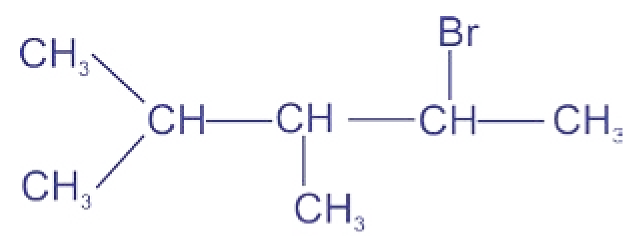

2,2-Dichlorobutane


2-Chloro-4-methylexane


1-Choro-2-methylpropane


2-Chloro-2-methylpropane


2-Chloro-4-methylpentance


2-Bromo-3,4-dimethylpentane

10.3 METHODS OF PREPARATION OF ALKYL HALIDES

Alkyl halides can be prepared by the halogenation of alkanes and by the addition of halogen acids to alkenes. These methods have already been discussed in the previous chapters. The best method for the preparation of alkyl halides is from alcohols.

1. From Alcohols

(a) Reaction of alcohols with halogen acids.

Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of $ZnCl_2$ which acts as a catalyst.

$$CH_3CH_2—OH + HX \xrightarrow{ZnCl_2} \underset{\text{Ethyl halide}}{CH_3CH_2—X} + H_2O$$

(b) Alcohols also react with thionyl chloride in pyridine as a solvent to give alkyl chlorides. This method is especially useful since the by-products (HC1, SO_2) are gases, which escape leaving behind the pure product.

$$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} R—Cl + SO_2 + H_2O$$

(c) Phosphorus trihalides or phosphorus pentahalides react with alcohols to replace -OH group by a halo group.

$$3CH_3—CH_2—OH + PBr_3 \longrightarrow 3CH_3—CH_2—Br + H_3PO_3$$

$$CH_3—CH_2—OH + PCl_5 \longrightarrow CH_3—CH_2—Cl + POCl_3 + HCl$$

2. An excellent method for the preparation of simple alkyl iodide is the treatment of alkyl chloride or alkyl bromide with sodium iodide. This method is particularly useful because alkyl iodides cannot be prepared by the direct iodination of alkanes.

$$RCl—NaI \longrightarrow RI + NaCl$$

$$RBr—NaI \longrightarrow RI + NaBr$$

10.4 REACTIVITY OF ALKYL HALIDES

An alkyl halide molecule (R — X) consists of two parts, an alkyl group with a partial positive charge on the carbon atom attached to halogen atom and the halide atom with a partial negative charge.

There are two main factors which govern the reactivity of R — X bond. These are:

i) C— X Bond energy
ii) C— X Bond polarity

Bond Energy

The following table shows the bond energies of C— X bonds in alkyl halides.

Bond	Bond Energy (kj/mole)
C — F	467
C — H	413
C — Cl	346
C — Br	290
C — I	228

The strength of the bonds show that iodo compound (with the weakest bonds) would be the most reactive one while fluoro compound will be the least reactive i.e., the order of reactivity of alkyl halides should be

R— I > R— Br > R— Cl > R— F

Bond Polarity

Electronegativities of halogen, carbon and hydrogen atoms present in alkyl halides are shown in the table.

Atom	Electronegativity
F	4.0
Cl	3.0
Br	2.8
I	2.5
H	2.1
C	2.5

The greatest electronegativity difference exists between carbon and fluorine atoms in alkyl fluorides.

If an electrophile is the attacking reagent then this difference suggests that alkyl fluorides would be the most reactive one. On the same lines, alkyl iodides should be the least reactive alkyl halides.

In the light of the above discussion it is clear that the two factors mentioned above predict different types of behaviour about the reactivity of alkyl halides. Experiments have shown that the strength of carbon halogen bond is the main factor which decides the reactivity of alkyl halides.

So the overall order of reactivity of alkyl halides for a particular alkyl group is:

Iodide > Bromide > Chloride > Fluoride

In fact the C-F bond is so strong that alkyl fluorides do not react under ordinary conditions.

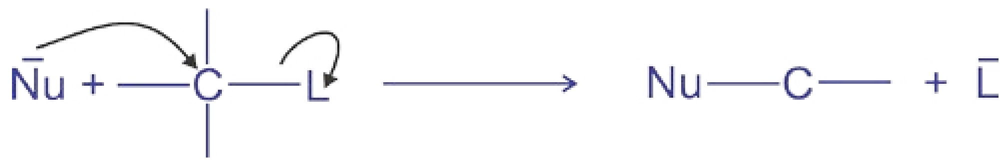
10.5 REACTIONS OF ALKYL HALIDES

The reactions of alkyl halides fall into two categories.

1. Those reactions in which the halogen is replaced by some other atom or a group (nucleophilic substitution, or S_N reactions).
2. Tnose which involve the removal of HX from the nanae (elimination, or E reactions).

10.5.1 Nucleophilic Substitution Reactions

Before discussing specifically the nucleophilic substitution reactions (S_N) of alkyl halides, let us look at the nucleophilic reaction in general. The overall process describing an S_N reaction is shown as follows:



In this equation the incoming group Nu is a nucleophile. Nucleophile means nucleus loving. It has an unshared electron pair available for bonding and in most cases it is basic in character. It may be negatively charged or neutral.

Examples of Nucleophiles

HO^-	Hydroxide ion	Cl^-	Chloride ion
$C_2H_5O^-$	Ethoxide ion	Br^-	Bromide ion
HS^-	Hydrogen sulphide ion	$\ddot{N}H_3$	Ammonia
SCN^-	Thiocyanate ion	CN^-	Cyanide ion
$H_2O:$	Water	I^-	Iodide ion
NH_2^-	Amino group		

Electrophile

It is a specie which attracts electrons (electron loving). The carbon atom of an alkyl group attached with the halogen atom and bearing a partial positive charge is called an electrophile or electrophilic center. An electrophile may be neutral or positively charged.

Animation 10.3: Electrophilic addition
Source & Credit: johnwiley

Leaving Group

L is also a nucleopile. It is called leaving group because it departs with an unshared pair of electrons. If we wish a S_N reaction to proceed in the forward direction the incoming nucleophile must be stronger than the departing one. Cl^-, Br^-, I^-, HSO_4^- are good leaving groups. Poor leaving groups are OH^-, $\overline{O}R$ and NH_2^-. Iodide ion is a good nucieophile as well as a good leaving group.

Substrate Molecule

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

10.5.2 Mechanism of Nucelophilic Substuitution Reactions

Alkyl halides may undergo nucleophilic substitution reactions in two different ways:

1. Nucleophilic Substitution Bimolecular (S_N2)
2. Nucleophilic Substitution Unimolecular (S_N1)

Nucleophilic substitution reactions on alkyl halides involve two main processes, the breakage of C — X bond and the formation of C — Nu bond. The mechanism of the nucleophilic substitution reactions depends upon the timing of these two processes.

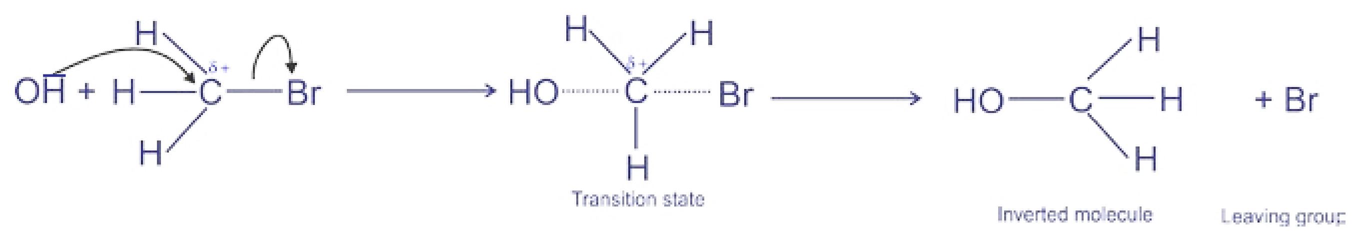
If the two processes occur simultaneously the mechanism is called S_N2 . If the bond breaks first followed by the formation of a new bond, the mechanism is called S_N1.

Nucleophilic Substitution Bimolecular (S_N2)

This is a single step mechanism. As soon as the nucleophile starts attacking the electrophilic carbon of the substrate, the bond with which the leaving group is attached, starts breaking. In other words the extent of bond formation is equal to the extent of bond breakage.

Another important feature of this mechanism is the direction of the attack of the attacking nucleophile. It attacks from the side which is opposite to the leaving group.

In order to give to the nucleophile enough room to attack, the substrate carbon atom changes its state of hybridization from tetrahedral sp^3 to planar sp^2. The attack of the nuclephile, the change in the state of hybridization and the departure of the leaving group, every thing occurs at the same time.



During the reaction the configuration of the alkyl halide molecule gets inverted. This is called inversion of configuration.

Molecularity of a reaction is defined as the number of molecules taking part in the rate determining step. Since in this mechanism, the reaction takes place in only one step which is also a rate determining step and two molecules are participating in this step, so it is called a bimolecular reaction.

Kinetic studies of the reactions involving S_N2 mechanism have shown that the rates of such reactions depend upon the concentrations of alkyl halide as well as the attacking nucleophile. Mathematically, the rate can be expressed as:

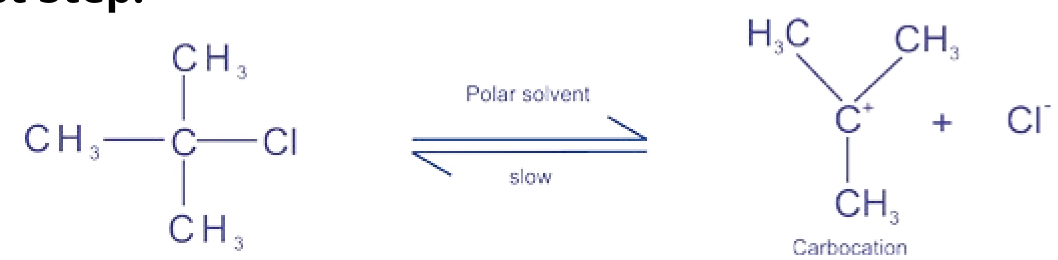
$$\text{Rate} = k\,[\text{Alkyl halide}]^1\,[\text{Nucleophile}]^1$$

Since the exponents of the concentration terms in the above expression are unity, so the order of a typical S_N2 reaction will be 1 + 1 = 2. Among the alkyl halides, the primary alkyl halides always follow S_N2 mechanism whenever they are attacked by nucleophiles.

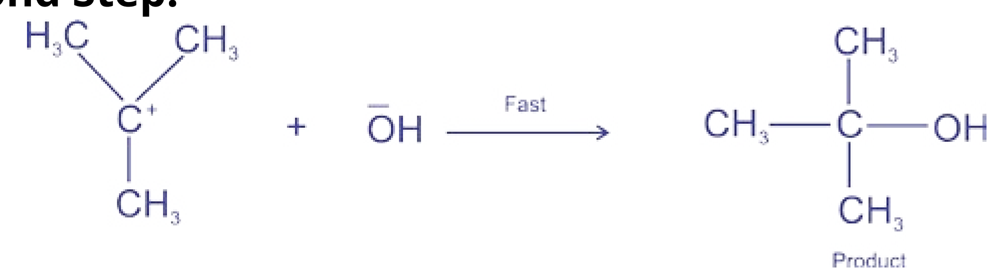
Nucleophilic Substitution Unimolecular (S_N1)

This type of mechanism involves two steps. The first step is the reversible ionization of the alkyl halide in the presence of an aqueous acetone or an aqueous ethyl alcohol. This step provides a carbocation as an intermediate. In the second step this carbocation is attacked by the nucleophile to give the product.

First Step:

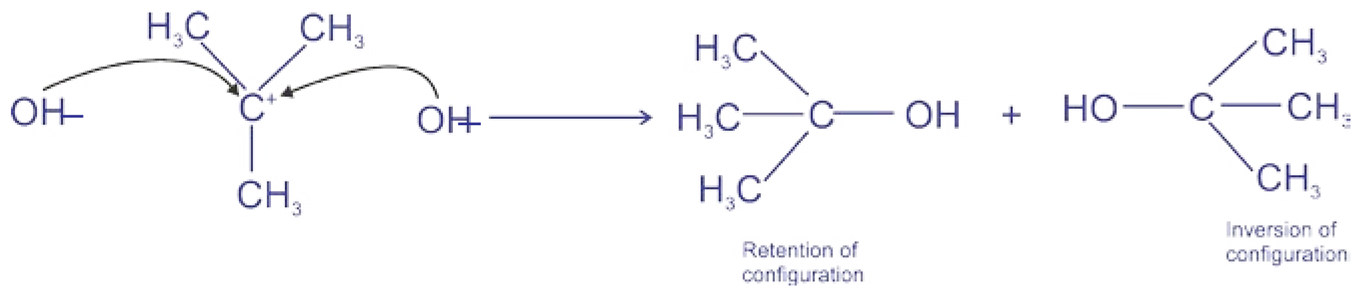


Second Step:



Since the first step involves the breakage of a covalent bond so it is a slow step as compared to the second step which involves the energetically favourable combination of ions. The first step is, therefore, called the rate-determining step. The mechanism is called unimolecular because only one molecule takes part in the rate determining step.

In S_N1 mechanism, the nucleophile attacks when the leaving group had already gone, so the question of the direction of the attack does not arise. Moreover, the intermediate carbocation is a planar specie allowing the nucleophile to attack on it from both the directions with equal ease. We, therefore, observe 50% inversion of configuration and 50% retention of configuration.



Reactions involving S_N1 mechanism show first order kinetics and the rates of such reactions depend only upon the concentration of the alkyl halide. The rate equation of such reactions can be written as follows.

Rate = k [Alkyl halide]

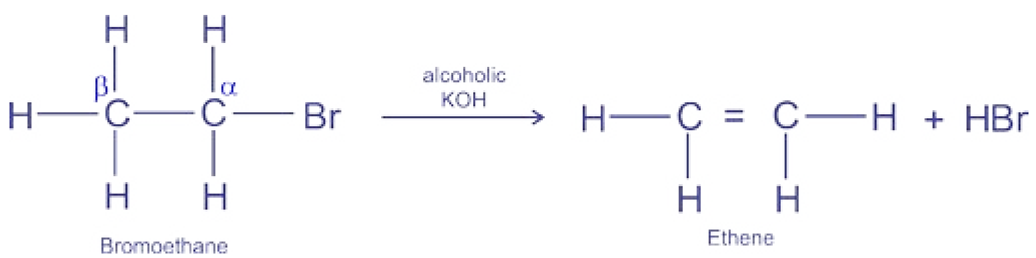
Tertiary alkyl halides when attacked by a nucleophile always follow S_N1 mechanism. Secondary alkyl halides, on the other hand, follow both S_N1 and S_N2 mechanisms.

10.5.3 β-Elimination Reactions

During nucleophilic substitution reactions, the attacking nucleophile attacks the electrophilic carbon atom of the alkyl halide. There is another site present in the alkyl halide molecule where the nucleophile can attack at the same time.Such a site is an electrophilic hydrogen atom attached to the β-carbon of the alkyl halide.

When the attack takes place on hydrogen, we get an alkene instead of a substitution product. Such a type of reactions are called elimination reactions.

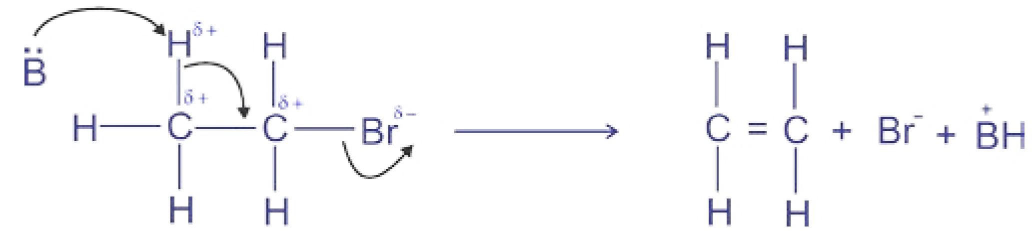
These reactions take place simultaneously with substitution reactions and often compete with them.



Like nucleophilic substitutions, the elimination reactions can also follow E2 or E1 mechanism.

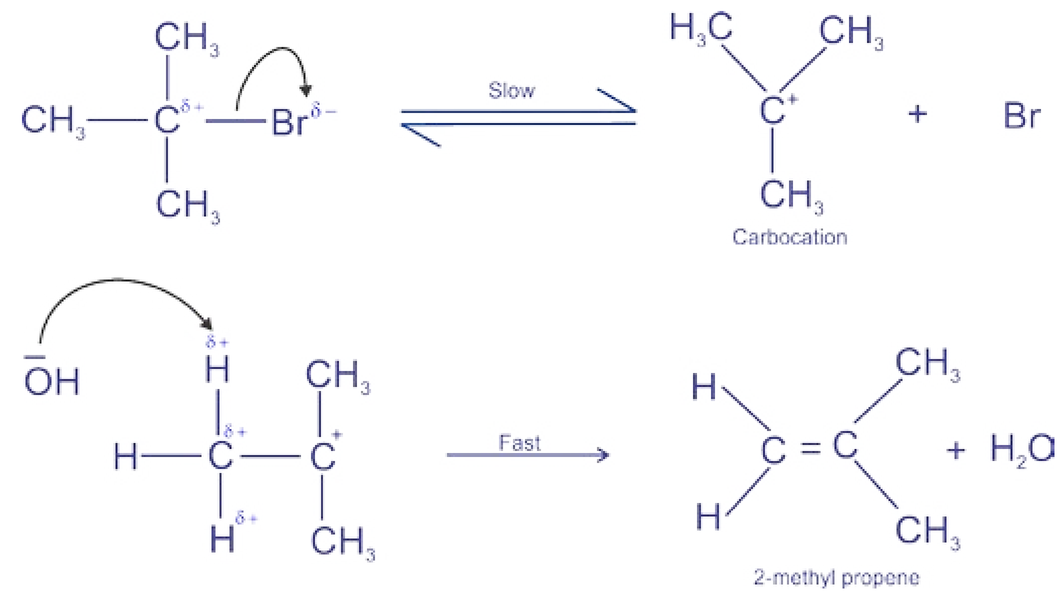
In E2 mechanism, the nucleophile attacks and the leaving group leaves at the same time with a formation of carbon carbon double bond.

The single step E2 elimination



Like S_N2 reactions, the molecularity of E2 reactions is also two and these reactions show second order kinetics.

In E1 mechanism, like S_N1 mechanism, the first step is the slow ionization of the substrate to give a carbocation. In the second step, the nucleophile attacks on hydrogen to give an alkene as a product



E2 mechanism is a bimolecular mechanism and the rates of those reactions which follow this mechanism depend upon the concentrations of the alkyl halide as well as the attacking nucleophile or a base. E1 mechanism, on the other hand, is a unimolecular mechanism and the rates of those reactions which follow this mechanism depend only upon the concentration of the alkyl halide molecule. Primary alkyl halides generally follow E2 mechanism whereas tertiary alkyl halides follow E I mechanism.

Examples of S_N reactions are given below.These reactions show the usefulness of alkyl halides as synthetic reagents.

Substrate	Attacking Nucleophile	Product
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	$\overline{O}H$	→ C_2H_5OH (Ethyl alcohol) + Br^-
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	I^-	→ C_2H_5I (Ethy liodide) + Br^-
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	CN^-	→ C_2H_5CN (Propane nitrile) + Br^-
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	NO_2^-	→ $C_2H_5NO_2$ (Nitroethane) + Br^-
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	CH_3O^-	→ $CH_3—CH_2—O—CH_3$ (Ethyl methyl ether) + Br^-
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	$\ddot{N}H_3$	→ $C_2H_5—NH_2$ (Ethylamine) + HBr
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	$CH_3—CH_2—\ddot{N}H_2$	→ $(CH_3—CH_2)_2NH$ (Diethylamine) + HBr
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	$(CH_3—CH_2)_2\ddot{N}H$	→ $(CH_3—CH_2)_3N$ (Triethylamine) + HBr
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	$(CH_3—CH_2)_3\ddot{N}$	→ $(CH_3—CH_2)_4N$ (Quaternary ethylammonium ion) + Br^-
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	$\overline{S}H$	→ C_2H_5SH (Ethyl thioalcohol) + Br^-
$CH_3—\overset{\delta^+}{C}H_2—Br^{\delta^-}$ +	$CH_3COO^-Na^+$	→ $CH_3COOC_2H_5$ (Ethyl acetate) + NaBr

Other reactions shown by alkyl halides are as follows:

1. Wurtz Synthesis

Alkyl halides react with sodium in ether solvent to give alkanes. The reaction is particularly useful for the preparation of symmetrical alkanes.

$$CH_3-CH_2-Cl + 2Na + Cl-CH_2-CH_3 \xrightarrow{Ether} \underset{\text{n-Butane}}{CH_3-CH_2-CH_2-CH_2-CH_3} + 2NaCl$$

2. Reduction of Alkyl Halides

Alkyl halides can be reduced with zinc in the presence of an aqueous acid such as HCl or CH_3COOH.

$$CH_3-CH_2-CH_2-Cl + Zn + H^+ + Cl \longrightarrow \underset{\text{Propane}}{CH_3-CH_2-CH_3} + ZnCl_2$$

3. Reaction with Sodium Lead Alloy (Na_4Pb)

Methyl chloride and ethyl chloride react with sodium lead alloy giving tetramethyl lead and tetraethyl lead,respectively. These compounds are important anti-knock agents and are used in gasoline.

$$4CH_3Cl + Na_4Pb \longrightarrow \underset{\text{Tetramethyl lead}}{(CH_3)_4Pb} + 4NaCl$$

$$4CH_3CH_2-Cl + Na_4Pb \longrightarrow \underset{\text{Tetramethyl lead}}{(CH_3CH_2)_4Pb} + 4NaCl$$

10.6 GRIGNARD REAGENT

Grignard reagents RMgX are derivatives of alkyl halides belonging to class of organo-metallic compounds. Grignard reagent was first prepared by Victor Grignard in 1900. These reagents are so important in organic synthesis that almost all the classes of organic compounds can be prepared from them. Due to their importance and applications Victor Grignard was awarded Nobel prize in chemistry.

Preparation:

Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of dry ether (alcohol free, moisture free).

$$\overset{\delta+}{R}-\overset{\delta-}{X} + Mg \xrightarrow{Ether} R-Mg-X$$

$$CH_3-CH_2-Br + Mg \xrightarrow{Ether} CH_3-CH_2-Mg-Br$$

Ethyl magnesium bromide

It is important that all the reactants must be absolutely dry and pure because Grignard reagents are so reactive that they may react with moisture or any impurity present. Reactivity of alkyl halides with magnesium is in the following order:

Alkyl iodide > Alkyl bromide > Alkyl chloride

And for a given halogen the order of reactivity is as follows:

$CH_3X > C_2H_5X > C_3H_7X$

Structure and Reactivity

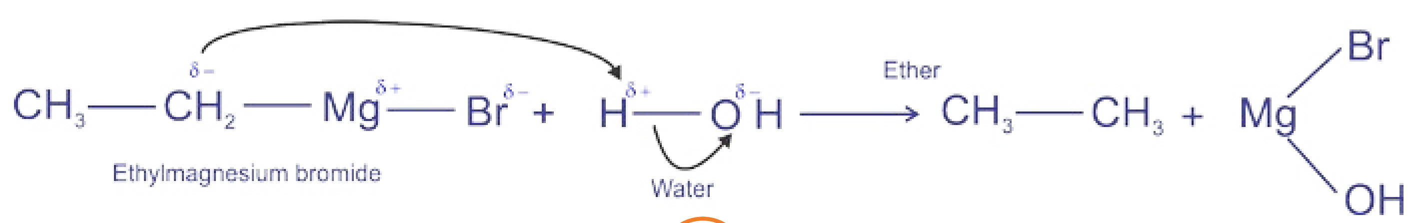
Grignard reagents are much reactive than most of the organic compounds. The reactivity is due to the nature of C - Mg bond which is highly polar.

$$CH_3\overset{\delta-}{C}H_2-\overset{\delta+}{Mg}-\overset{\delta-}{X}$$

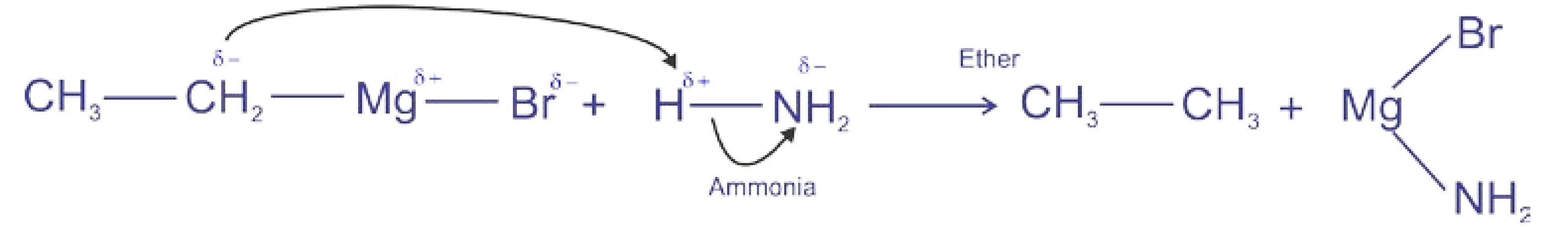
Magnesium is more electropositive than carbon and the C-Mg bond though covalent is highly polar, giving alkyl carbon the partial negative charge. This negative charge is an unusual character which makes the alkyl groups highly reactive towards electrophile centres. Mostly reactions shown by Grignard reagent are exothermic.

Reactions

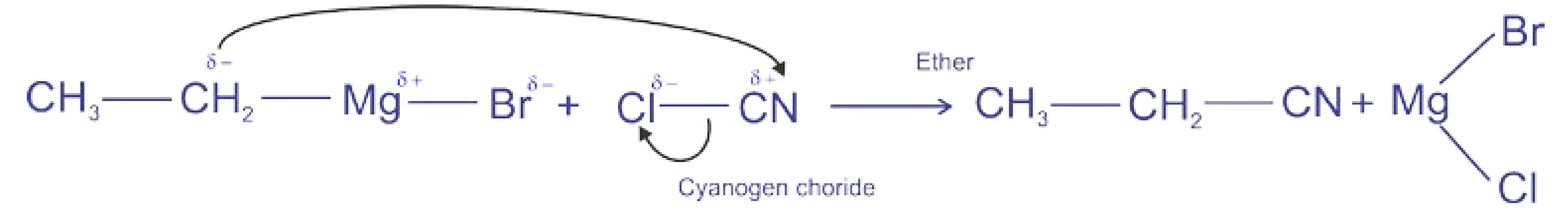
(i) **With Water**



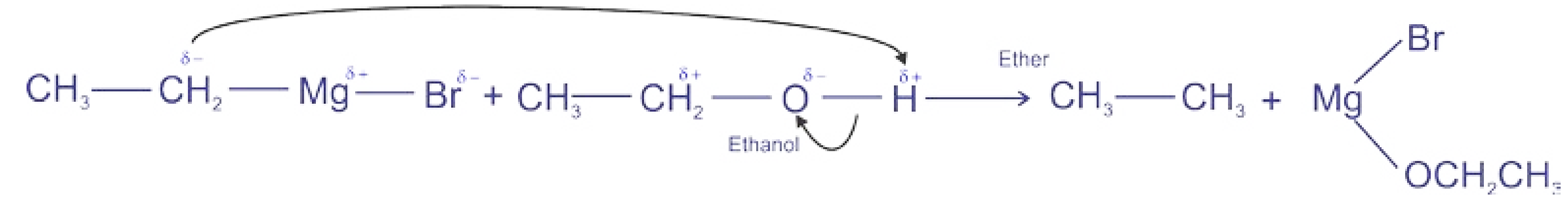
(ii) **With ammonia**



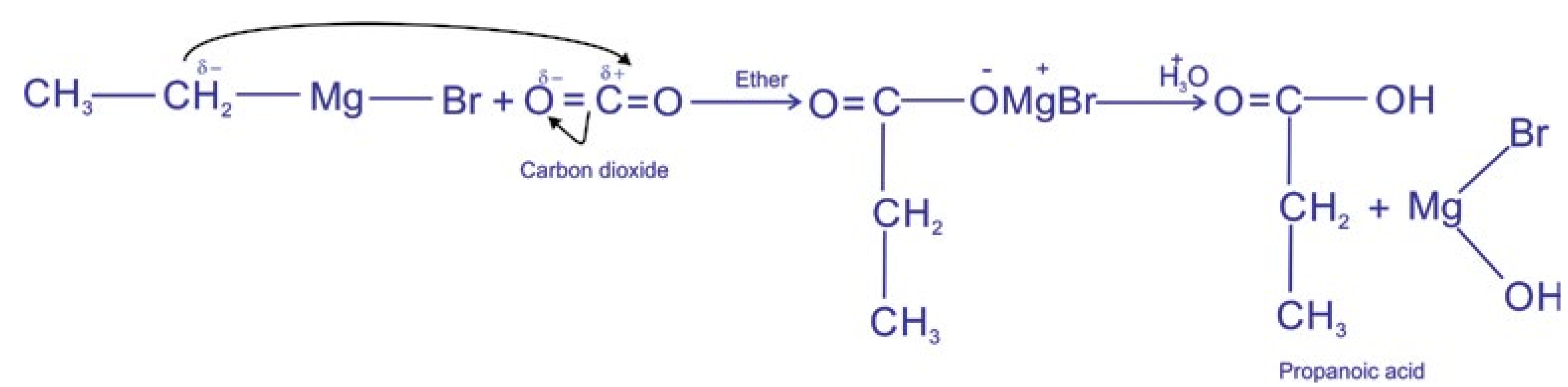
(iii) **With cyanogen chloride**



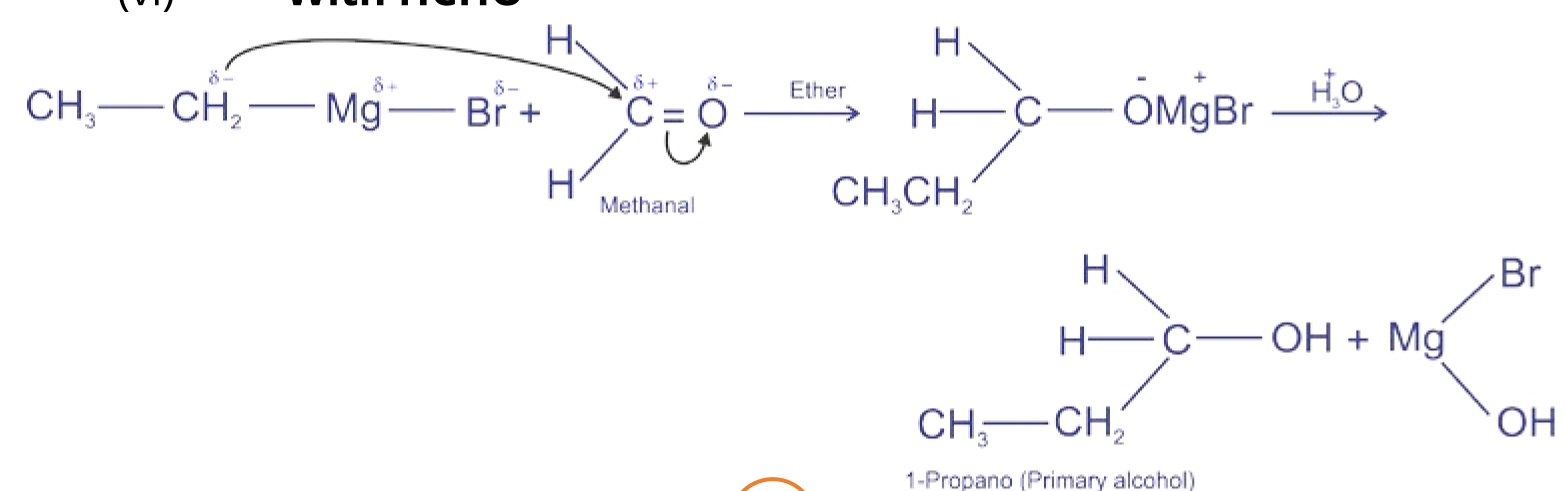
(iv) **With alcohols**



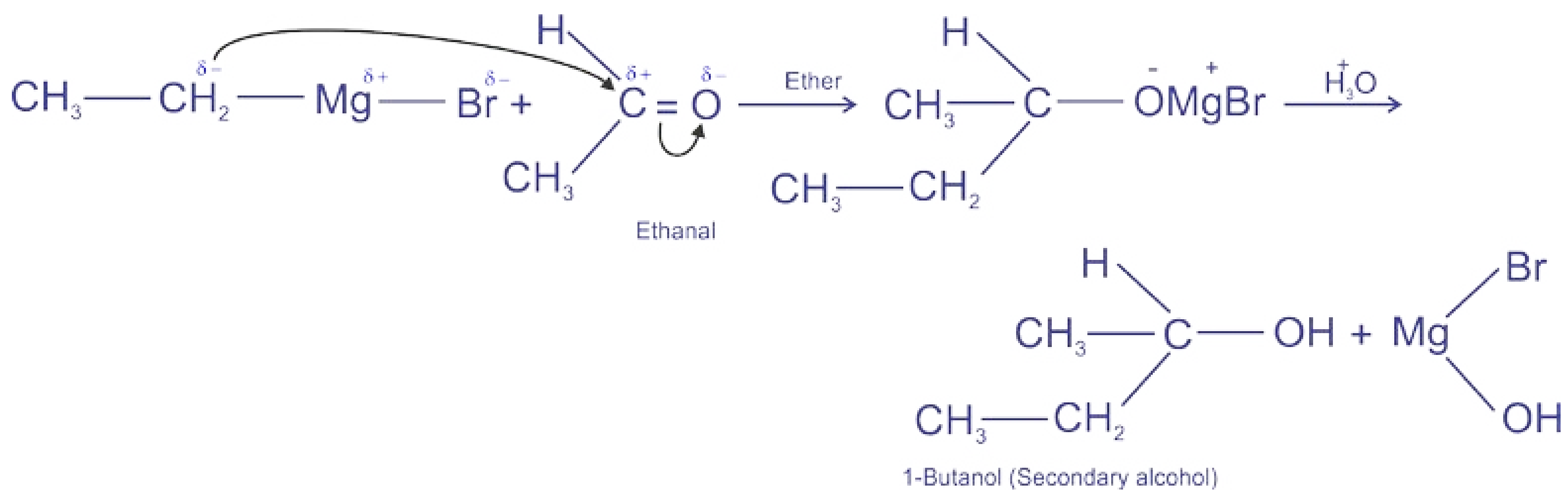
(v) **With CO_2**



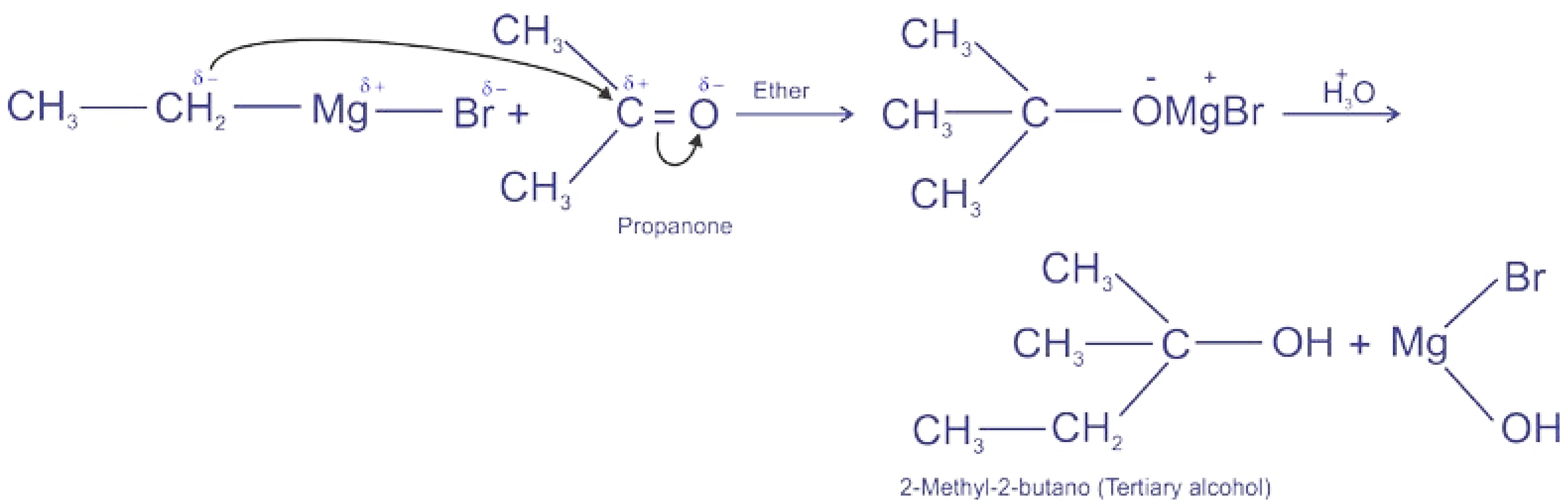
(vi) **With HCHO**



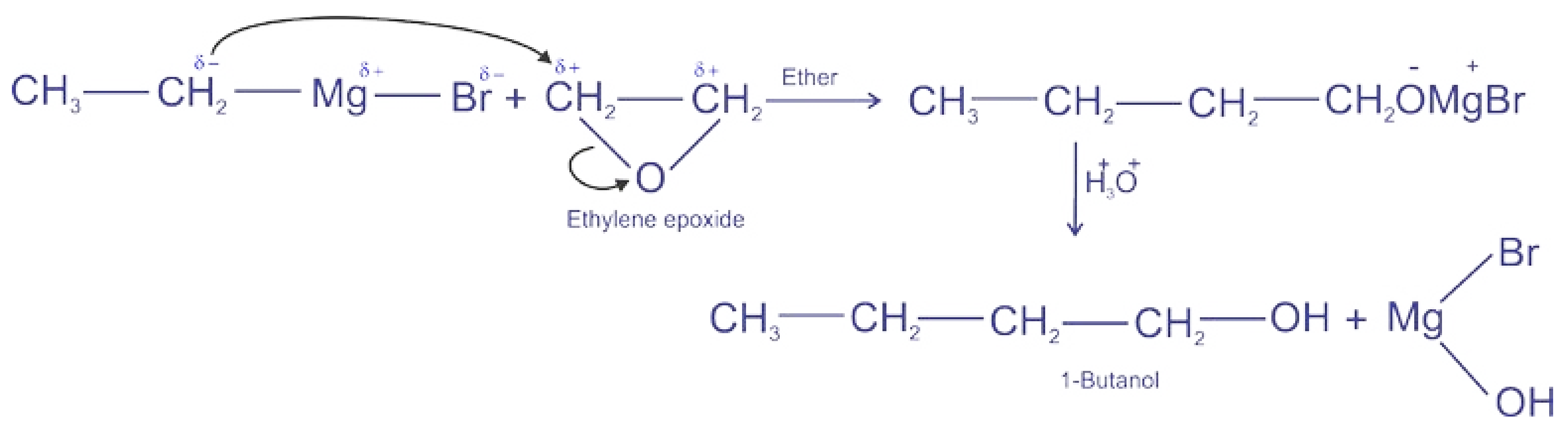
(vii) **With CH_3CHO**



(viii) **With CH_3COCH_3**



(ix) **With Epoxide**



Simulation 10.3: Interactive Periodic Table
Source & Credit: learnerstv

KEY POINTS

1. Monohalo derivates of alkanes are called alkyl halides.
2. The general formula of alky 1 halides is $C_nH_{2n+1}X$.
3. The best method for the preparation of alkyl halides is by the reactions of alcohols with inorganic halides like $SOCl_2$, PX_3 and PX_5.
4. Alkyl halides are very reactive class of organic compounds. They undergo nucleophilic substitution reactions and elimination reactions in the presence of a nucleophile or a base.
5. Nucelophilic substitution reactions can take place in two distinct ways. A one step mechanism is called S_N2 while a two step mechanism is called S_N1. S_N1 reactions show first order kinetics whereas S_N2 reactions show 2nd order kinetic.
6. Nucleophilic substitution reactions take place simultaneously with elimination reactions and often compete with them.
7. Elimination of two atoms or groups from adjacent carbon atoms in the presence of a nucleophile or a base is called elimination reaction. Like nucleophilic substitution, (3-elimination reaction also take place in two distinct ways E2 and E1.
8. Grignard reagent can be prepared by adding alkyl halide in a stirred suspension of magnesium metal in diethyl ether.
9. Grignard reagent has a reactive nucleophilic carbon atom which can react with electrophilic centres to give the products in high yields.
10. Primary, secondary and tertiary alcohols can be best prepared by reacting Grignard reagent with formaldehyde, any other aldehydes and ketones, respectively.

EXERCISE

Q.1. Fill in the blanks.

i) In tertiary alkyl halides the halogen atom is attached to a carbon which is further attached to __________ carbon atoms directly.

ii) The best method for the preparation of alkyl halides is the reaction of _________ with inorganic reagents.

iii) An alkyl group with a partial positive charge on the carbon atom is called____________ centre.

iv) The mechanism is called __________if it involves one molecule in the ratedetermining step.

v) Molecularity of a reaction is defined as the number of molecules taking part in the ______________.

vi) The molecularity of E2 reactions is always two and the reactions show ________ order kinetics.

vii) Wurtz synthesis is useful for the preparation of____________ alkanes.

viii) Grignard reagents are prepared by the reaction of magnesium metal with alkyl halides in the presence of___________.

Q.2. Indicate True or False.

i) In secondary alkyl halides, the halogen atom is attached to a carbon which is further attached to two carbon atoms directly.

ii) Alcohols react with thionyl chloride in ether as solvent to give alkyl halides.

iii) Order of reactivity of alkyl halides for a particular alkyl group is: Iodide > Bromide > Chloride > Fluoride

iv) In S_N2 reactions the attacking nucleophile always attacks from the side in which the leaving group is attached.

v) Methyl magnesium iodide on hydrolysis yields ethyl alcohol.

vi) Primary, secondary and tertiary amines react with Grignard reagents in the sameway.

vii) The reactions of secondary alkyl halides may follow both S_N1 and S_N2 mechanisms.

viii) S_N1 mechanism is a one stage process involving a simultaneous bond breakage and bond formation.

ix) In β-elimination reactions, the two atoms or groups attached to two adjacent carbon atoms are lost under the influence of an electrophile.

x) The reactivity order of alkyl halides is determined by the strength of carbon-halogen bond.

Q. 3. Multiple choice questions. Encircle the correct answer.

i) In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms.
(a) Two (b) Three (c) One (d) Four

ii) The reactivity order of alkyl halides for a particular alkyl group is:
(a) Fluoride > Chloride > Bromide > Iodide
(b) Chloride > Bromide > Fluoride > Iodide
(c) Iodide > Bromide > Chloride > Fluoride
(d) Bromide > Iodide > Chloride > Fluoride

iii) When CO_2 is made to react with ethyl magnesium iodide, followed by acid hydrolysis, the product formed is:
(a) Propane (b) Propanoic acid (c) Propanal (d) Propanol

iv) Grignard reagent is reactive due to:
(a) the presence of halogen atom (b) the presence of Mg atom
(c) the polarity of C -Mg bond (d) none of the above

v) S_N2 reactions can be best carried out with:
(a) Primary alkyl halides (b) Secondary alkyl halides
(c) Tertiary alkyl halides (d) All the three

vi) Elimination bimolecular reactions involve:
(a) first order kinetics (b) second order kinetics
(c) third order kinetics (d) zero order kinetics

vii) For which mechanisms, the first step involved is the same.
(a) E1 and E2 (b)E2andS_N2 (c)$S_N1$andE2 (d) E1 and S_N1

viii) Alkyl halides are considered to be very reactive compounds towards nucleophiles, because:
(a) they have an electrophilic carbon
(b) they have an electrophilic carbon and a good leaving group
(c) they have an electrophilic carbon and a bad leaving group
(d) they have a nucleophilic carbon and a good leaving group

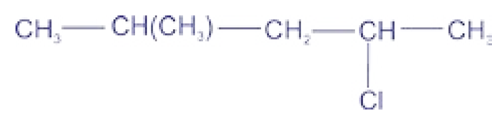
ix) The rate of E1 reaction depends upon:
(a) the concentration of substrate
(b) the concentration of nucleophile
(c) the concentration of substrate as well as nucleophile
(d) None of the above

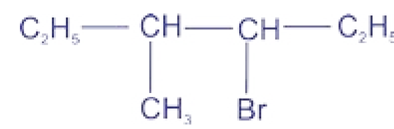
x) Which one of the following is not a nucleophile :
(a) H_2O (b) H_2S (c) BF_3 (d) NH_3

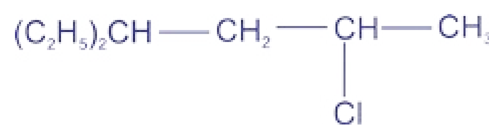
Q.4. Define alkyl halide. Which is the best method of preparing alkyl halides?

Q.5. Write down a method for the preparation of ethyl magnesium bromide in the laboratory?

Q.6. Give IUPAC names to the following compounds.

i) 

ii) 

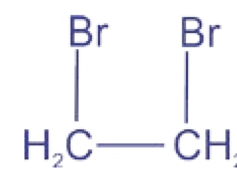
iii) 

iv) $(CH_3)_3C - CH_2 - Cl$

v) $(CH_3)_2CHBr$

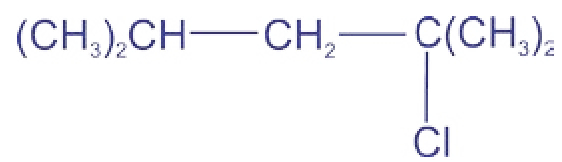
vi) $(CH_3)_2CH - CH_2 - CH(C_2H_5)CH_2Cl$

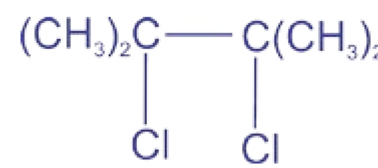
vii) CBr_4

viii) 

ix) CH_2Cl_2

x) $(CH_3)_3C - CH_2 - CH_2 - CH_2 - Br$

xi) 

xii) 

xiii) $(CH_3CH_2)_3CBr$

Q.7. Draw all the possible structures that have the molecular formula $C_6H_{13}Cl$. Classify each as primary, secondary or tertiary chloride. Give their names according to IUPAC system.

Q.8. Using ethyl bromide as a starting material how would you prepare the following compounds. Give also the inorganic reagents and conditions necessary to carry out these reactions:

(a) n-Butane
(b) Ethyl alcohol
(c) Ethyl cyanide
(d) Ethane
(e) Ethene
(f) Propanoic acid
(g) Propane

Q.9. Write a detailed note on the mechanism of nucleophilic substitution reactions.

Q.10. What do you understand by the term β-elimination reaction. Explain briefly the two possible mechanisms of 3-elimination reactions.

Q.11. What products are formed when the following compounds are treated with ethyl magnesium bromide, followed by hydrolysis in the presence of an acid,

i) HCHO
ii) CH_3CHO
iii) CO_2
iv) $(CH_3)_2CO$
v) $CH_3—CH_2—CHO$
vi) ClCN

Q. 12. How will you carry out the following conversions.

i) $CH_4 \longrightarrow CH_3CH_2COOH$

ii) $CH_3—CH_3 \longrightarrow (CH_3—CH_2)_4N^+ Br$

iii) $CH_2 = CH_2 \longrightarrow CH_3—CH_2—CH_2—CH_2—OH$

iv) $CH_3CH_2CH_2Cl \longrightarrow CH_3—CH = CH_2$

v) $CH_3COOH \longrightarrow CH_3CH_2COOH$

CHAPTER

11

ALCOHOLS, PHENOLS AND ETHERS

Animation 11.1: Hanau Alcohol Torch
Source and Credit : reddit

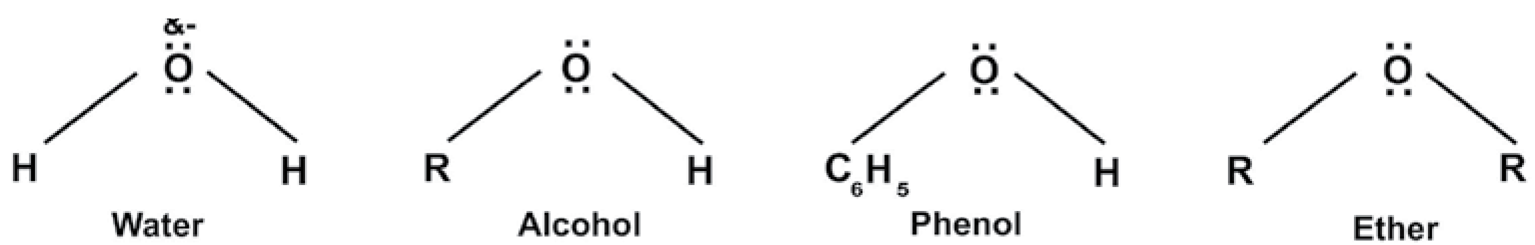
IN THIS CHAPTER YOU WILL LEARN:

1. How to name simple monohydric and polyhydric alcohols and their classification as primary, secondary and tertiary alcohols.
2. The important synthetic reactions leading to alcohols and industrial processes for the manufacture of methanol and ethanol.
3. The nature of OH group and its reactivity when O-H bond is broken and when C-O bond is broken.
4. To distinguish chemically between the primary, secondary and tertiary alcohols.
5. The methods of preparation of phenol and its acidic nature.
6. The importance of phenol as starting material for the preparation of five industrially important compounds.
7. How to name ethers and preparation of diethyl ether.
8. The physical . and chemical behaviour of diethyl ether and its inertness towards chemical reagents.

11.1 INTRODUCTION

Alcohols, phenols and ethers are classes of organic compounds which are much closer to water in structure and hence considered as derivatives of water.

Animation 11.2: Alcohol
Source and Credit : rationalwiki



Alcohols and phenols are much more close to one another in structure and proper ties. Both contain hydroxyl (-OH) group so they may also be termed as hydroxy derivatives of alkanes and benzene respectively. In ether both hydrogens of water are replaced by alkyl or phenyl groups.

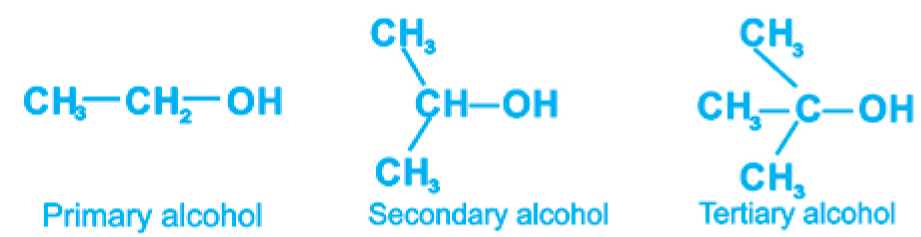
11.2 ALCOHOLS

They are represented by a general formula ROH where R is an alkyl group which maybe $CH_3—$,CH_3CH_2 — , $(CH_3)_2C$ H — and C_6H_5 — CH_2— ,etc.

Classification

Alcohols are classified into monohydric and polyhydric alcohols. Monohydric alcohols contain one -OH group while polyhydric alcohols may contain two, three or more OH groups and named as dihydric or trihydric alcohols, etc.

Monohydric alcohols are further classified into primary, secondary and tertiary alcohols. In primary alcohols, -OH functional group is attached with primary carbon atom, in secondary alcohols with secondary carbon atom and in tertiary alcohols it is attached with a tertiary carbon atom.



11.2.1 NOMENCLATURE OF ALCOHOLS

There are two systems of naming alcohols

Common or Trivial Names

(a) Lower and simpler alcohols are usually known by their common or trivial names, obtained by adding the name of alcohol after the name of the alkyl group to which the OH group is attached, e.g.,

CH_3OH	C_2H_5OH	C_6H_5 CH_2 OH
Methyl alcohol	Ethyl alcohol	Benzyl alcohol

(b) I.U.RA.C Names

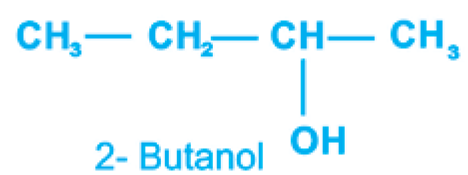
In this system the alcohols are named according to the following rules.
(i) The longest chain of carbon atoms containing the hydroxyl group is taken as parent hydrocarbon. The ending 'e' of alkane is replaced by ol, e.g;

CH_3OH	C_3H_7OH	$C_5H_{11}OH$
Methanol	Propanel	Pentanol

(ii) The position of OH group is indicated by a number placed before the name. The carbon chain is numbered, starting from the end where carbon atom attached with OH group gets the lowest possible number, e.g;

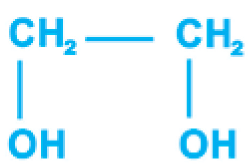
$CH_3—CH_2—CH_2—CH_2—OH$

1-Butanol

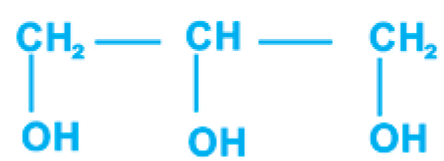


2- Butanol

(iii) If more than one OH groups are attached, they are indicated by an appropriate suffix diol, triol, etc., e.g;



1,2-Ethanediol (Glycol)



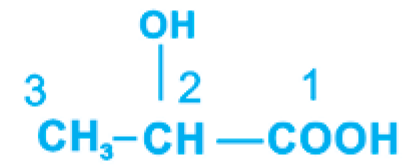
1,2,3- Propanetriol (Glycerol)

(iv) The unsaturated alcohols are numbered in such a way that hydroxyl group rather than the point ot unsaturation gets the lower number, e.g.

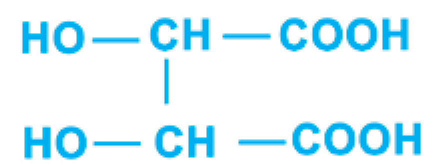
$$\overset{4}{CH_3}—\overset{3}{CH}=\overset{2}{CH}—\overset{1}{CH_2OH}$$

2-Buten-1- ol

(v) When hydroxyl group is not a preferred functional group as in hydroxy acids, aldehydes and ketones, the substituent name hydroxy is used as a prefix to indicate the position of OH group, e.g.;



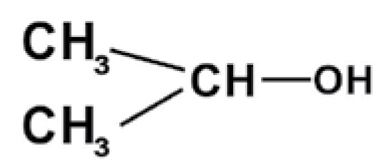
2-Hydroxy propanoic Acid (Lactic Acid)



2,3-Dihydroxy butane-1,4- dioic acid (Tartaric Acid)

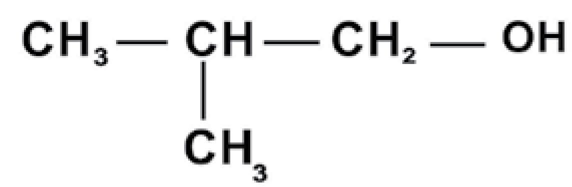
The names of some alcohols in the two systems are given below

Formula	Common Name	IUPAC Name
CH_3OH	Methyl alcohol	methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	Propyl alcohol	1-Propanol

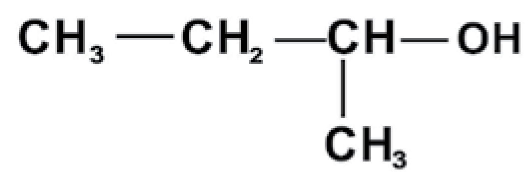


Isopropyl alcohol 2- Proponal

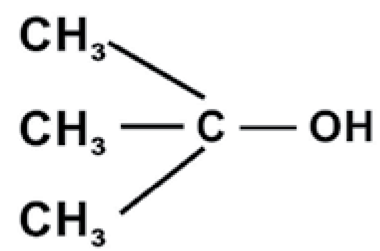
$CH_3—CH_2—CH_2—CH_2—OH$ n-Butyl alcohol 1-Butanol



iso-Butyl alcohol 2-Methyl -1-proponal



sec-Butyl alcohol 2- Butanol



ter- Butyl alcohol 2-Methyl-2-propanol

11.2.2 Industrial Preparation of Alcohols

Methanol

Formerly methanol was prepared by distillation of wood. That is why it is also called as wood spirit. Now-a-days methanol is prepared from carbon monoxide and hydrogen or water gas as follows:

$$CO+2H_2 \xrightarrow[450°C:200atm]{(ZnO+Cr_2O3)} CH_3OH$$

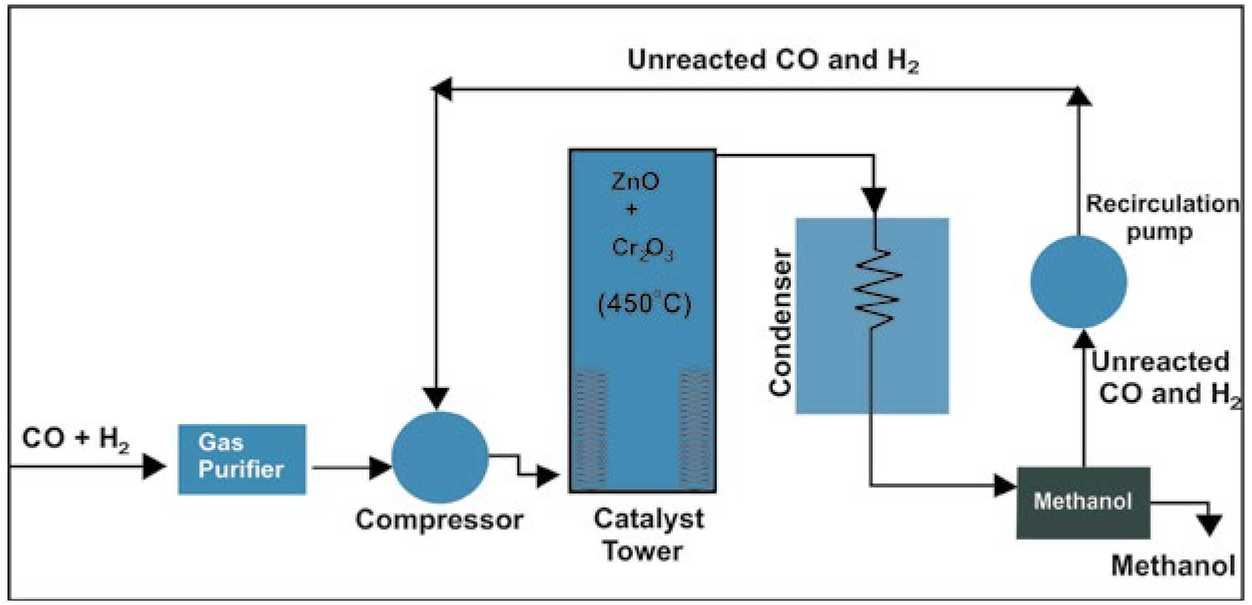


Fig. 11.1 Flow sheet diagram for the manufacturing of methanol

First of all a mixture of carbon monoxide and hydrogen is purified. It is compressed under a pressure of 200 atmospheres and taken into a reaction chamber by means of coiled pipes Here the catalyst is heated upto 450-500 °C. Gases react to form methanol vapours. These vapours are passed through a condenser to get methanol. Unreacted gases are recycled through compressor to reaction chamber.

Animation 11.3: ethyl methanoate
Source and Credit : dynamicscience

Ethanol

Ethanol is prepared on industrial scale world over, by the process of fermentation. Fermentation is a biochemical process which occurs in the presence of certain enzymes secreted by microorganisms such as yeast. Optimum temperature for this process of fermentation is 25-35°C. Moreover, proper aeration, dilution of solution and the absence of any preservative are essential conditions for fermentation. In Pakistan ethanol is prepared by the fermentation of molasses starch grains or fruit juices.

From Molasses

The residue obtained after the crystallization of sugar from concentrated sugar cane juice is called molasses. It undergoes fermentation in the presence of enzymes present in yeast to give ethanol.

$$\underset{\text{Molasses}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{Yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

From Starch

From Starch

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)} + nH_2O \xrightarrow[\text{Yeast}]{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Yeast}]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Alcohol obtained by fermentation is only upto 12% and never exceeds 14% because beyond this limit enzymes become inactive. This alcohol is distilled again and again to obtain 95% alcohol which is called rectified spirit. Absolute alcohol can aioo be obtained by redistillation of rectified spirit in the presence of CaO which absorbs its moisture.

Denaturing of Alcohol

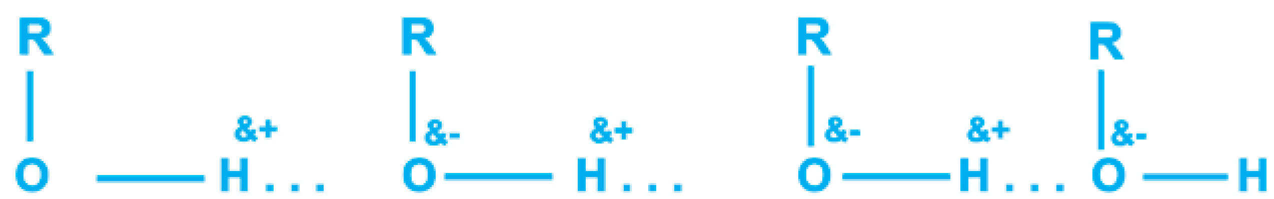
Sometimes ethanol is denatured by addition of 10% methanol to avoid its use for drinking purposes. Such alcohol is called methylated spirit. A small quantity of pyridine or acetone may also be added for this purpose.

Other Methods of Preparation of Alcohols

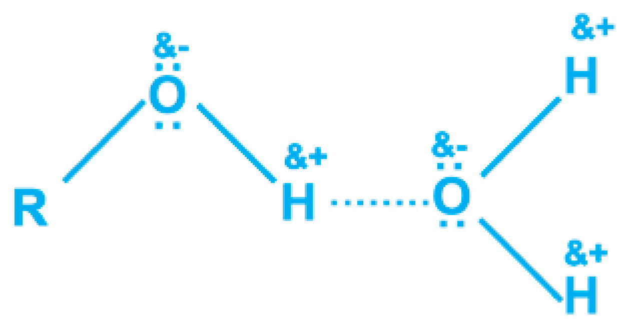
Alcohols can be obtained by the hydration of aikenes and by the reaction of Grignard reagents with aldehydes or ketones. Both these methods have already been discussed in the previous chapter.

11.2.3 Physical Properties

Lower alcohols are generally colourless toxic liquids with characteristic sweet smell and burning taste They are readily soluble in water but solubility decreases in higher alcohols. The solubility of alcohols is due to hydrogen bonding which is prominent in lower alcohols but diminishes in higher alcohols.



Hydrogen bonding in alcohol



Hydrogen bonding between water and alcohol

Melting and boiling points of alcohols are higher than corresponding alkanes. Methyl alcohol and ethyl alcohol are liquids while methane and ethane are gases. This is also due to hydrogen bonding which is present in alcohols but absent in alkanes.

11.2.4 Reactions of Alcohols

Alcohols react with other reagents in two ways
(i) Reactions in which C — O bond breaks
(ii) Reactions in which O — H bond breaks

Which bond will break depends upon the nature of the attacking reagent.
If a nucleophile attacks, it is the C — O bond which breaks. On the other hand, if an electrophile attacks on alcohol, it is the O — H bond which breaks.

$$CH_3{-}CH_2^{\delta+}OH^{\delta-} \xrightarrow{\text{Nucleophile}} CH_3{-}CH_2^{+} + OH^{-}$$

$$CH_3{-}CH_2{-}O^{\delta-}{-}H^{\delta+} \xrightarrow{\text{Electrophile}} CH_3{-}CH_2{-}O^{-} + H^{+}$$

The order of reactivity of alcohols when C — O bond breaks:

Tertiary alcohol > Secondary alcohol > Primary alcohol

The order of reactivity of alcohols when O — H bond breaks:

CH_3OH > Primary alcohol > Secondary alcohol > Tertiary alcohol

11.2.5 Reactions in w hich C — O Bond is Broken.

1 $$\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{pyridine}} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + SO_2 + HCl$$

2 $$C_2H_5OH + HCl \xrightarrow{ZnCl2} C_2H_5Cl + H_2O$$

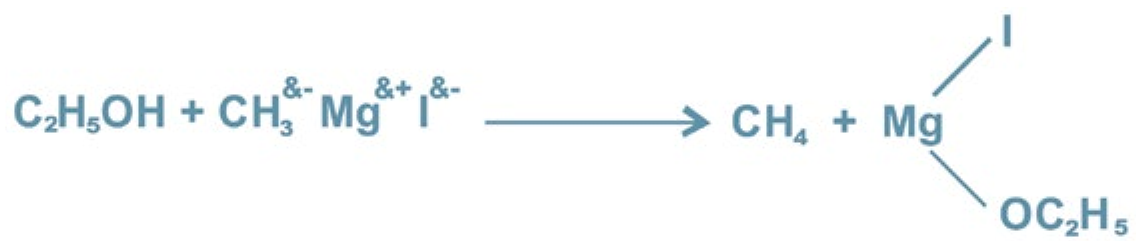
3 $$C_2H_5OH + HNH_2 \xrightarrow{ThO2} C_2H_5NH_2 + H_2O$$

Ethyl amine

11.2.6 R eactions Involving the Cleavage of O — H bond.

1 $$2C_2H_5OH + 2Na \rightarrow 2C_2H_5O^-N^+a + H_2$$

Sodium cthoxide

2 

3 $$C_2H_5OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

Ethyl acetate

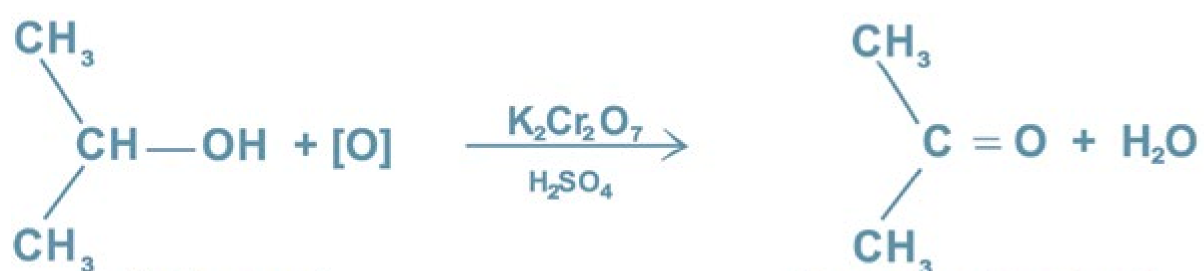
11.2.7 Some Other Reactions of Alcohols

(i) Oxidation

Oxidation of alcohols convert them into aldehydes and ketones. The best reagent for this purpose is acid dichromate.

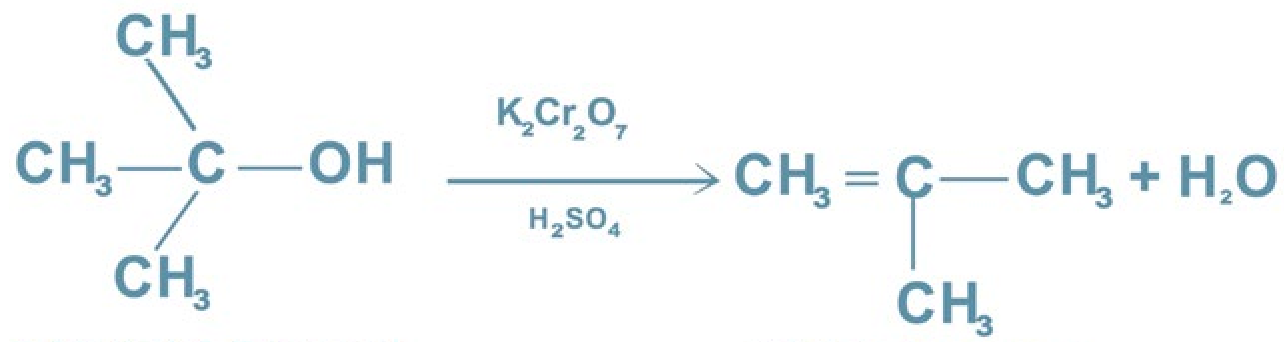
$$CH_3\text{-}CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3\text{-}CHO + H_2O$$

E thanal (acetaldehyde)



2- Propanol   Propanone (acetone)

Tertiary alcohols are resistant to oxidation. In the presence of acid dichromate they undergo elimination reactions to give alkenes.



2-Methyl-2-Propanol   2-Methylpropene

(ii) Dehydration

Alcohols react with con. H_2SO_4 and give different products at different temperatures.

$$C_2H_5OH \xrightarrow[180^\circ c]{conc.H_2SO_4} CH_2 = CH_2 + H_2O$$

Ethanol

$$2C_2H_5OH \xrightarrow[140^\circ C]{conc.H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

Diethyl ether

(iii) Reactions with Phosphorus Halides PCl_3, PCl_5

$$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$$

$$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$$

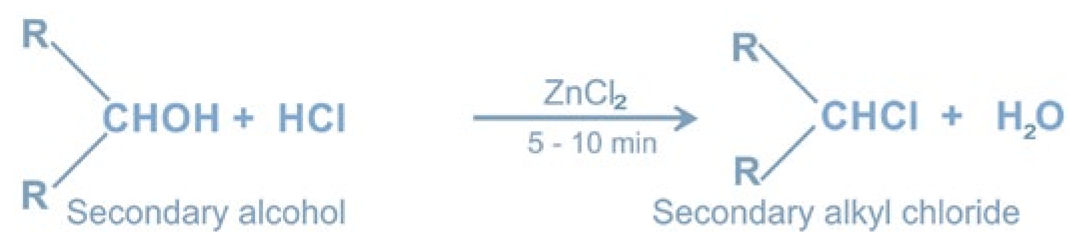
11.3 DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

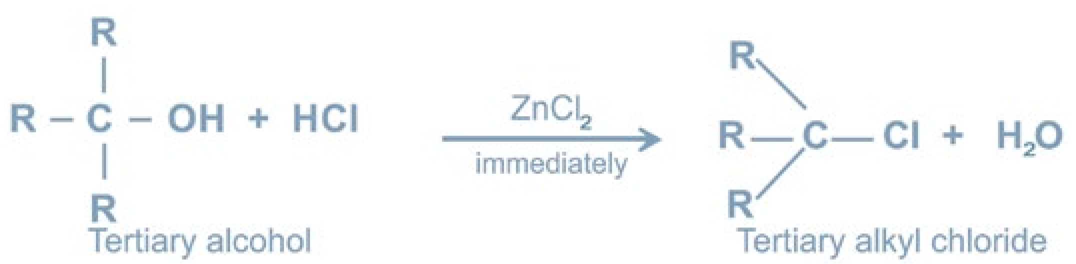
Lucas Test

Primary, secondary and tertiary alcohols are identified and distinguished by reacting them with con. HCI in anhydrous $ZnCl_2$. An oily layer of alkyl halides separates out in these reactions.

1. Tertiary alcohols form an oily layer immediately
2. Secondary alcohols form an oily layer in five tc ten minutes.
3. Primary alcohols form an oily layer only on heating.

$$\underset{\text{Primary alcohol}}{R{-}CH_2{-}OH} + HCl \xrightarrow[\text{Heat}]{ZnCl_2} \underset{\text{Primary alkyl chloride}}{R{-}CH_2{-}Cl} + H_2O$$





Distinction between Methanol and Ethanol

Ethanol gives iodoform with iodine in the presence of NaOH. Formation of yellow crystals indicate that the alcohol is ethanol. Methanol does not give iodoform test.

$$C_2H_5OH + 4I_2 + 6NaOH \rightarrow \underset{\text{Iodoform}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

$$CH_3OH + I_2 + NaOH \rightarrow \text{No yellow ppt}$$

11.4 USES OF ALCOHOLS

Methanol is used as a solvent for fats oils, paints, varnishes. It is also used as antifreeze in the radiators of automobiles and for denaturing of alcohol.
Ethanol is used as a solvent, as a drink and as a fuel in some countries. Moreover it. is used in pharmaceutical preparations and as a preservative for biological specimen.

11.5 PHENOL

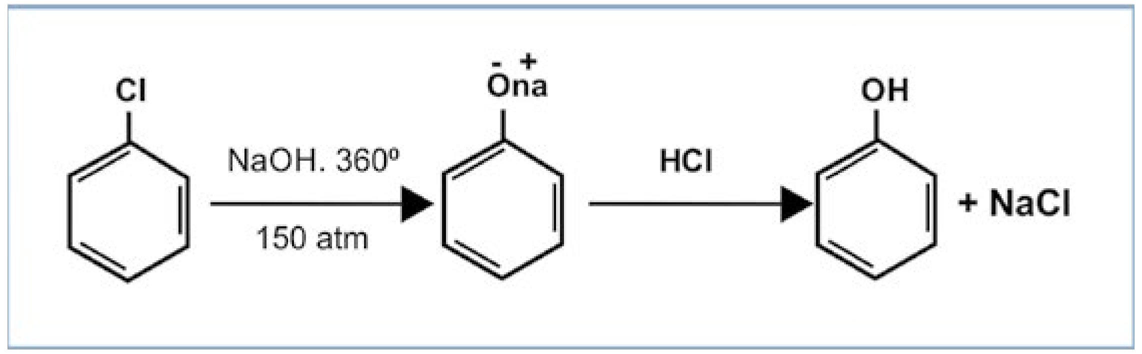
Aromatic compounds which contain one or more OH groups directly attached with carbon of benzene ring are called Phenols. The simplest example is phenol which is also known as Carbolic acid i.e. C_6H_5OH. It was first obtained from coaltar by Runge in 1834.

11.5.1 Preparation of Phenol

1) From Chlorobenzene (Dow's Method)

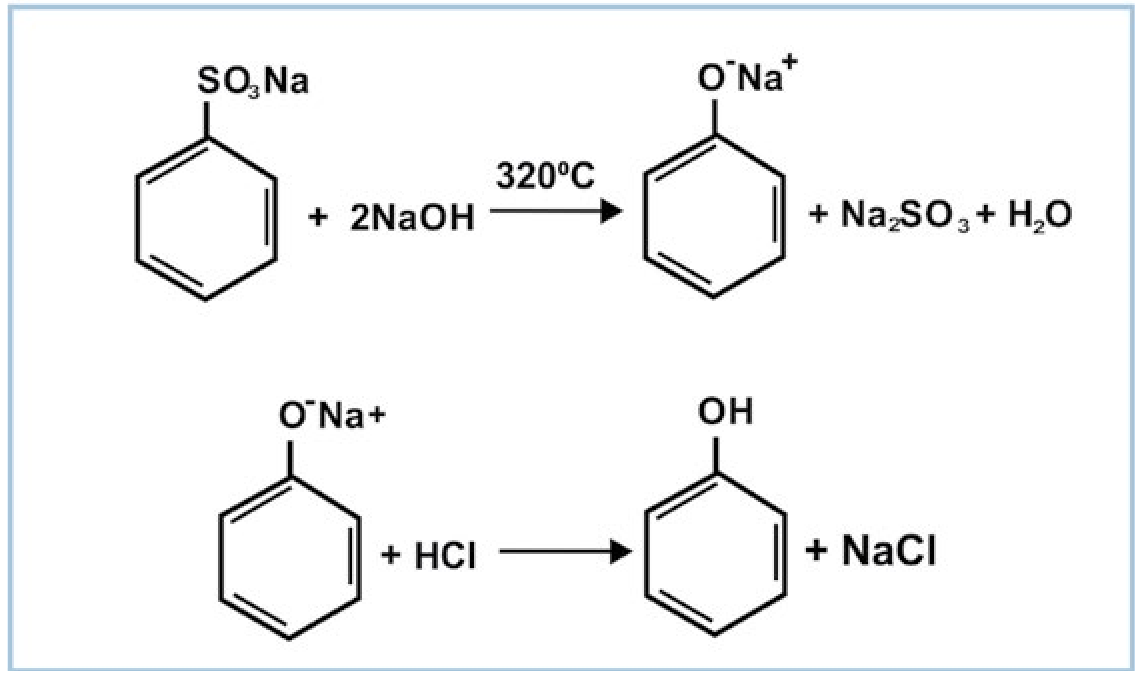
In this method chlorobenzene is treated with 10% NaOH at 360°C and 1I50 atmospheres pressure. Sodium phenoxide is produced which on treating with HCI gives phenol.

Animation 11.4: Phenol
Source and Credit : chem



2) From Sodium Salt of Benzen e Sulphonic Acid

Sodium salt of benzene sulphonic acid reacts with NaOH aT 320°C tc give sodium phenoxide which cn treatment with HC1 gives phenol.



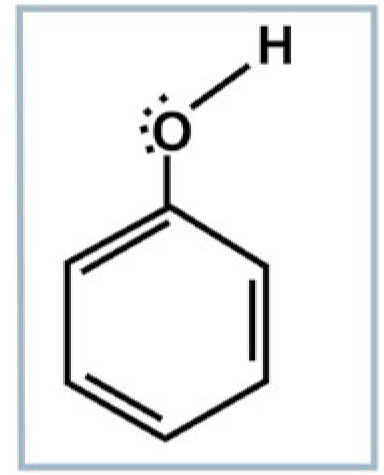
The phenol is recovered by steam distillation.

11.5.2 Physical Properties

Phenol is a colourless, crystalline, deliquescent solid with characteristic phenolic odour having melting point 41°C and boiling point 182°C. It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5°C. It is poisonous and used as a disinfectant in hospitals and washrooms.

Animation 11.5: Physical Properties of phenol
Source and Credit : chemwiki

11.5.3 Reactions of Phenol



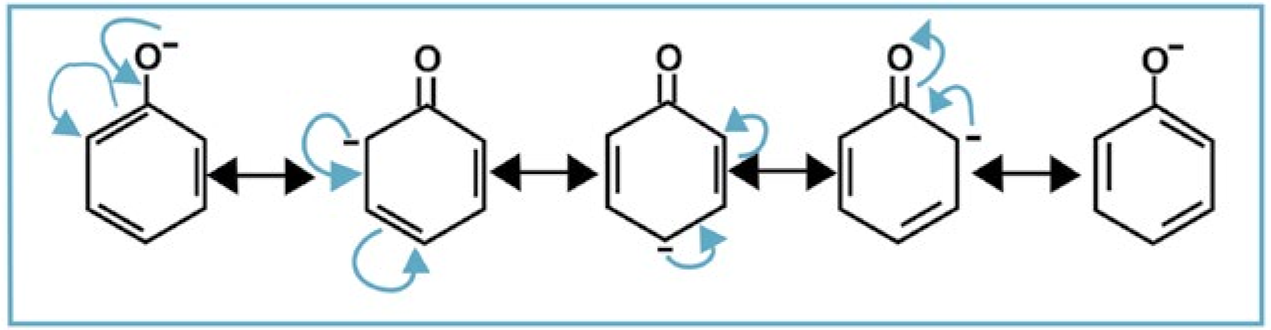
Phenol shows two type of reactions.
1. Reactions due to — OH group
2. Reactions due to benzene ring

Phenols are less reactive to nucleophiles so nucleophilic attack is less favoured, i.e - OH is not easy to replace while electrophilic attack on the ring is easy.

11.5.4 Acidic Behaviour of Phenol

Phenol is much more acidic than alcohols but less acidic than carboxylic acids. It dissolves readily in alkalies but it is too weak to affect the litmus paper or to evolve CO_2 from carbonates. Its dissociation constant (K_a) is 1.3×10^{-10}.
Phenol is partially soluble in water and its solution has a pH of around 5 or 6. This makes phenol different from aliphatic alcohols.

The reason why phenol is acidic lies in the nature of the phenoxide ion. The negative charge on oxygen atom can become involved with the π-electron cloud on the benzene ring. The negative charge is thus delocalized in the ring and the phenoxide ion becomes relatively stable. This type of delocalization is not possible with alcohols.



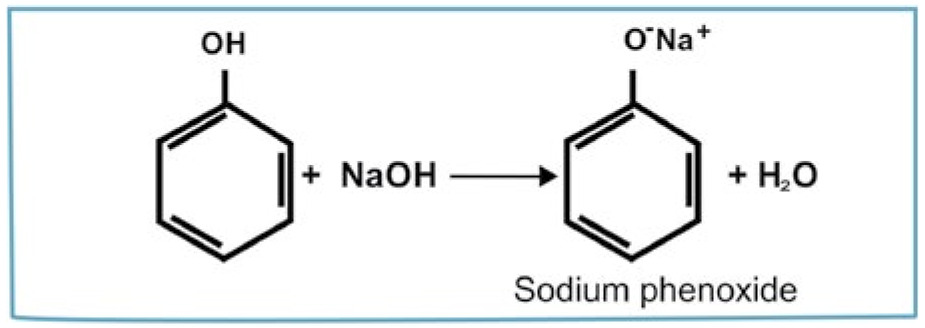
Relative acidic strength of alcohol, phenol, water and carboxylic acid is as follows,

carboxylic acid > phenol > water > alcohol

11.5.5 Reactions of Phenol Due to - OH Group.

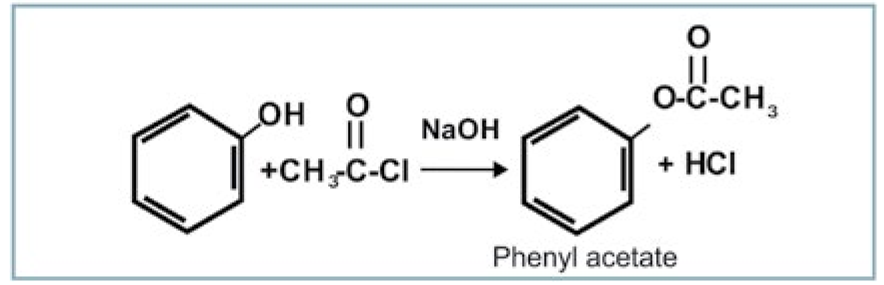
Salt Formation

Phenol reacts with alkalies to form salts, e.g;

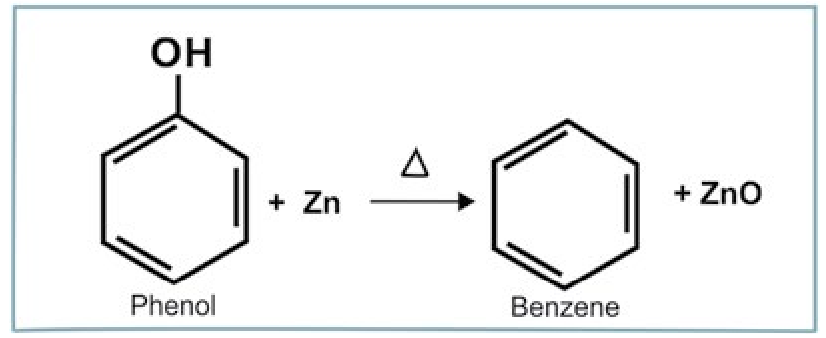


Ester Formation

Phenol reacts with acetyl chloride in the presence of a base to form ester.



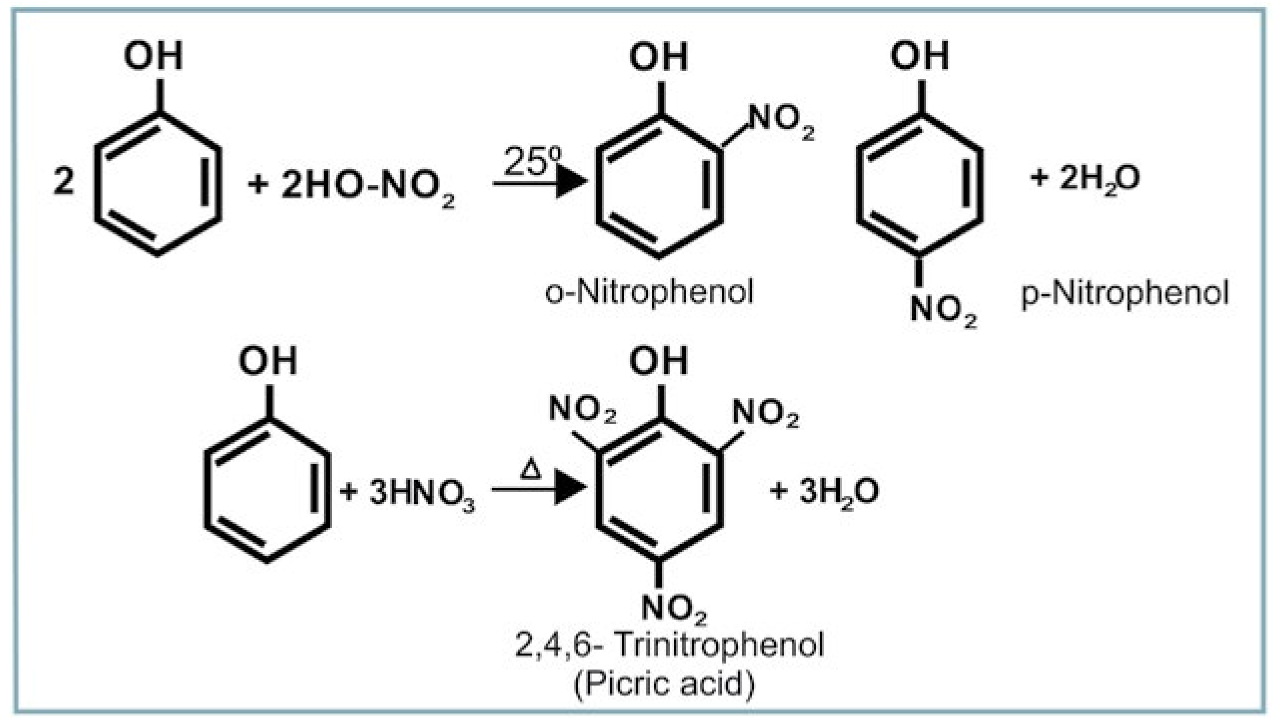
Reduction with Zn



11.5.6 Reactions of Phenol Due to Benzene Ring

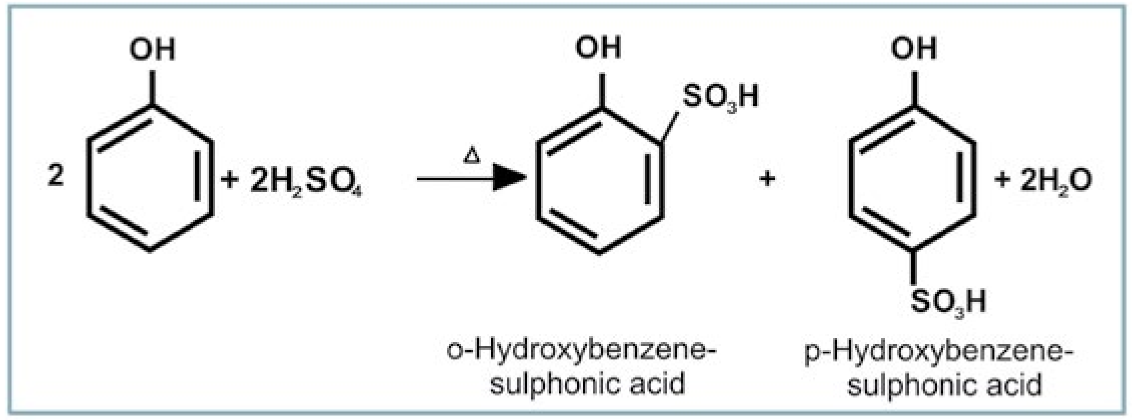
Nitration

Phenol reacts with dil. and conc. HNO_3 at different temperatures as follows.



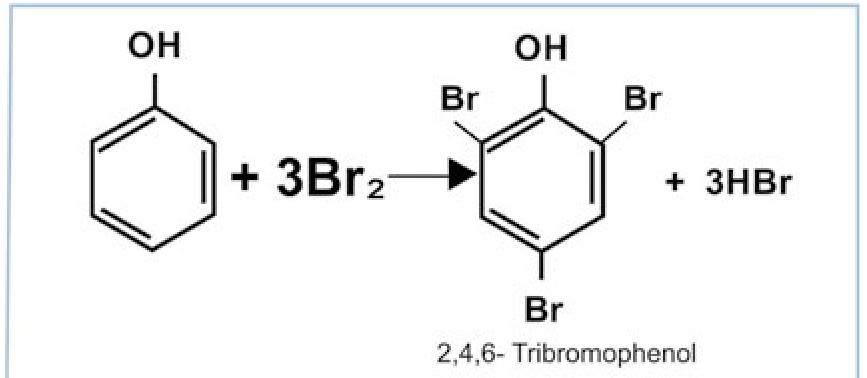
Sulphonation

Phenol reacts with conc. H_2SO_4 at room temperature giving ortho and para hydroxy benzene sulphonic acids.



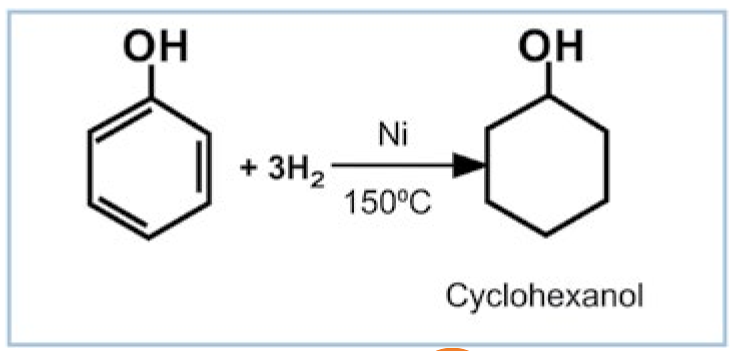
Halogenation

An aqueous solution of phenol reacts with bromine water to give white ppt. of 2,4,6- tribromophenol.



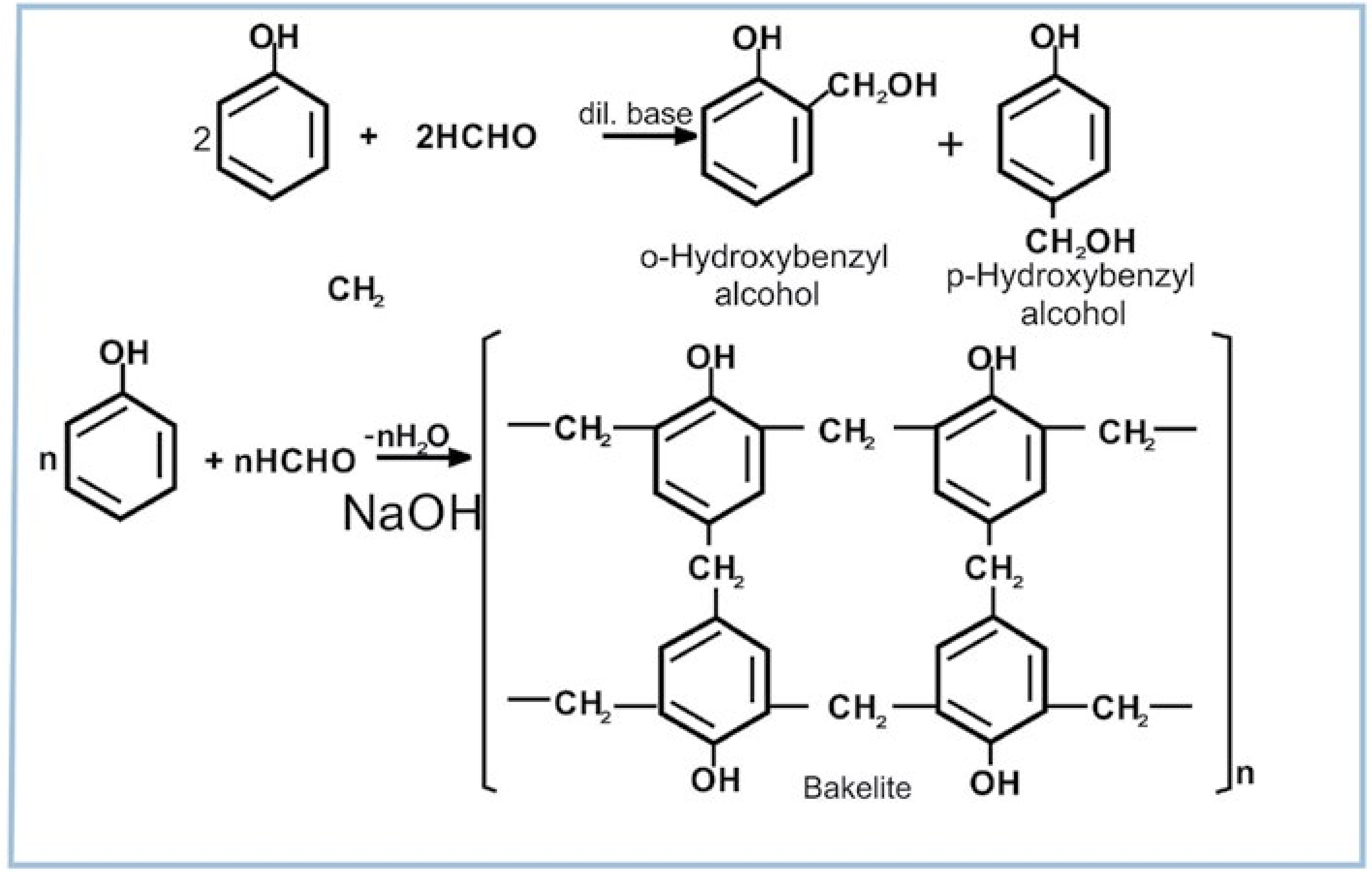
Hydrogenation

When hydrogen is passed through phenol at 150°C in the presence of Ni catalyst it gives cyclohexanol.



Reaction with formaldehyde

Phenol reacts with formaldehyde (methanal) in the presence of acid or alkali to give hydroxy benzyl alcohol which on further reaction with other phenol molecules yield a polymer called bakelite.



11.6 ETHERS

Ethers are classified into two categories

1. Simple or symmetrical ethers, which contain two same alkyl groups e.g. di-methyl ether CH_3OCH_3 and diethyl ether $CH_3 — CH_2 — O — CH_2 — CH_3$.
2. Mixed or unsymmetrical ethers, which contain different alkyl or phenyl groups, e.g., ethyl methyl ether $CH_3 — O — CH_2 — CH_3$.

11.6.1 Nomenclature

Ethers are named either by I.U.P.A.C. system or by common names. In I.U.P.A.C. system the large alkyl (R) group is taken as parent molecule and given the last name (suffix) while the smaller alkyl group along with oxygen is used as prefix and given the name alkoxy (e.g.methoxy, ethoxy, propoxy, etc).

I. U.P. A. C. names are not common as they are difficult. Usually ethers are known by their common names, as given below;

Formula	Common Names	I.U.P.A.C
CH_3OCH_3	Dimethyl ether	Methoxy methane
$CH_3OC_2H_5$	Methyl ethylether	Methoxy ethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxy ethane
$C_2H_5O\ CH_2 — CH_2 — CH_3$	Ethyl n-propylether	Ethoxy propane
$CH_3OC_6H_5$	Methyl phenyl ether	Methoxy benzene

11.6.2 Preparation of Ethers

Ethers are prepared from alcohols either directly or indirectly. Usually they are obtained by the following methods.

(i) By Williamsons synthesis

Alcohols are reacted with metallic sodium to form alkoxides. This alkoxide ion is a strong nucleophile and readily reacts with alkyl halide to produce an ether.

$$2C_2H_5OH + 2Na \rightarrow 2C_2H_5O^-Na^+ + H_2$$

$$C_2H_5O^-Na^+ + C_2H_5Br \rightarrow C_2H_5OC_2H_5 + NaBr$$

(ii) Alkyl halides are heated with dry silver oxide to form ethers

$$2C_2H_5Br + Ag_2O \rightarrow C_2H_5OC_2H_5 + 2AgBr$$

11.6.3 Physical Properties

Usually ethers are volatile liquids, highly inflammable with low boiling points. They are slightly soluble in water but freely soluble in organic solvents. Ether molecules do not show hydrogen bonding with one another but they show weak hydrogen bonding with water molecules due to which they are slightly soluble in water.

11.6.4 Chemical Reactivity

Ethers are comparatively inert substances. The reagents like ammonia, alkalies, dilute acids and metallic sodium, have no action on ethers in cold state. Moreover, they are not oxidized or reduced easily. However ethers show some reactions, e.g.

1. With hydrogen iodide ethers give alcohols which can react further to give alkyl iodides.

$$C_2H_5OC_2H_5 + HI \longrightarrow C_2H_5 — \overset{+}{\underset{|\atop H}{O}} — C_2H_5 + I^-$$

Oxonium ion

$$C_2H_5 — \overset{+}{\underset{|\atop H}{O}} — C_2H_5 + I^- \longrightarrow C_2H_5OH + C_2H_5I$$

2. Ethers also react with hot phosphorus pentachloride to give alkyl chloride.

$$C_2H_5OH + 4I_2 + 6NaOH \rightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

KEY POINTS

1. Alcohols and Phenols are hydroxy derivatives of aliphatic and aromatic hydrocarbons.
2. General formula for alcohol is ROH, for Phenol is Ph OH, and for ether it is ROR.
3. Alcohols are usually named by replacing 'e' for the alkane with 'ol'.
4. In Pakistan ethanol is prepared commercially from molasses.
5. Fermentation is a biochemical phenomenon which may occur naturally or artificially.
6. Ethyl alcohol obtained by fermentation is less than 12% concentrated.
7. Ethyl alcohol gives different products when reacts with H_2SO_4 of different concentrations.
8. Ethyl alcohol is used as a solvent, as a beverage and as a fuel.
9. Primary, secondary and tertiary alcohols can be distinguished by Lucas test.
10. Picric acid is a phenol which behaves like an acid.

EXERCISE

1. Primary, secondary and tertiary alcohols can be identified by______ test.
2. Oxidation of_________ alcohols give ketones.
3. Alcohols on heating with________ give alkenes at high temperature.
4. Alcohols have_______ boiling points than ethers due to stronger hydrogen bonding.
5. Williamsons synthesis is used to prepare_______ .
6. _______is also called wood spirit.
7. Carbolic acid is the other name of_______ .
8. Primary, secondary and tertiary alcohols can be prepared by reacting Grignard reagent with_______ , _______ and _______.
9. Alcohols and_______react to produce esters.
10. _______ is used as anti-freezing agent in automobile radiator.
11. The process of conversion of starch into alcohol with the help of microorganisms is called_______ .
12. Ketones on reduction give_______ alcohols.

Q.2. Indicate True or False

1. Methylated spirit contains 95% methyl alcohol and 5% ethyl alcohol.
2. Ethyl alcohol is a very good anti-freezing agent.
3. Methanol is also called wood spirit.
4. Only 14% ethyl alcohol can be prepared by fermentation.
5. Ethers do not show hydrogen bonding.
6. Alcohols are more acidic than phenols.
7. Phenol is more soluble in water than lower alcohols.
8. Alcohols are more basic than ethers.
9. Ethers have higher boiling points than alcohols and phenols.
10. Methanol and ethanol can be distinguished by iodoform test.

Q.3. Multiple Choice Questions. Encircle the correct answer.

i) Which compound shows hydrogen bonding
a) C_2H_6 b) C_2H_5Cl c) CH_3-O-CH_3 d) C_2H_5OH

ii) Which compound shows maximum hydrogen bonding with water?
a) CH_3OH b) C_2H_5OH c)CH_3-O-CH_3 d) C_6H_5OH

iii) Which compound is more soluble in water
a) C_2H_5OH b) C_6H_5OH c) CH_3COCH_3 d) n-Hexanol

iv) Which compound will have the maximum repulsion with H_2O?
a) C_6H_6 b) C_2H_5OH c) $CH_3CH_2CH_2OH$ d) CH_3— O — CH_3

v) Ethanol can be converted into ethanoic acid by
a) Hydrogenation b) Hydration c) Oxidation d) Fermentation

vi) Which enzyme is not involved in fermentation of starch?
a) Diastase b) Zymase c) Urease d)Invertase

vii) Which compound is called a universal solvent?
a) H_2O b) CH_3OH c) C_2H_5OH d) CH_3— O — CH_3

viii) Methyl alcohol is not used
a) as a solvent
b) as an anti-freezing agent
c) as a substitute for petrol
d) for denaturing of ethyl alcohol

ix) Rectified spirit contains alcohol methyl about
a) 80% b) 85% c) 90% d) 95%

x) According to Lewis concept ethers behave as
a) Acid
b) Base
c) Acid as well as a base
d) None of them

Q.4. What are alcohols. How are they classified? How will you distinguish between primary, secondary and tertiary alcohols?

Q.5. How is methyl alcohol obtained on large scale? How it may be distinguished from ethyl alcohol?

Q.6. What is fermentation? Which compound may be obtained on industrial scale by fermentation?

Q.7. Explain the following terms.
Absolute alcohol, Methylated spirit, Rectified spirit, Denaturing of alcohols.

Q.8. How does ethyl alcohol react with the following reagents?
i) Conc.H_2SO_4 ii) Na iii) PCl_5 iv) CH_3COOH v) $SOCl_2$

Q.9. How will you obtain primary, secondary and tertiary alcohols by reacting Grignard reagent with suitable carbonyl compounds.

Q.10. How will you distinguish between
i) an alcohol and a phenol
ii) an alcohol and an ether
iii) methanol and ethanol
iv) a tertiary alcohol and a primary alcohol
v) 1-propanol and 2-propanol

Q.11. Give reasons for the followings:
i) Ethyl alcohol is a liquid while methyl chloride is a gas.
ii) Ethanol has higher boiling point than diethyl ether.
iii) Absolute alcohol cannot be prepared by fermentation process.
iv) Ethanol gives different products with conc. H_2SO_4 under different conditions.
v) Water has higher boiling point than ethanol.

Q.12. How will you convert
i) Methanol into ethanol
ii) Ethanol into methanol
iii) Ethanol into isopropyl alcohol
iv) Formaldehyde into ethyl alcohol
v) Acetone into ethyl alcohol

Q.13. Explain the following terms using ethyl alcohol as an example.
i) Oxidation ii) Dehydration iii) Esterification
iv) Ether formation

Q.14. Compare the reactions of phenol with those of ethanol. Discuss the difference if any.

Q.15. Arrange the following compounds in order of their increasing acid strength and give reasons.

H_2O, C_2H_5OH, C_6H_5OH , C_6H_5COOH

Q.16. Write down two methods for preparing phenol. What is the action of following on phenol.

HNO_3, NaOH, Zn, Bromine water

Q.17. Give the uses of phenols. How bakelite is prepared from it.

Q.18. (a) Write I.U.P.A.C. names ofthe following compounds.

$(CH_3)_2$ CH - OH, $(CH_3)_2CHCH_2OH$,
$(CH_3)_3COH$, C_2H_5 - CH - OH, (with CH_3 attached to CH)

(b) Write structure formulas for the following compounds.

Glycol, Glycerol, Carbolic Acid, Acetophenone, Picric Acid

Q.19. (a) Name the following compounds

$CH_3 - CH_2 - CH_2 - O - CH_3$, $C_6H_5 - O - C_6H_5$

$(CH_3)_2CH - O - CH(CH_3)_2$, $CH_3 - O - C_6H_5$

$CH_3 - CH_2 - CH_2 - O - CH_2 - CH_3$

(b). Write down structural formulas of the following compounds.Methoxy ethane, ethoxy benzene, sodium ethoxide, sodium phenoxide, propoxy propane.

CHAPTER

12

ALDEHYDES AND KETONES

In This Chapter You Will Learn:

1. How to name aldehydes and ketones.
2. General methods for the preparation of aldehydes and ketones.
3. How are formaldehyde and acetaldehyde commercially prepared.
4. The relationship between structure and reactivity of carbonyl group.
5. The reactions of aldehydes and ketones and their mechanism.
6. How to identify aldehydes and ketones.
7. Tests for the distinction between aldehydes and ketones.

12. 1 INTRODUCTION

Organic compounds containing the carbonyl functional group, $>C=O$, are called carbonyl compounds. In a carbonyl group, a carbon atom is bonded to oxygen with a double bond.

In aldehydes, the carbonyl group is bonded to at least one hydrogen atom, and so it occurs at the end of a chain.

An aldehyde can be represented by the general formula,

$R-\overset{\overset{O}{||}}{C}-H$,where R may be H or an alkyl group.

In ketones, the carbonyl group is bonded to two carbon atoms, and so it occurs within a chain. A ketone may be represented by the general formula,

The homologous series of both aldehydes and ketones have the general formula, $C_nH_{2n}O$.

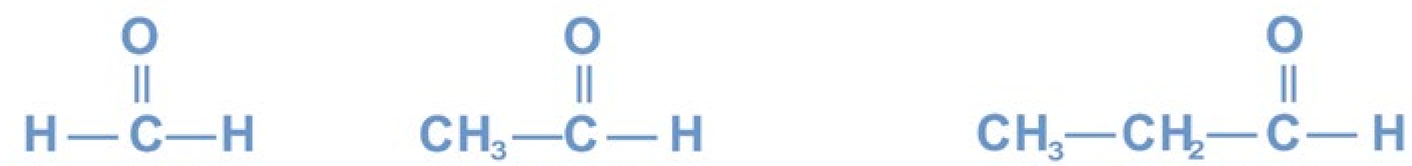
Aldehydes and ketones are present in many naturally occurring compounds. The aldehyde group is present in most sugars. They are the principal constituents of a number of essential oils used as fragrances and flavours. Ketonic group is present in camphor and menthone.

12.2 NOMENCLATURE

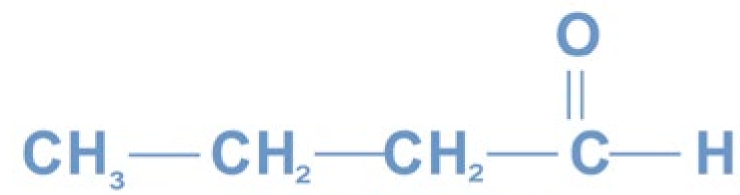
a. Aldehydes

Common Names:

The common names of aldehydes are obtained from the common names of carboxylic acids containing the same number of carbon atoms. The ending -ic acid in the common name of the acid is replaced by the word aldehyde.

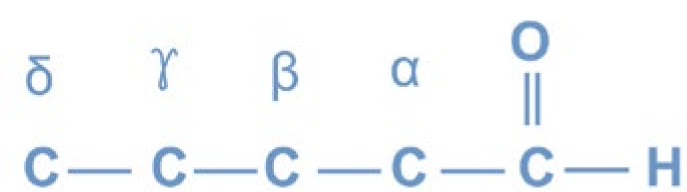


Formaldehyde Acetaldehyde Propionaldehyde



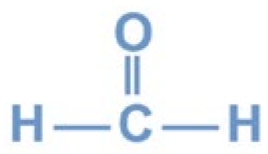
Butyraldehyde

The positions of other groups on the chain are indicated by Greek letters (α, β, γ, δ). Lettering starts on the carbon adjacent to the carbonyl group,

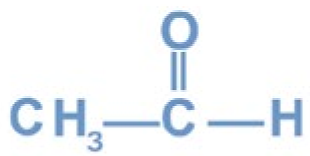


IUPAC Names:

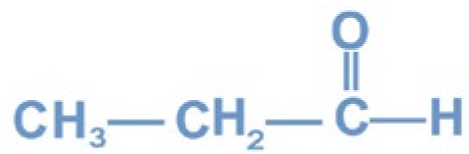
The **IUPAC** names of aldehydes are derived from the names of alkanes having the same number of carbon atoms. The letter - e in the name of the alkane is replaced with al The positions of other groups on the chain are indicated by using numbers. Numbering starts from the carbonyl carbon. Aromatic aldehydes are not given **IUPAC** names.



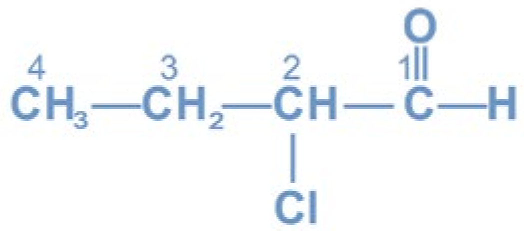
Methanal



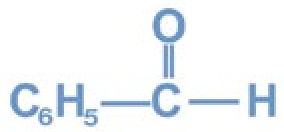
Ethanal



Propanal



2-Chlorobutanal

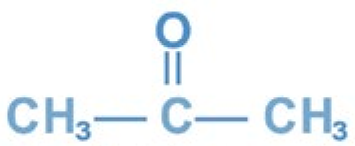


Benzaldehyde

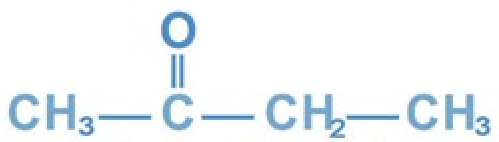
b. Ketones

Common Names

The common names of ketones are obtained by separately writing the names of the alky! groups attached to the carbonyl carbon. The word ketone is then added as a separate word. The names of the alkyl groups are written alphabetically. When the two alkyl groups are the same, the prefix di - is added before the name of the alkyl group.



Dimethyl ketone (Acetone)

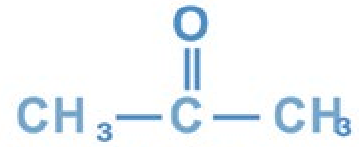


Ethyl methyl ketone

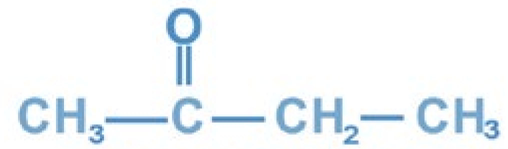
The positions of other groups are indicated by Greek letters, the α - carbon atom being the one adjacent to the carbonyl group. If the two alkyl groups in a ketone are the same, the ketone is said to be symmetrical, if unlike, unsymmetrical.

IUPAC Names

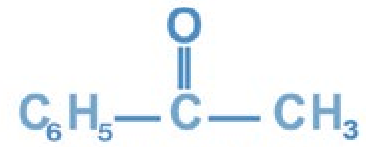
The IUPAC names of ketones are derived from the names of alkanes having the same number of carbon atoms. The letter e in the name of alkane is replaced with the suffix -one. The positions of the carbonyl group and of other groups on the chain are indicated by numbers. Numbering is started from that end whjch is nearest to the carbonyl group. Aromatic ketones are not given IUPAC names.



2-Propanone (Propanone)



2-Butanone (Butanone)



Acetophenone

12.3 PREPARATION OF ALDEHYDES AND KETONES

Aldehydes are obtained by the oxidation of primary alcohols whereas ketones by the oxidation of secondary alcohols. Ketones are also prepared by hydration of alkynes.

a. Preparation of Formaldehyde (Formalin)

(i) Laboratory Method

Formaldehyde is prepared in the laboratory by passing a mixture of methyl alcohol vapours and air over platinised asbestos or copper or silver catalyst at 300 ^{0}C.

$$2CH_3OH + O_2 \xrightarrow[300^oC]{\text{Pt-asbestos}} 2H-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2H_2O$$

Set up the apparatus as shown in Fig. (12.1). Air is drawn through methyl alcohol with the help of a suction pump. Methyl alcohol is oxidised to gaseous formaldehyde which is absorbed in water. The resulting mixture is called formalin. Formalin is a mixture of 40 % formaldehyde, 8% methyl alcohol and 52 % water.

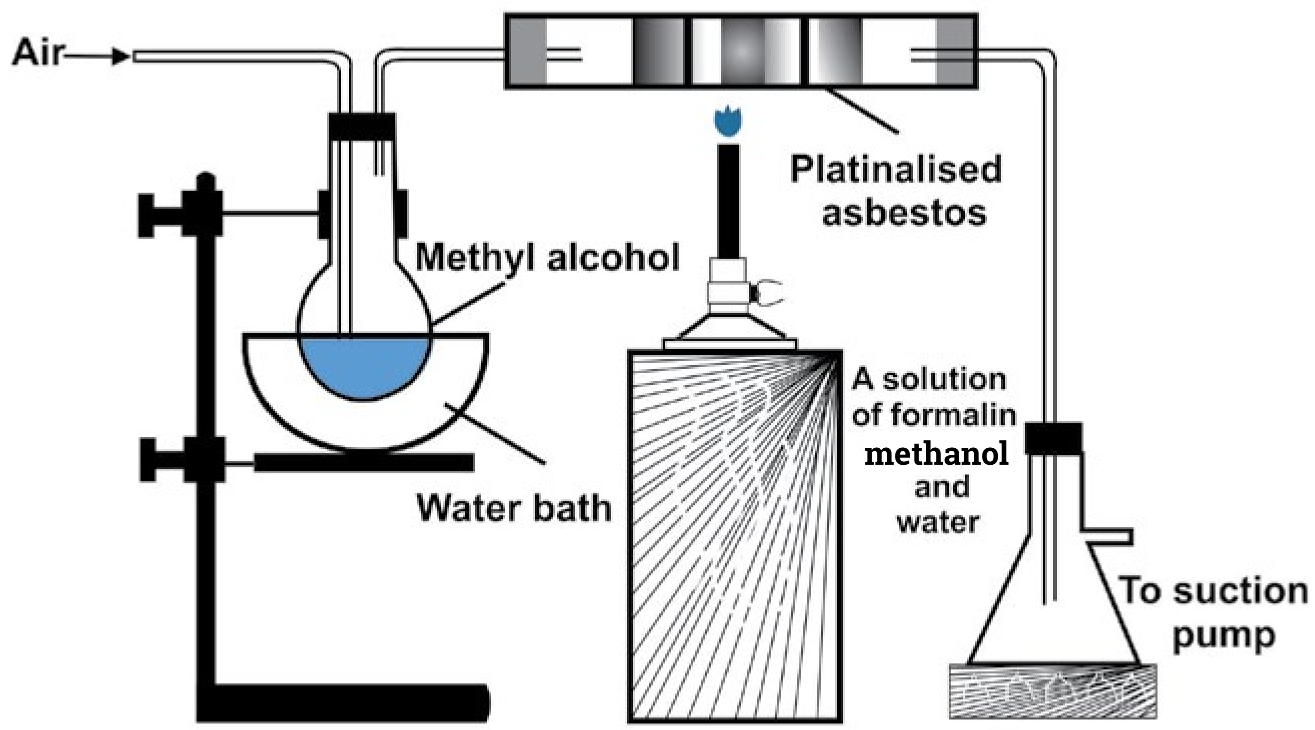


Fig. 12.1 Preparation of Formaldehyde (formalin)

(ii) Industrial Method

Formaldehyde is manufactured by passing a mixture of methanol vapours and air over iron oxide-molybdenum oxide or silver catalyst at 500 °C.

$$2CH_3OH + O_2 \xrightarrow[500^oC]{FeO,\ Mo_2O_3} 2H-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2H_2O$$

b. Preparation of Acetaldehyde

(i) Laboratory method

Acetaldehyde is prepared in the laboratory by the oxidation of ethyl alcohol with acidified sodium dichromate solution.

$$CH_3CH_2OH + [O] \xrightarrow[\triangle]{Na_2Cr_2O_7 + H_2SO_4} C_3H\ CHO + H_2O$$

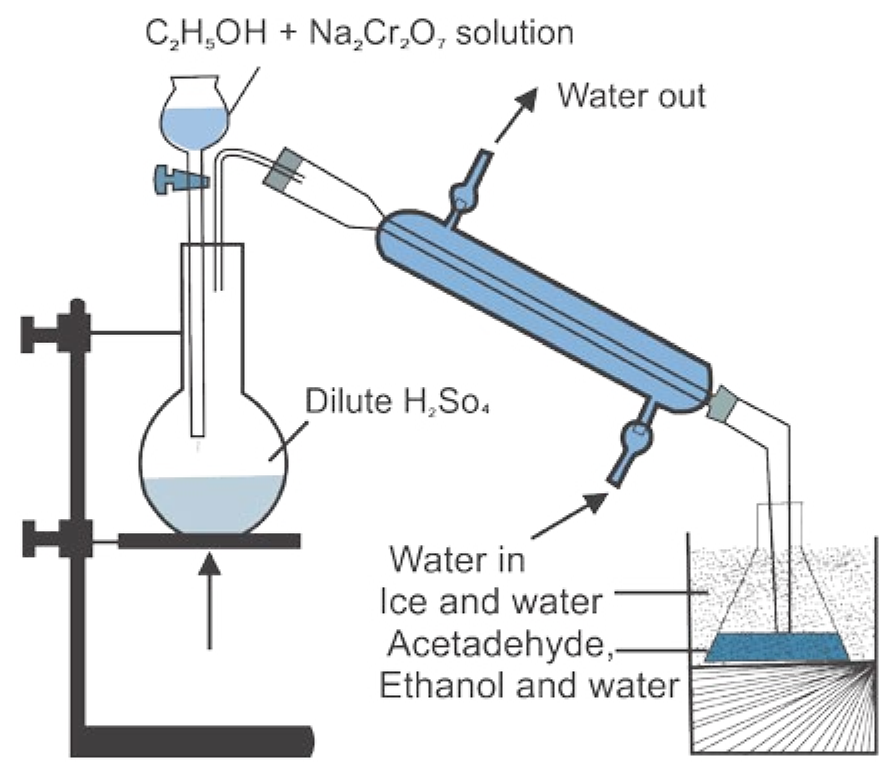


Fig. 12.2 Preparation of Acetaldehyde

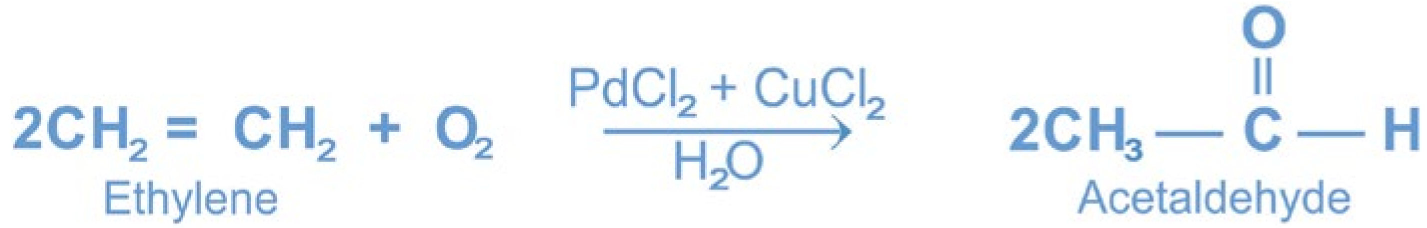
A mixture of ethyl alcohol and sodium dichromate solution is run into boiling dilute sulphuric acid. Immediately a vigorous reaction takes place and the acetaldehyde formed in liquid state is immediately distilled off. This prevents the oxidation of acetaldyde to acetic acid. Ethyl alcohol remains in solution until it is oxidised. Pure acetaldehyde is obtained by redistillation.

Acetaldehyde can also be prepared by the dry distillation of a mixture of calcium salts of formic acid and acetic acid.

$$\left(H-\overset{\overset{\displaystyle O}{\|}}{C}-O\right)_2Ca + \left(CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O\right)_2Ca \xrightarrow{Heat} 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2CaCO_3$$

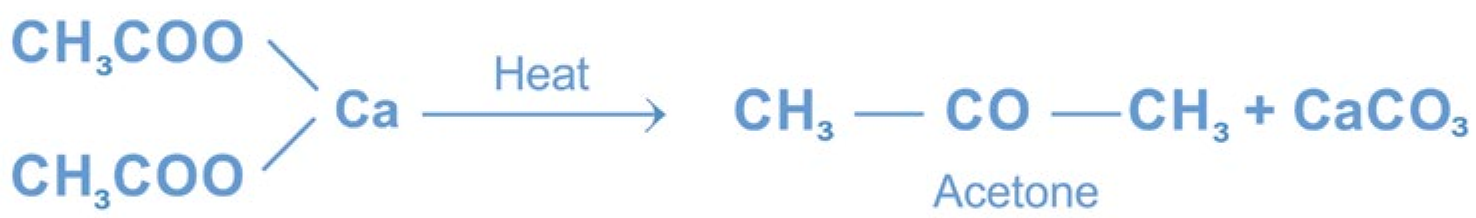
(ii) Industrial Method

Acetaldehyde is prepared industrially by air oxidation of ethylene using palladium chloride catalyst with a cupric chloride promoter.



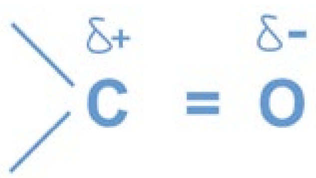
C. Preparation of Acetone

Acetone is prepared by dry distillation of calcium acetate.



12.4 REACTIVITY OF CARBONYL GROUP

The carbonyl group has a σ-bond and a π-bond. Thus it can undergo addition reactions. Most reagents react with the carbonyl group by adding to it. As oxygen is more electronegative, it tends to attract the π electrons to itself. This attraction makes the carbonyl group a polar group. The oxygen atom has a partial negative charge on it and is nucleophilic, whereas the carbon atom has a partial positive charge and is electrophilic,



Nucleophilic Addition Reactions of Aldehydes and Ketones

As a result of the unsymmetrical electronic distribution about the carbonyl group, the nucleophilic reagent can start the initial attack on the carbon. It appears that whether the initial attack is to be by a nucleophilic reagent or by an electrophilic reagent depends upon a particular reaction and upon the conditions under which that reaction is carried out. Therefore, most of the reactions of the carbonyl group will be considered to be nucleophilic addition reactions.

In these reactions of aldehydes and ketones, the negative part of the reagent combines with the electrophilic carbon of the carbonyl group, whereas the positive part, which is usually hydrogen goes to the oxygen. The nucleophilic addition reactions of carbonyl group are catalysed by bases or acids. Remember that whether the addition is base-catalysed or acid-catalysed, the adduct is the same. A base catalyst increases the nucleophilic character of the reagent, while an acid-catalyst promotes the nucleophilic attack by increasing the positive character (electrophilic character) of the carbonyl carbon atom.

12.5 REACTIONS OF CARBONYL COMPOUNDS

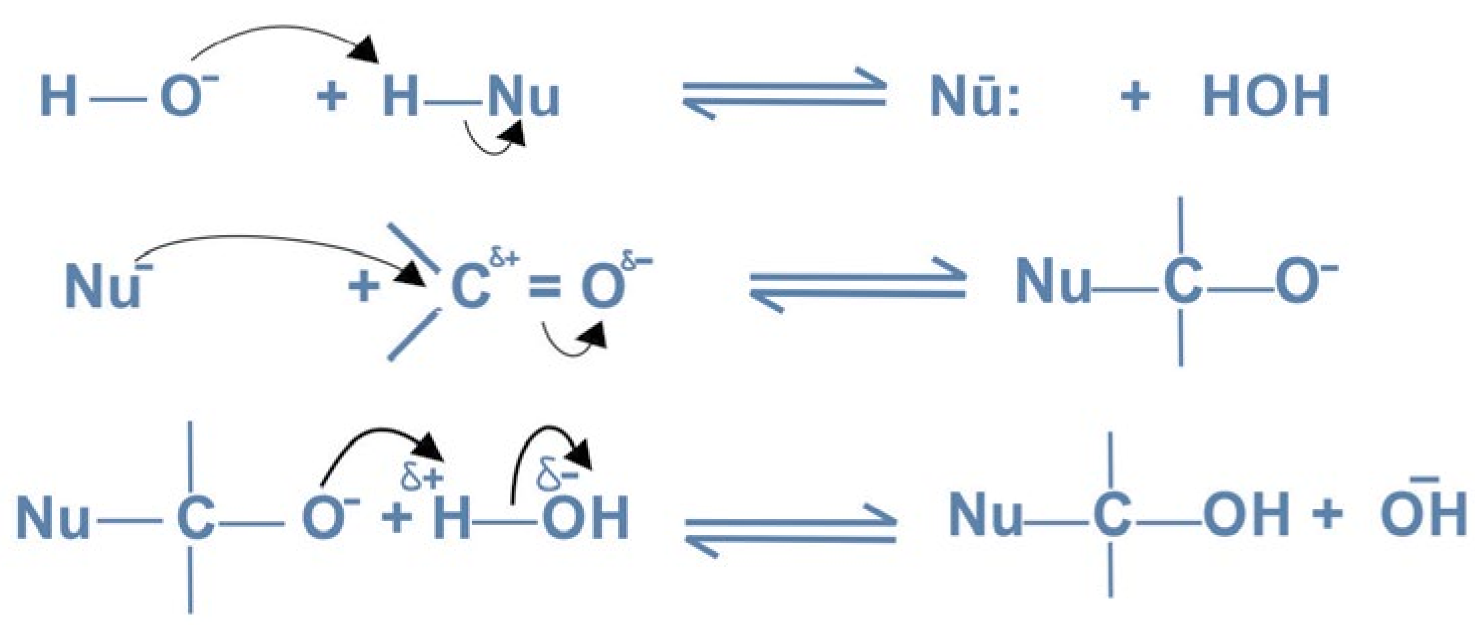
12.5.1 Nucleophilic Addition Reactions

The characteristic reactions of carbonyl compounds are nucleophilic addition reactions.

(a) Base-Catalysed Addition Reactions

A base-catalysed nucleophilic addition reaction will take place with a strong nucleophilic reagent. The base reacts with the reagent and generates the nucleophile. The addition is initiated by the attack of a nucleophile on the electrophilic carbon of the carbonyl group. The general mechanism of the reaction is as follows:

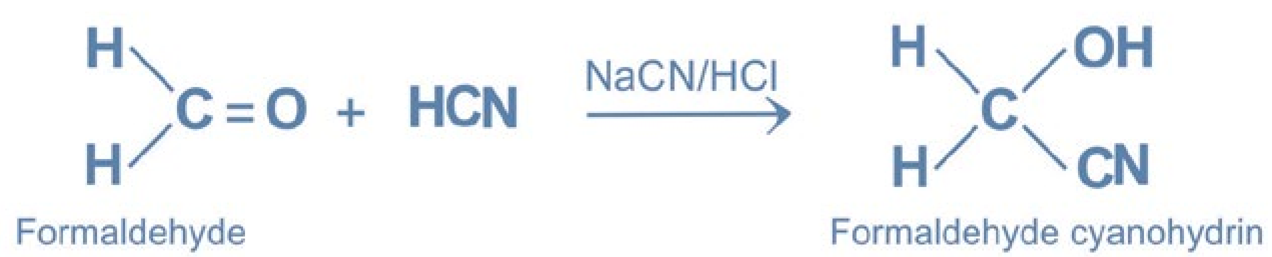
General mechanism:



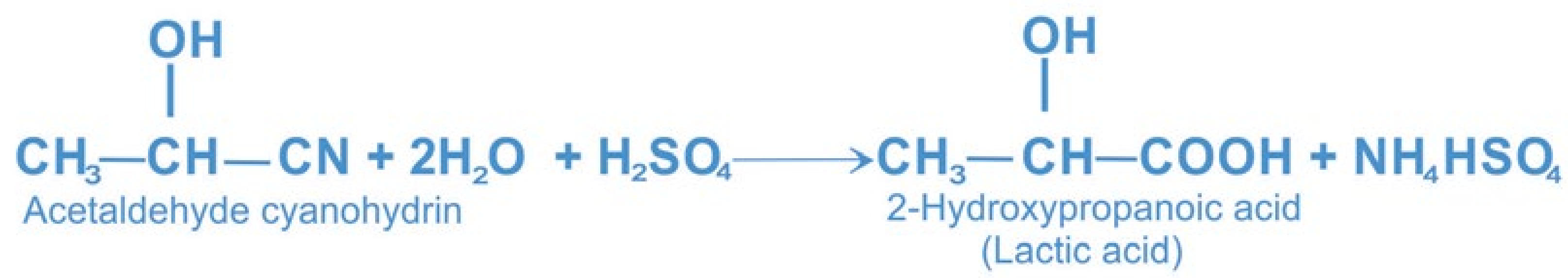
The base-catalysed nucleophilic addition reactions of aldehydes and ketones are the following:

1. Addition of Hydrogen Cyanide

Hydrogen cyanide adds to aldehydes and ketones to form cyanohydrins. The reaction is carried out by adding slowly a mineral acid to an aqueous solution of sodium cyanide. The acid generates HCN from sodium cyanide *in situ.*



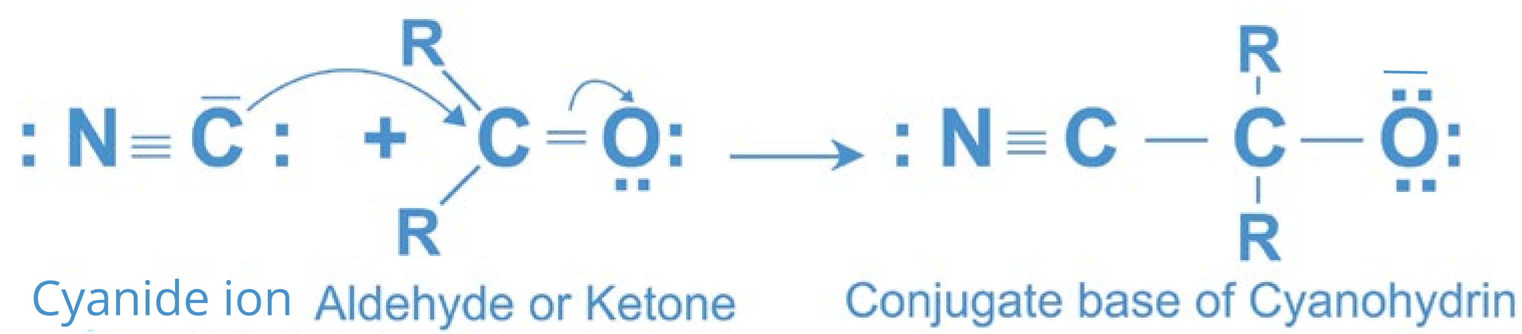
The cyano group, — C ≡ N is hydrolysed by an aqueous acid into a carboxylic acid through an acid amide.

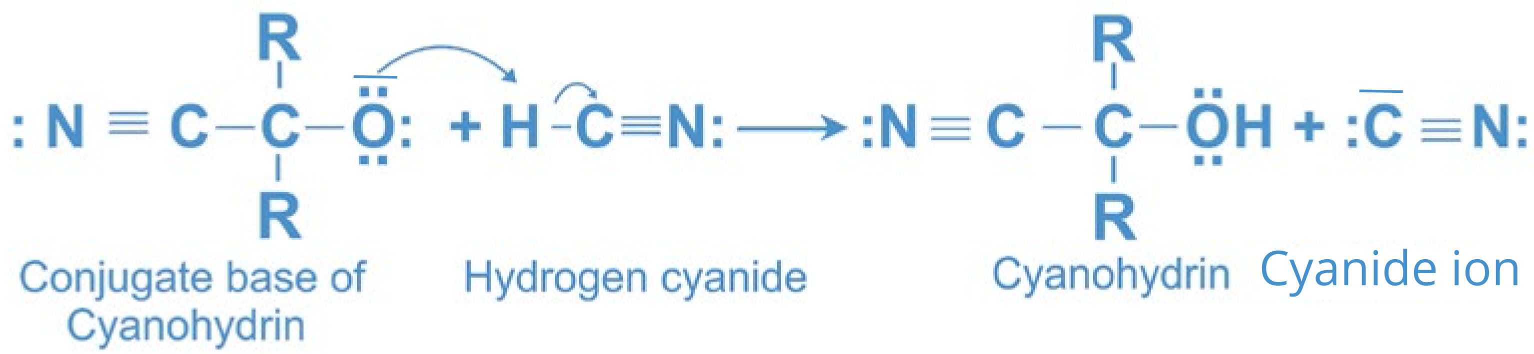


The reaction is used in the synthesis of α-hydroxy acids that contain one carbon atom more than the number of carbon atoms in the starting aldehydes or ketones.

Mechanism:

Nucleophilic attack by the negatiely charged carbon of cyanide ion at the carbonyl carbon of the aldehyde and ketone. Hydrogen cyanide itself is not very nucleophilic and does not ionize to from cyanide to a significant extent. Thus , a source of cyanide ion such as NaCN or KCN is used. The mechanism of the reaction is as follows:





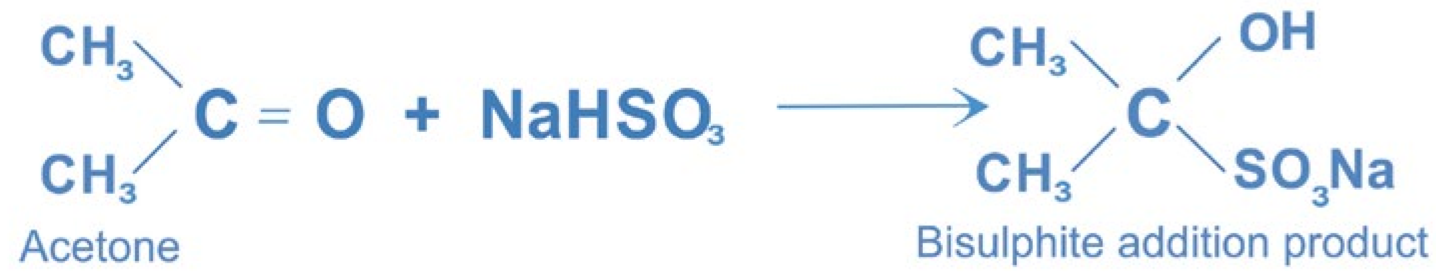
The hydroxide ion liberated in the formation of cyanohydrin reacts with undissociated hydrogen cyanide and produces more cyanide ions, which in turn react with more carbonyl compound.

2. Addition of Grignard Reagents

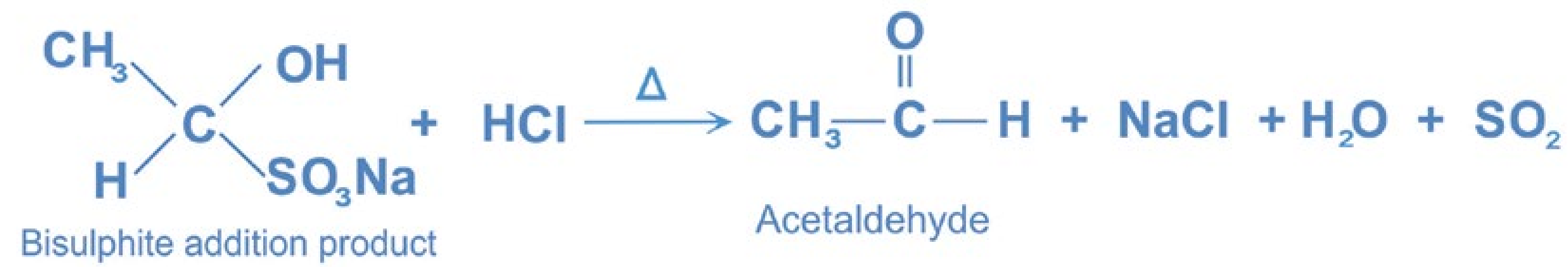
Grignard reagents add to aldehydes and ketones to form adducts which on hydrolysis with a dilute mineral acid (HCl, H_2SO_4) give alcohols. The reaction has already been studied in chapter 10.

3. Addition of Sodium Bisulphite

Aldehydes and small methyl ketones react with a saturated aqueous solution of sodium bisulphite to form a crystalline white precipitate of sodium bisulphite adduct.



Bisulphite on heating with a dilute mineral acid (HCl or H_2SO_4), regenerates the parent aldehyde or ketone.



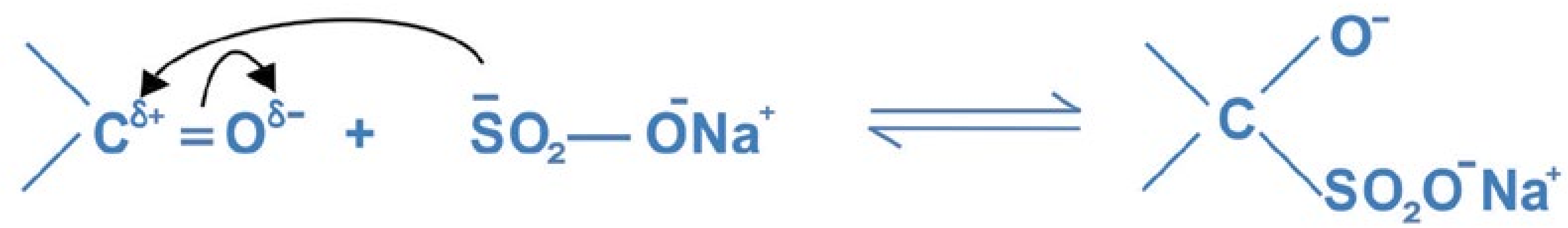
The reaction is used for the separation and purification of carbonyl compounds from non-carbonyl compounds such as alcohols.

Mechanism:

Sodium bisulphite ionises to form sulphite ions.

$$NaHSO_3 \rightleftharpoons \bar{S}O_2—O^- + H^+ + Na^+$$

The sulphite ion acts as a nucleophile, since the sulphur atom is more nucleophilic than oxygen, a C—S bond is formed.



Proton is attached to the negatively charged oxygen atom to form bisulphite addition product.

Bisulphite addition product

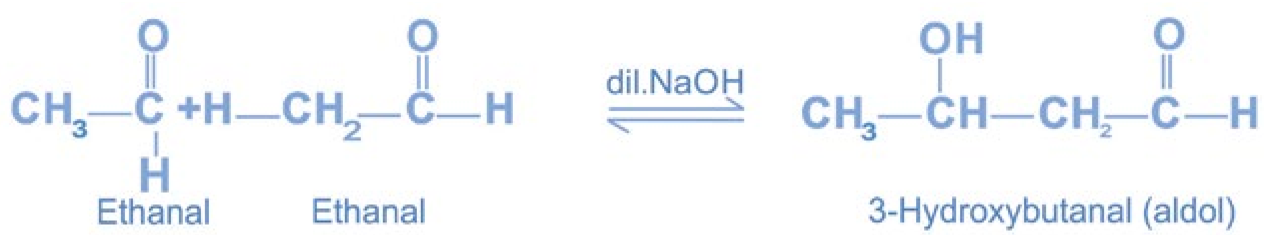
Ketones in which both alkyl groups are larger than methyl do not react with sodium bisulphite.

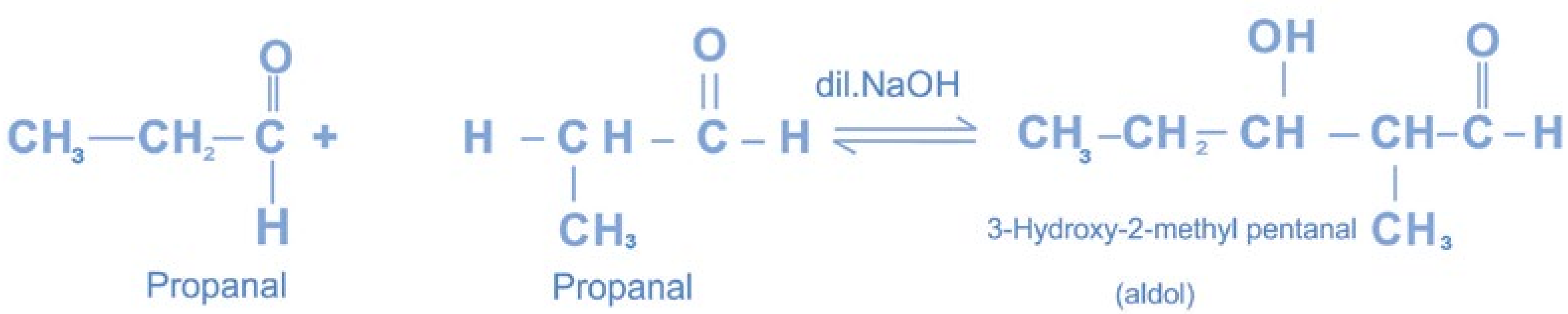
4. Condensation Reactions

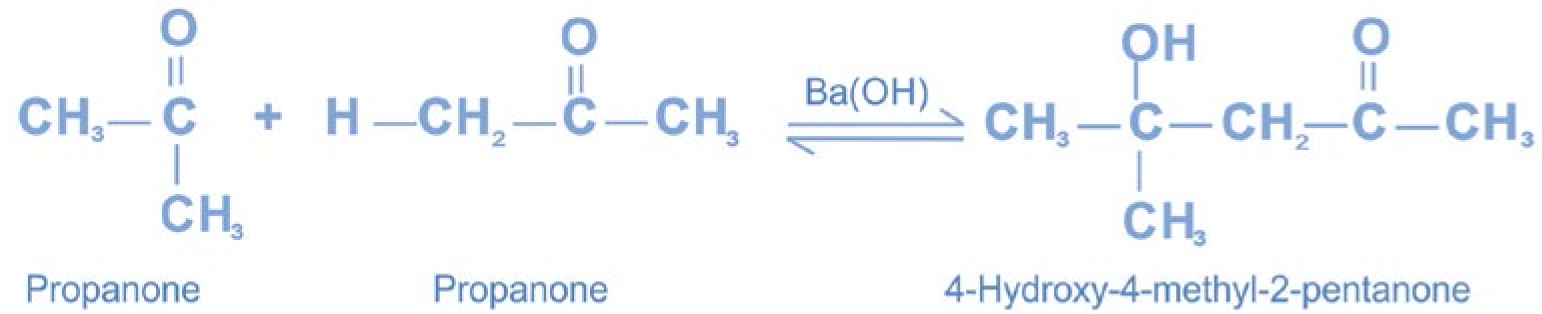
The reactions in which two molecules of the same or different compounds combine to form a new compound with or without the elimination of a small molecule like H_2O or NH_3, are called condensation reactions.

(i) Aldol Condensation

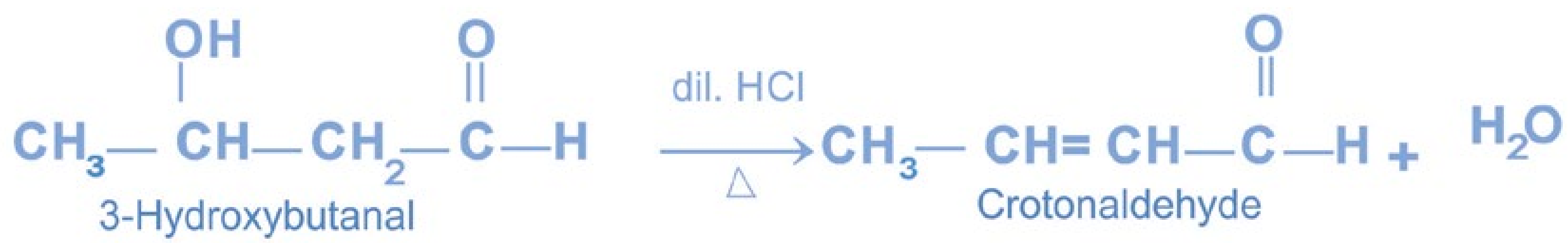
Aldehydes and ketones possessing α-hydrogen atoms react with a cold dilute solution of an alkali to form addition products known as aldols. The name 'aldol' is given to the product because it contains both aldehyde and alcohol functional groups. Note that the name aldol condensation is reserved for the reaction that starts with two identical carbonyl compounds. Two molecules of the same carbonyl compound condense to form an aldol.







The aldol compound readily loses water on heating in the presence of dilute acid to form an unsaturated carbonyl compound. A carbon-carbon double bond is formed between the α- and β- carbon atoms.



Mechanism of Aldol Condensation:

The hydroxide ion acts as a base. It removes a proton from α-carbon of one molecule of the carbonyl compound to form a carbanion.

The carbanion acts as a nucleophile. It attacks the electrophilic carbonyl carbon atom of the unchanged second molecule to form an alkoxide ion.

The alkoxide ion removes a proton from water to form aldol.

$$CH_3-\overset{O^-}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H + \overset{\delta+}{H}-\overset{\delta-}{OH} \longrightarrow CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}-H + \overline{O}H$$

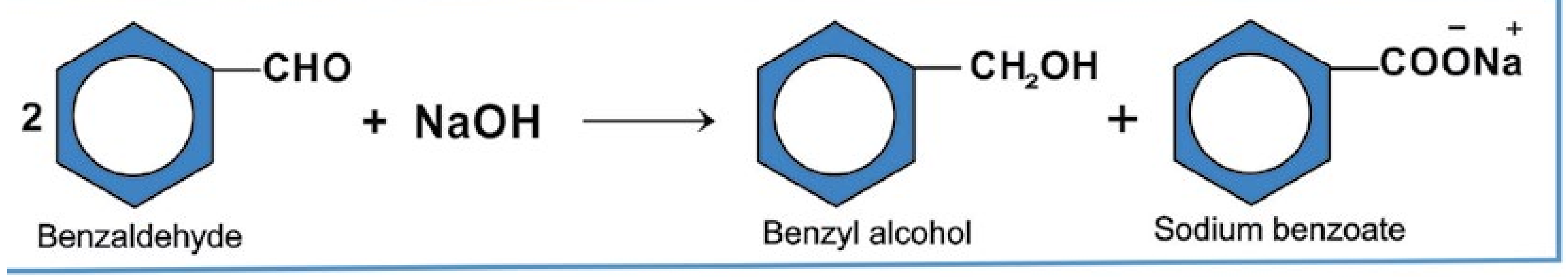
Alkoxide ion — 3-Hydroxybutanal (aldol)

The basic catalyst hydroxide ion is regenerated.

5. Cannizzaro's Reaction

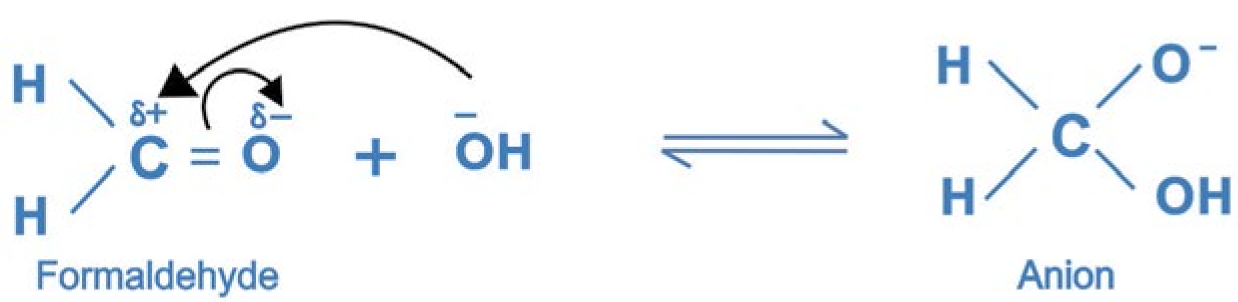
Aldehydes that have no α-hydrogen atoms undergo Cannizzaro's reaction. It is a disproportionation (self oxidation-reduction) reaction. Two molecules of the aldehyde are involved, one molecule being converted into the corresponding alcohol (the reduced product) and the other into the acid in the salt form (the oxidation product). The reaction is carried out with 50 percent aqueous solution of sodium hydroxide at room temperature.

$$2H-\overset{O}{\overset{\|}{C}}-H + NaOH \longrightarrow CH_3OH + H-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Na}$$

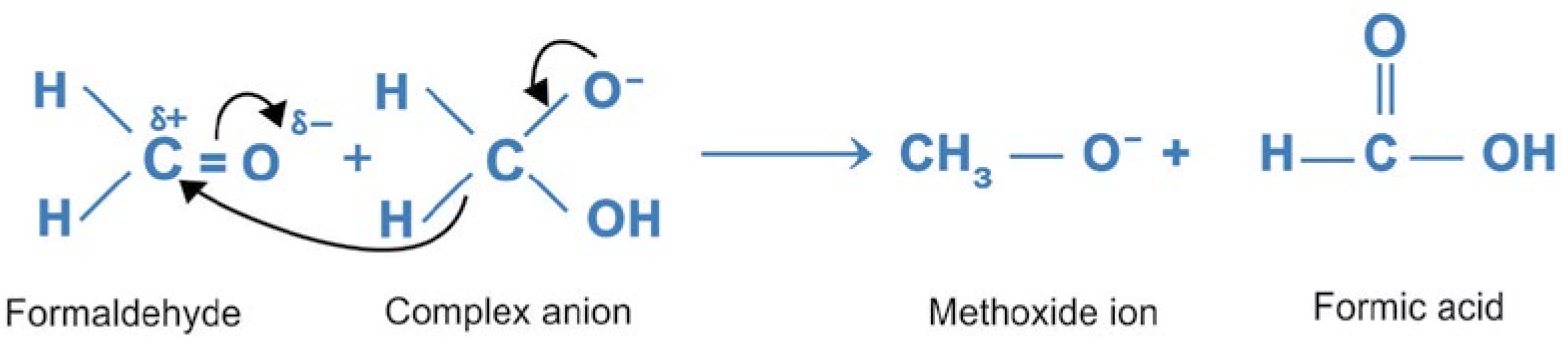


Mechanism:

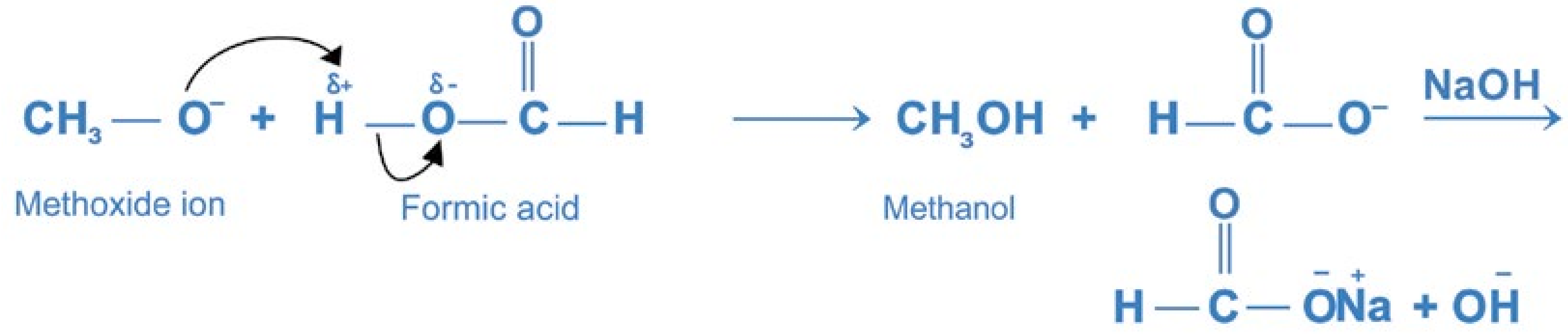
The hydroxide ion acts as a nucleophile. It attacks on the electrophilic carbonyl carbon to form a complex anion.



The anion transfers a hydride ion to second molecule of formaldehyde.



The presence of the negative charge on oxygen of the anion helps in the loss of hydride ion.The methoxide ion acts as a base and abstacts a proton from formic acid to form methanol and formate ion.



The formate ion in the presence of alkali gives a salt of the acid.

6. Haloform Reaction

Only acetaldehyde and methyl ketones react with halogens in the presence of sodium hydroxide to give haloform and sodium salt of the acid. The term haloform is used for the reaction because a haloform (chloroform, bromoform or iodoform) is one of the products.

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3X_2 + 4NaOH \longrightarrow CHX_3 + RCOONa + 3NaX + 3H_2O$$

R = alkyl, aryl or hydrogen; Halogen; Haloform; Sod.carboxylate

$$CH_3-\overset{O}{\overset{\|}{C}}-H + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$$

Acetaldehyde; Iodine; Iodoform (yellow ppt); Sod. formate

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$$

Acetone, Iodine → Iodoform, Sod. acetone

Secondary alcohols containing the hydroxyl group on the second carbon atom also undergo this reaction. Ethanol is the only primary alcohol that gives this reaction.

$$R-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + RCOONa + 5NaI + 5H_2O$$

Secondary alcohol → Iodoform, Sod. carboxylate

$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5NaI + 5H_2O$$

Ethanol → Iodoform, Sod.formate

From a synthetic point of view the haloform reaction affords a convenient method for converting a methyl ketone to a carboxylic acid containing one carbon atom less than the parent compound.

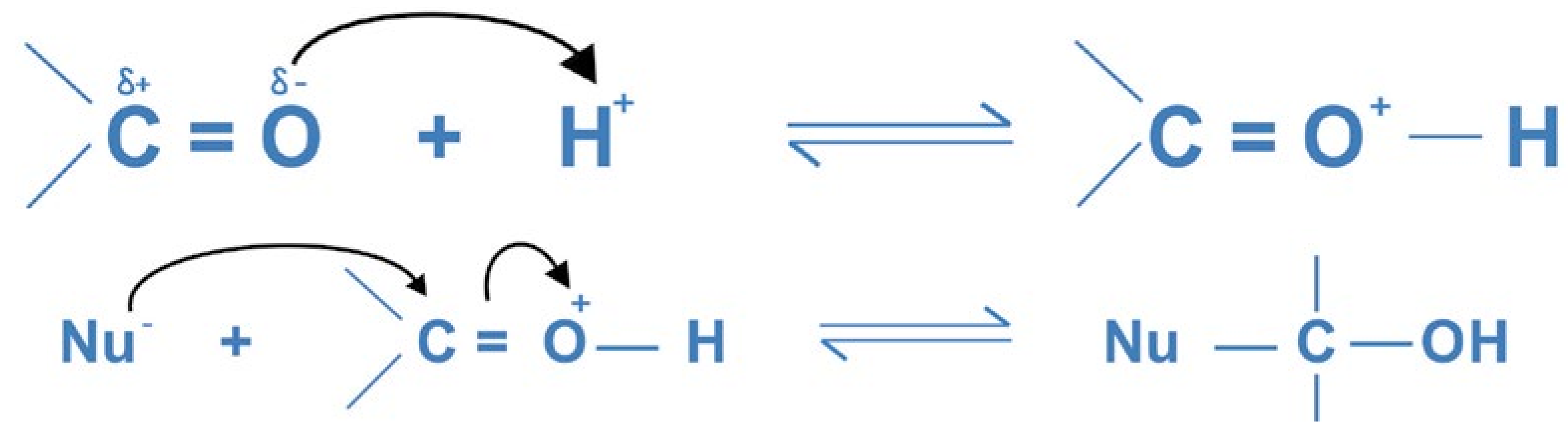
Iodoform Test:

The haloform reaction using iodine and aqueous sodium hydroxide is called the iodoform test. It results in the formation of water insoluble iodoform which is a yellow solid. Iodoform test is used for distinguishing methyl ketones from other ketones. It is also used to distinguish ethanol from methanol and other primary alcohols. It can be used to distinguish acetaldehyde from other aldehydes.

(b) Acid-Catalysed Addition Reactions

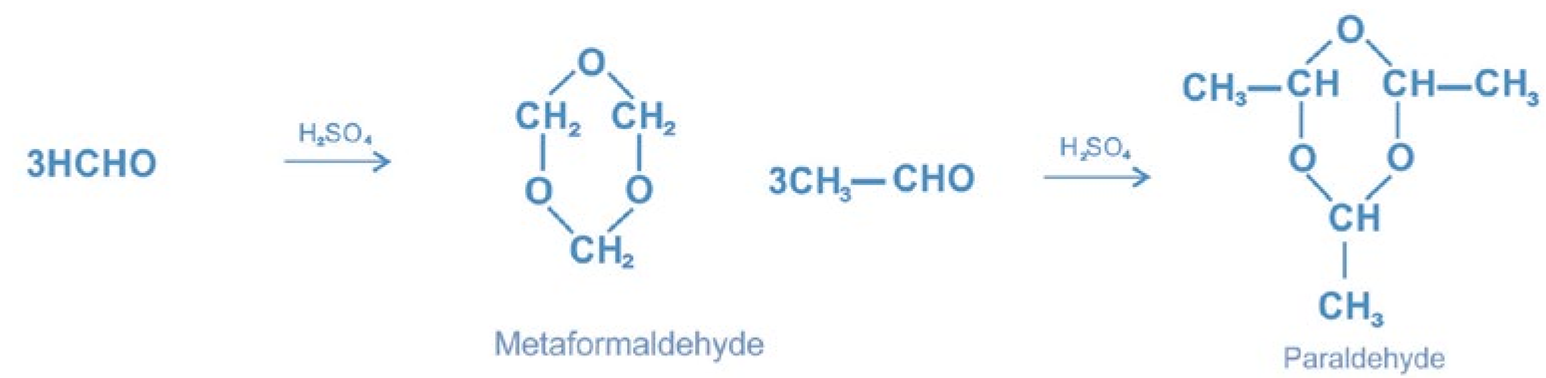
The acid catalysed nucleophilic addition reaction will take place with a weak nucleophilic reagent. The addition is initiated by the proton (H^+) liberated by the acid. The proton combines with the carbonyl oxygen atom and increases the electrophilic character of the carbonyl carbon. As a result, the attack of the weaker nucleophile on the electrophilic carbon becomes easier.

The general mechanism of the reaction is as follows.



The acid- catalysed nucleophilic addition reactions of aldehydes and ketones are the following.

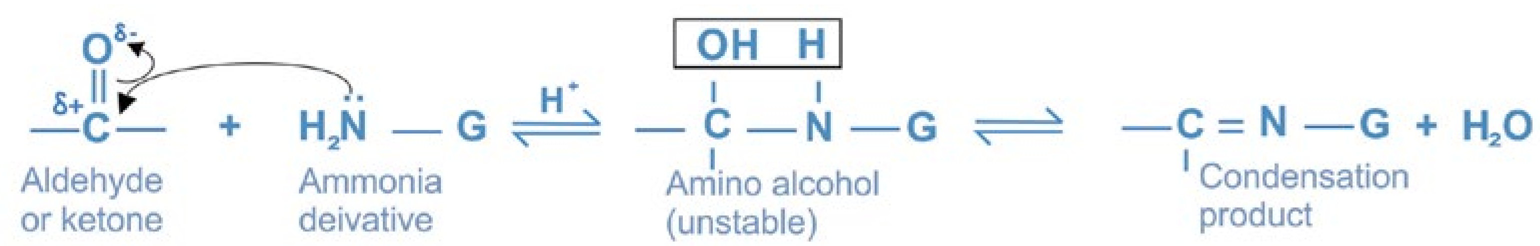
1. Both formaldehyde and acetaldehyde polymerize in the presence of dil. H_2SO_4 to give metaformaldehyde and paraldehyde respectively.



2. Reactions of Ammonia Derivatives

Aldehydes and ketones react with ammonia derivatives, $G — NH_2$ to form compounds containing the group, >C = N— G and water. The reaction is known as condensation reaction or addition - elimination reaction because water is lost after addition occurs. The reaction is acid catalysed.

The general reaction is:



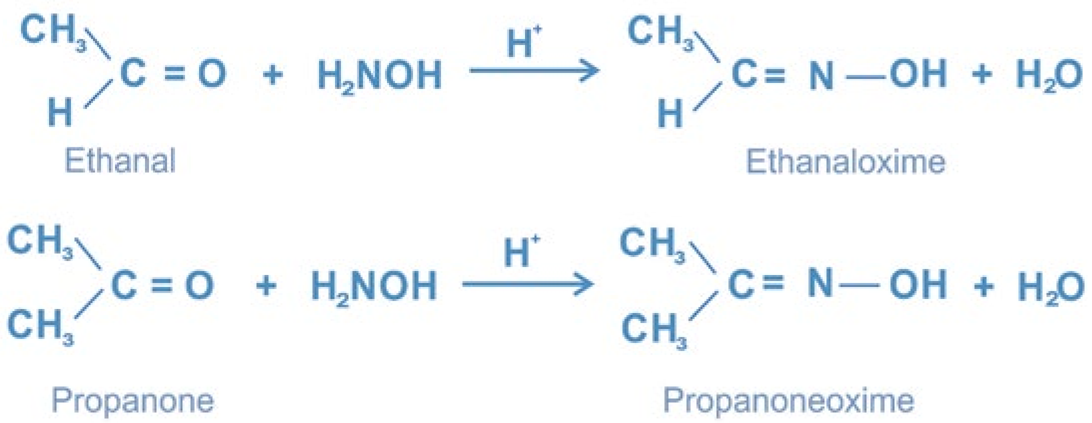
Where G = $\ddot{O}H$, $-\ddot{N}H_2$, $-\ddot{N}HC_6H_5$, $-\ddot{N}HCONH_2$, etc.

Some commonly used ammonia derivatives are hydroxylamine, NH_2OH, hydrazine, NH_2NH_2, phenylhydrazine, $C_6H_5NHNH_2$, semicarbazide, $NH_2NHCONH_2$, and 2,4- dinitrophenylhydrazine, $NH_2NHC_6H_3(NO_2)_2$.

The reactions of the above stated ammonia derivatives with aldehydes and ketones are as follow.

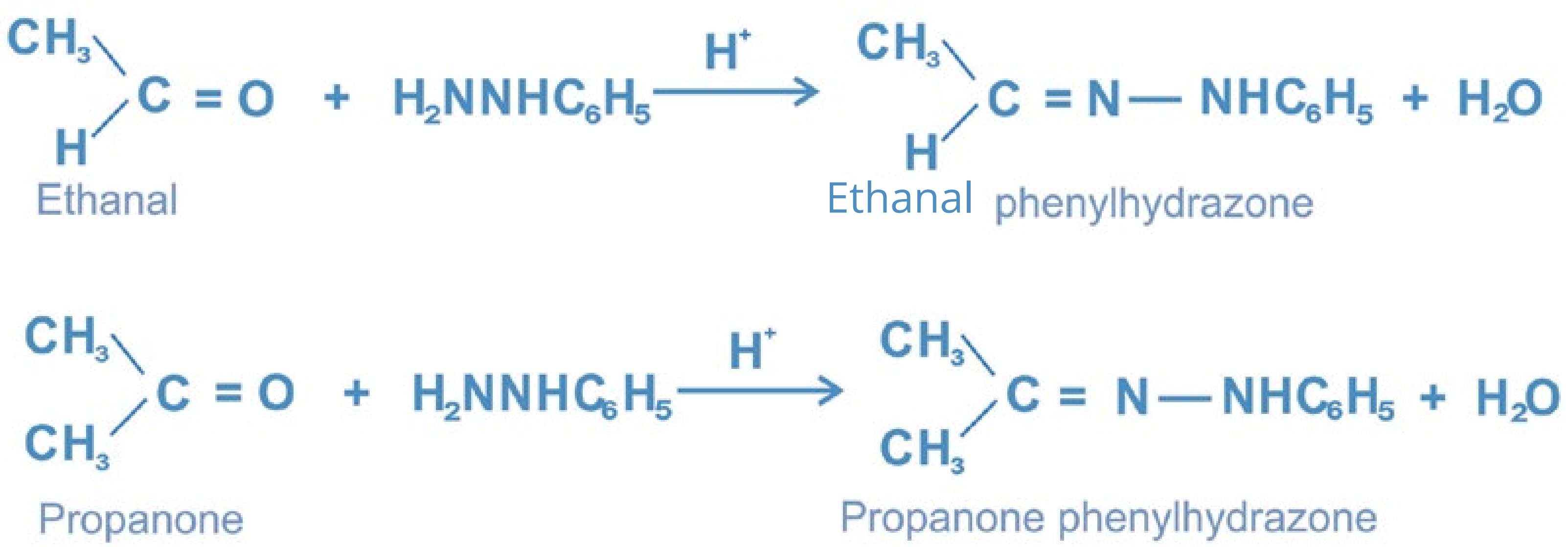
(i) Reaction with Hydroxylamine

Aldehydes and ketones react with hydroxylamine to form oximes in the presence of an acid.



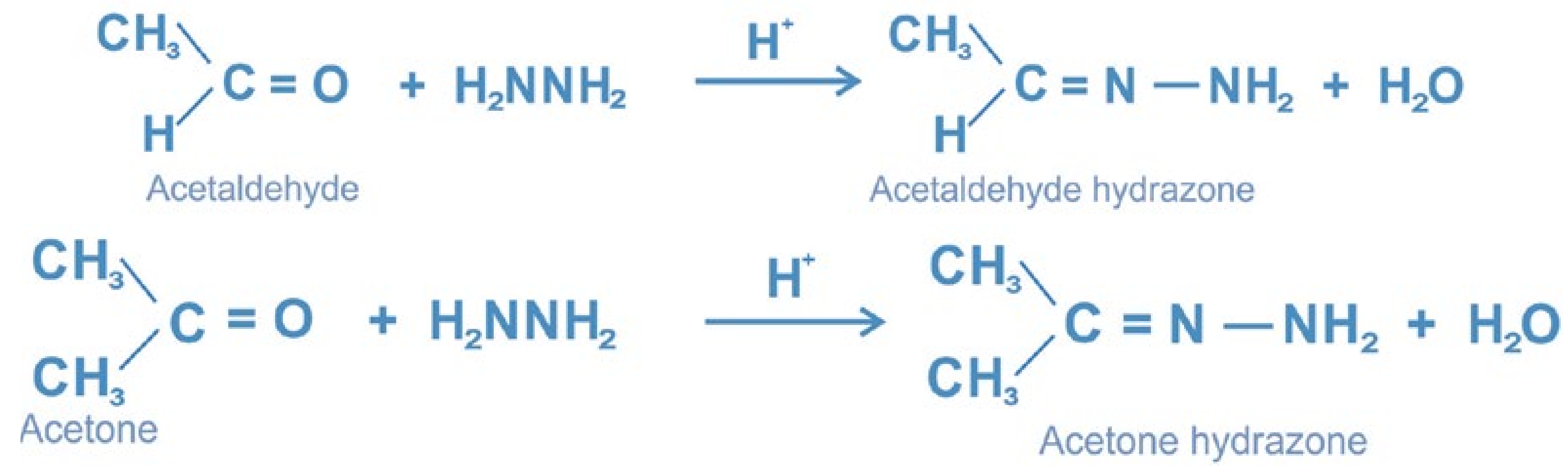
(ii) Reaction with Phenylhydrazine

Aldehydes and ketones react with phenylhydrazine to form phenylhydrazones in the presence of an acid



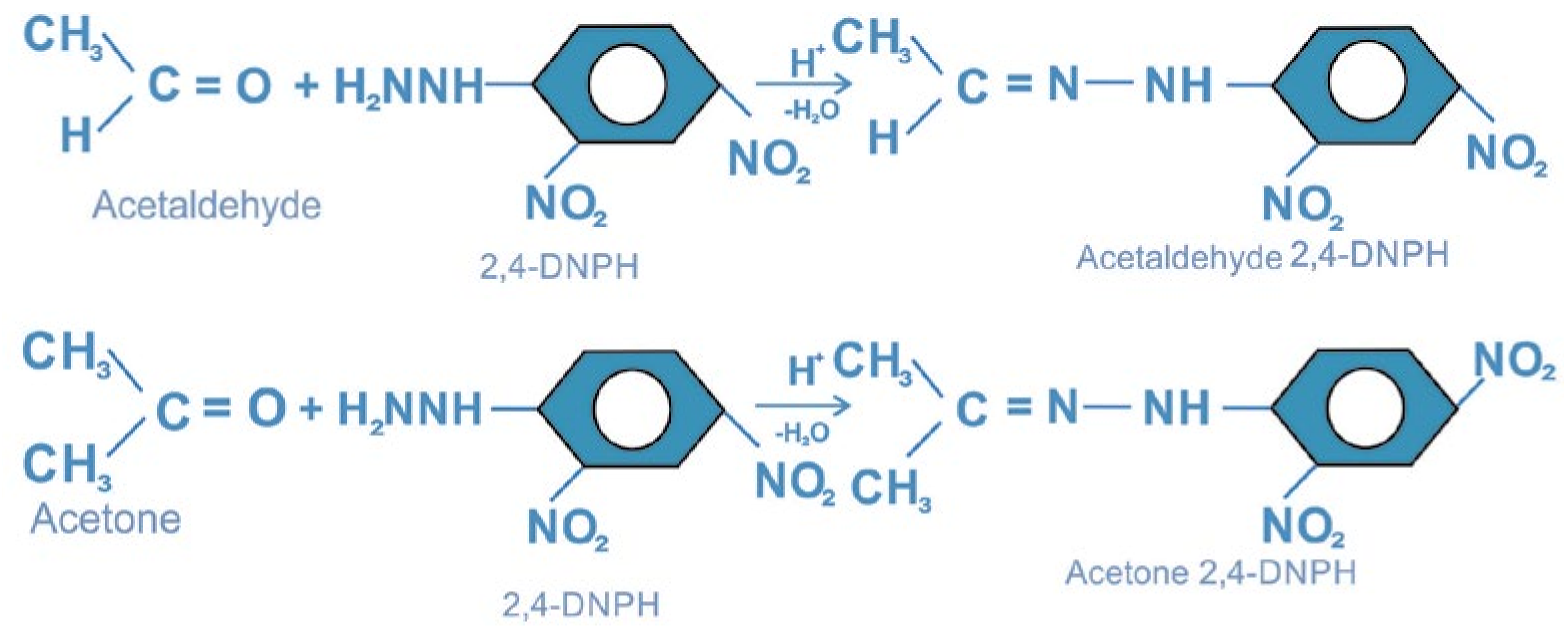
(iii) Reaction with Hydrazine

Aldehydes and ketones react with hydrazine to form hydrazones in the presence of an acid.



(iv) Reaction with 2 , 4 -Dinitrophenylhydrazine [2 ,4-DNPH]

Aldehydes and ketones react with 2, 4-dinitrophenyhydrazine to form 2, 4- dinitrophenylhydrazones in the presence of an acid.

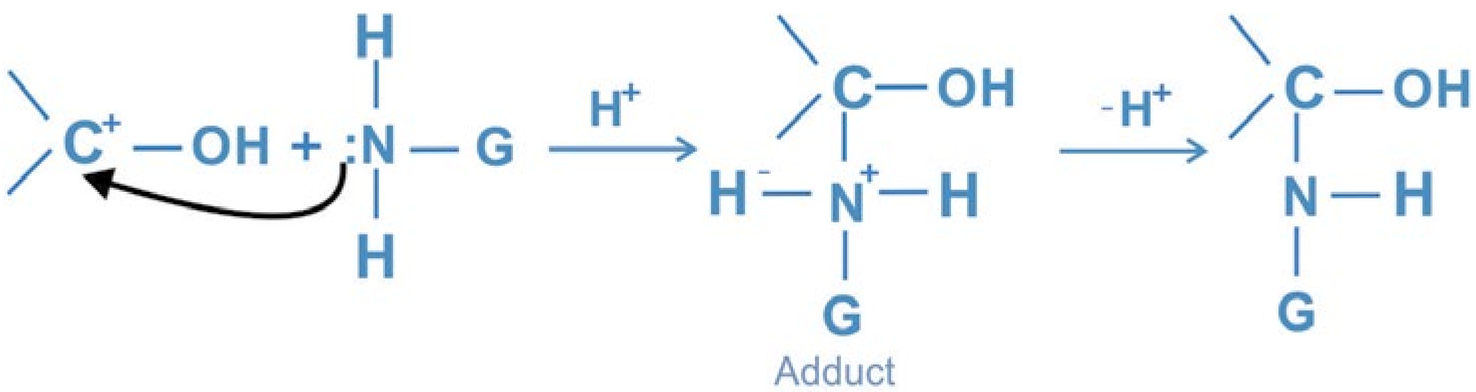


The reaction can be used for the identification of aldehydes and ketones because 2, 4-dinitrophenylhydrazones are usually yellow or orange crystalline solids

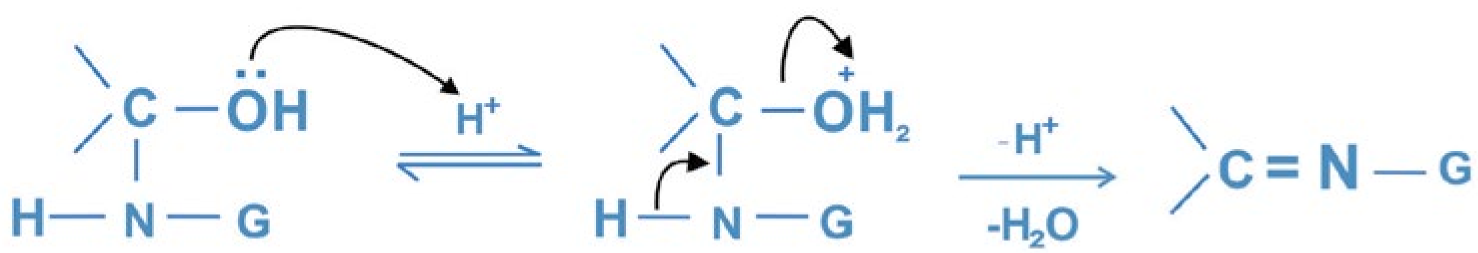
Mechanism of the Reactions of Ammonia Derivatives

Step (i) Protonation of oxygen of the carbonyl group.

Step (ii) Nucleophilic attack of nitrogen of ammonia derivative on the electrophilic positively charged carbon and deprotonation of the adduct.



Step (iii) Protonation of oxygen of hydroxyl group followed by the removal of water.

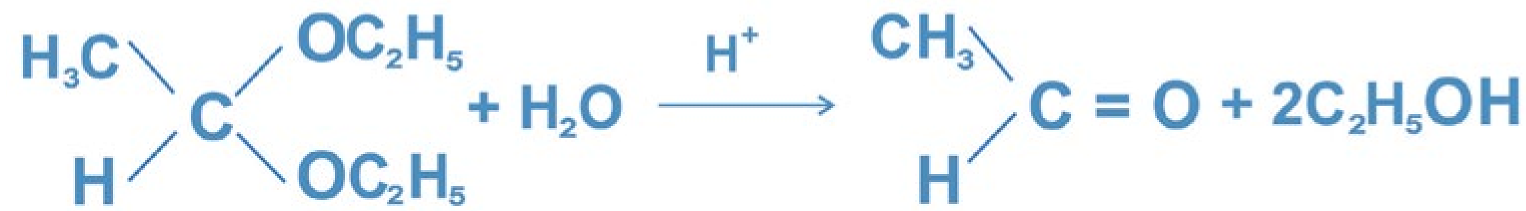


9. Addition of Alcohols

Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetals. The hydrogen chloride gas acts as a catalyst. Both the alcohol and the hydrogen chloride gas must be dry.

1,1-Diethoxyethane (an acetal)

The reaction may be used to protect the aldehyde group against alkaline oxidising agents. To regenerate aldehyde, the acetal is hydrolysed in the presence of an acid.



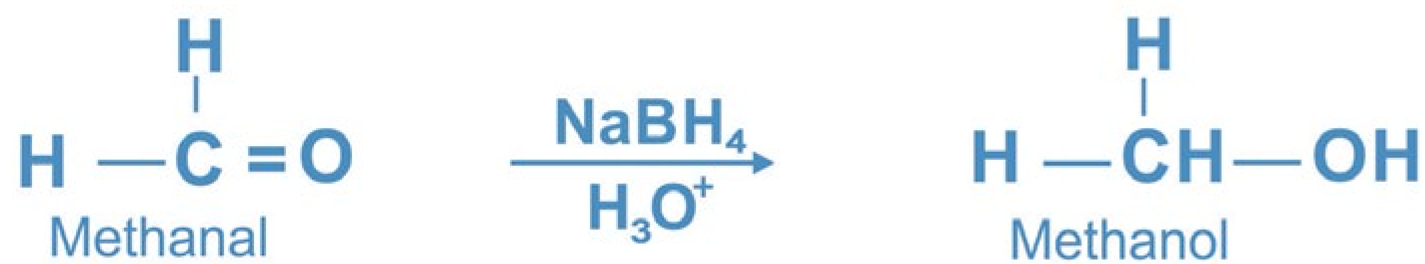
Ketones do not react under these conditions.

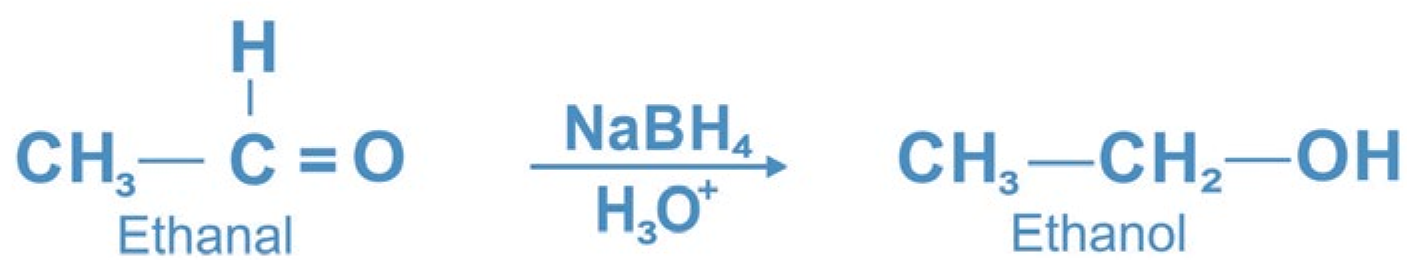
12.5.2 Reduction Reactions

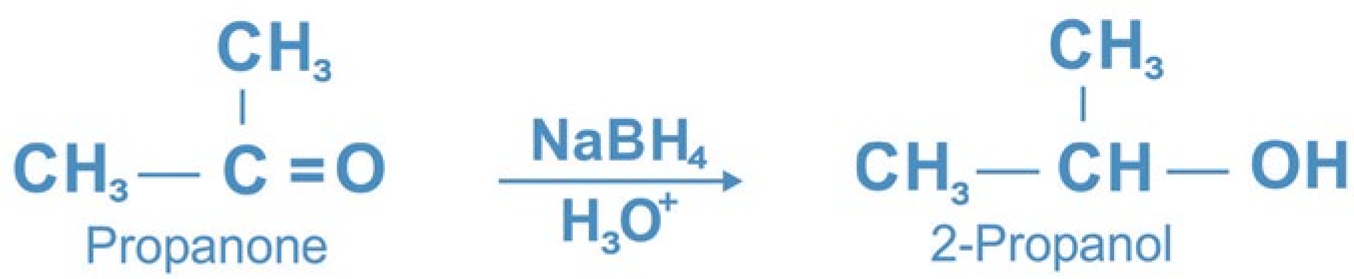
Aldehydes and ketones can both be reduced. Aldehydes are reduced to primary alcohols whereas ketones to secondary alcohols. The carbonyl group is converted into an alcohol.

(i) Reduction with Sodium Borohydride

Aldehydes and ketones are reduced to alcohols with sodium borohydride, $NaBH_4$. The reaction is carried out in two steps: reaction of the carbon compound with $NaBH_4$ under anhydrous Conditions and then hydrolysis.



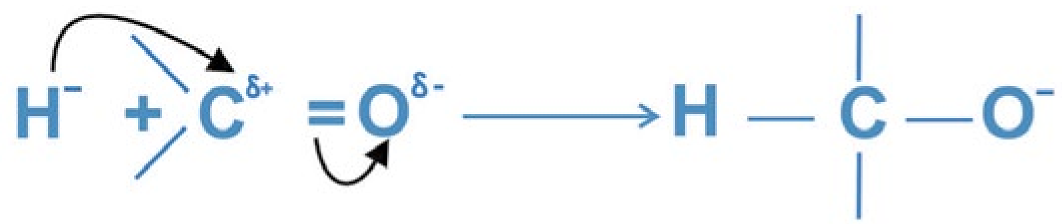




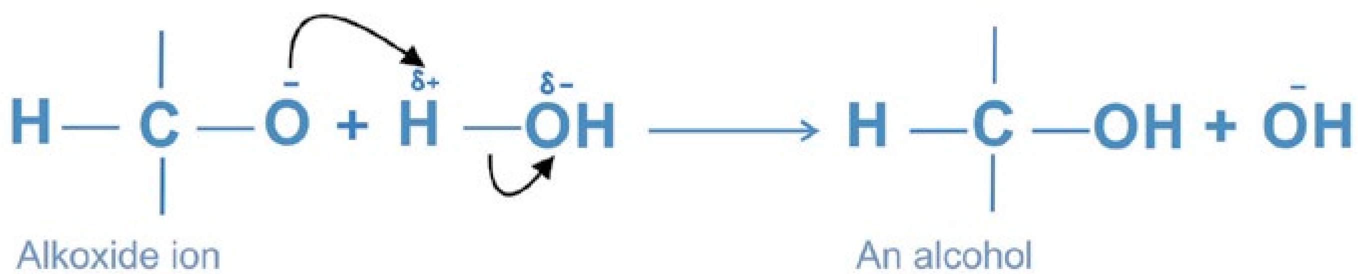
Sodium borohydride reduces the carbon-oxygen double bond but not the carbon-carbon multiple bond.

Mechanism:

The tetrahydridoborate (III) ion, $\overline{BH_4}$ is source of hydride ion, H^-.The hydride ion acts as a nucleophile.It attacks on the electrophilic carbon of the carbonyl group to give an alkoxide ion.

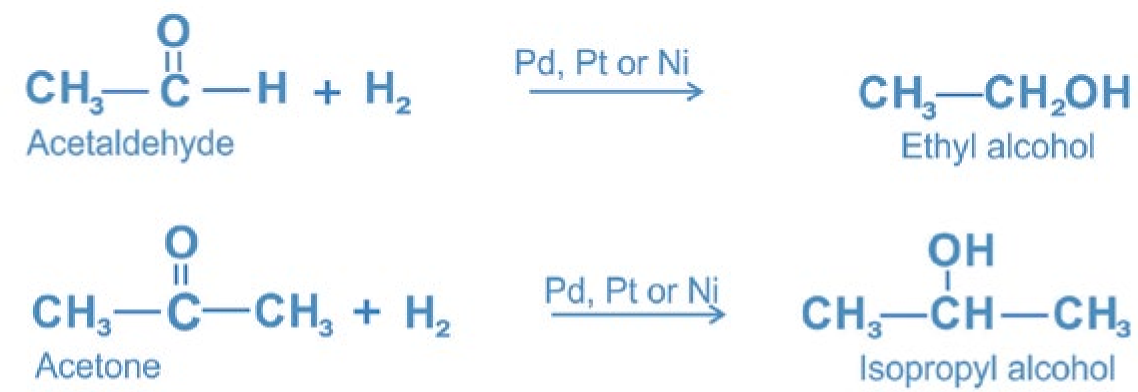


The alkoxide ion is protonated with water to give an alcohol.



(ii) Catalytic Reduction

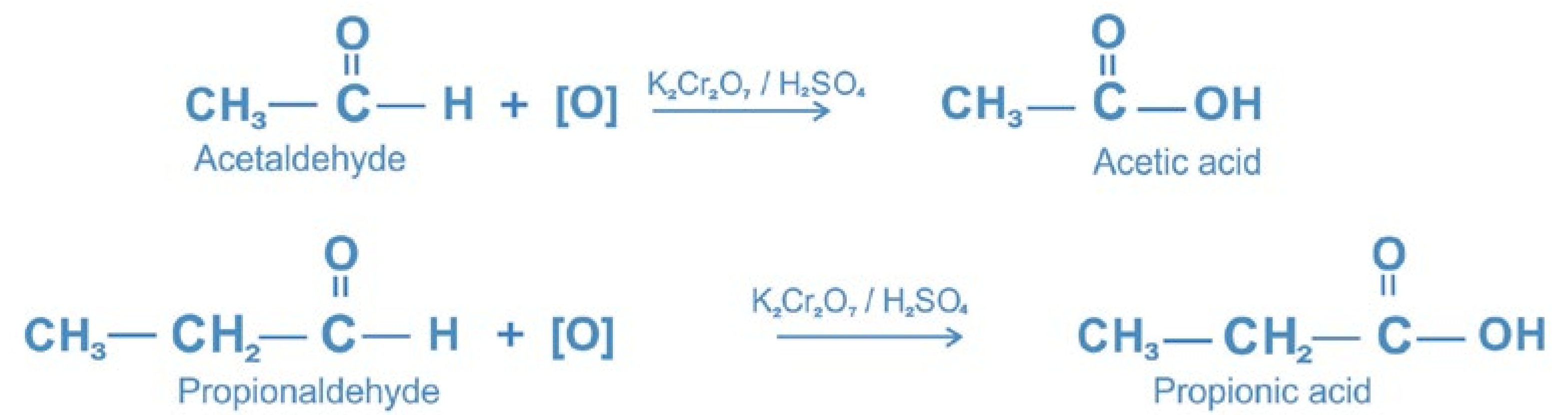
Aldehydes and ketones on reduction with hydrogen in the presence of a metal catalyst like Pd, Pt or Ni form primary and secondary alcohols respectively. Hydrogen is added across the carbonyl group.



12.5.3.Oxidation Reactions

(i) Oxidation of Aldehydes:

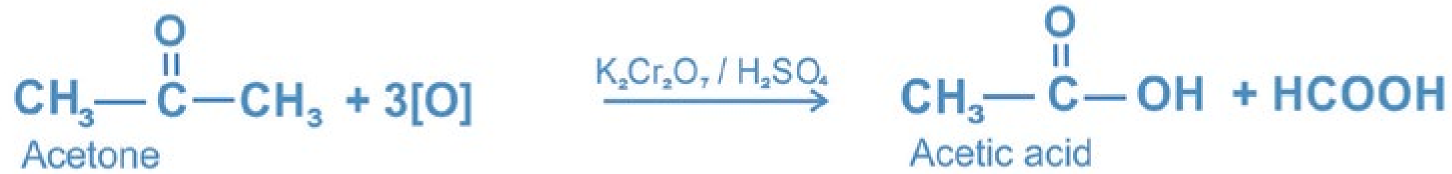
Aldehydes are easily oxidised by mild oxidising agents like Tollen's reagent, Fehling's solution and Benedict's solution. They are oxidised to carboxylic acids by strong oxidising agents such as $K_2Cr_2O_7$ / H_2SO_4 , $KMnO_4$ / H_2SO_4, and dilute nitric acid. The hydrogen atom attached to the carbonyl group in aldehydes is oxidised to OH group.



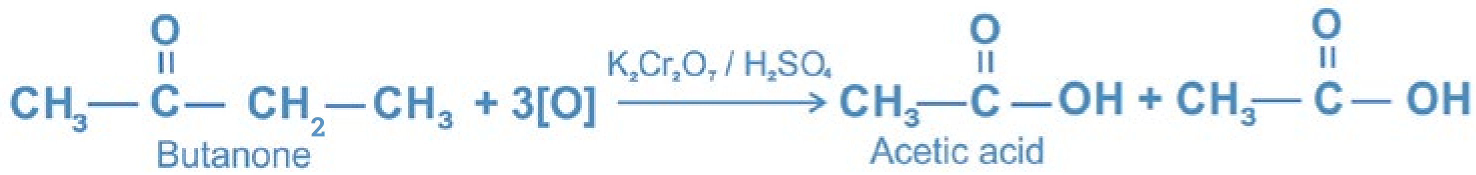
The carboxylic acid has the same number of carbon atoms as are present in the parent aldehyde.

(ii) Oxidation of Ketones:

Ketones do not undergo oxidation easily because they require breaking of strong carbon - carbon bond. They give no reaction with mild oxidising agents. They are only oxidised by strong oxidising agents such as $K_2Cr_2O_7$ / H_2SO_4 , $KMnO_4$ / H_2SO_4, and conc. HNO_3. In oxidation of ketones, only the carbon atoms adjacent to the carbonyl group are attacked. The carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidised. In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidised and a mixture of two carboxylic acids is always obtained.



However, in case of unsymmetrical ketones, the carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidised and the carbonyl group remains with the smaller alkyl group.



12.6 IDENTIFICATION OF CARBONYL COMPOUNDS

Detection tests for aldehydes and Ketones.

1. 2,4 DNPH Test: Aldehydes and ketones form a yellow or red precipitate with 2,4 dinitrophenylhdrazine solution.

2. Sodium Bisulphite Test: Aldehydes and small methyl ketones form a crystalline white precipitate with saturated sodium bisulphite solution.

3. Tollen's Test [Silver Mirror Test]: Aldehydes form silver mirror with Tollen's reagent (ammoniacal silver nitrate solution). Add Tollen's reagent to an aldehyde solution in a test tube and warm. A silver mirror is formed on the inside of the test tube.

High quality mirrors are manufactured by using this principle. Ketones do not give this test.

$$AgNO_3 + 3NH_4OH \rightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + 2H_2O$$

$$R\text{—}CHO + 2[Ag(NH_3)_2]OH \rightarrow R\text{-}COONH_4 + \underset{\text{Silver mirror}}{2Ag} + 2NH_3 + H_2O$$

4. Fehling's Solution Test [an alkaline solution containing a cupric tartrate complex ion]: Aliphatic aldehydes form a brick-red precipitate with Fehling's solution. To an aldehyde solution, add Fehling's solution and boil. A brick red precipitate of cuprous oxide is formed. Ketones do not give this test.

$$AgNO_3 + 3NH_4OH \rightarrow [Ag(NH_3)_2]OH + \underset{\text{Brick-red-ppt}}{NH_4NO_3} + 2H_2O$$

5. Benedict's Solution Test |an alkaline solution containing a cupric citrate complex ion]: Aliphatic aldehydes form a brick-red precipitate with Benedicts's solution. To an aldehyde solution, add Benedict's solution and boil. A brick-red precipitate of cuprous oxide is formed

$$RCHO + 2Cu(OH)_2 + NaOH \rightarrow RCOONa + Cu_2O + 3H_2O$$

Ketones do not give this test.

6. Sodium Nitroprusside Test:
Ketones produce a wine red or orange red colour on adding alkaline sodium nitroprusside solution dropwise. Aldehydes do not give this test.

12.7 USES

(a) Uses of Fomaldehyde

(i) It is used in the manufacture of resins like urea-formaldehyde and plastics such as bakelite.
(ii) It is used in the manufacture of dyes such as indigo, para-rosaniline, etc.
(iii) Its 40% aqueous solution called formalin is used as an antiseptic, a disinfectant, a germicide, a fungicide and for preserving animal specimens and sterlising surgical instruments.
(iv) It is used as a decolourising agent in vat dyeing.
(v) It is used in the silvering of mirrors.
(vi) It is used in making medicine urotropine used as a urinary antiseptic.
(vii) It is used in making formamint (formaldehyde + lactose) used as throat lozenges.
(viii) It is used in the processing of anti-polio vaccine.

(b) Uses of Acetaldehyde

1. It is used in the production of acetic acid, acetic anhydride, n-butanol, ethanol, 2-ethyl-1-hexanol, vinyl acetate, paraldehyde, ethylacetate, etc. Brick-red-ppt
2. It is used to make acetaldehyde ammonia used as a rubber-accelerator.
3. It is used to make chloral hydrate, ethanol trimer and tetramer. Chloral hydrate and ethanol trimer are both used as hypnotic drugs whereas ethanol tetramer is used as a slug poison.
4. It is used as an antiseptic inhalent in nasal infections.
5. It is used in silvering of mirrors.
6. It is used to make phenolic resins and synthetic drugs.

KEY POINTS

1. Aldehydes and ketones contain the carbonyl group, C = 0 as the functional group.
2. Both aldehydes and ketones can be prepared by the oxidation of primary and secondary alcohols respectively.
3. Both aldehydes and ketones undergo nucleophilic addition reactions. In these reactions, the negative part of the reagent combines with the electrophilic carbon of the carbonyl group whereas the positive part goes to the oxygen atom. They are base catalysed addition reactions.
4. Two molecules of the same carbonyl compound condense to form an aldol. Aldehydes and ketones containing α-hydrogen atoms undergo this reaction in the presence of dilute sodium hydroxide.
5. Aldehydes that have no α-hydrogen atoms undergo Cannizzaro's reaction in the presence of concentrated sodium hydroxide.
6. Acetaldehyde and only methyl ketones react with halogens in the presence of sodium hydroxide to give haloform. It provides a useful method for converting a methyl ketone to a carboxylic acid containing one carbon atom less than the parent methyl ketone. Iodoform test is used for distinguishing methyl ketones from other ketones.
7. Aldehydes and ketones react with ammonia derivatives, $G - NH_2$ to form condensation products containing the group, C = N - G and water. The reaction is acid-catalysed.
8. Aldehydes and ketones are reduced to alcohols with sodium borohydride. Aldehydes and ketones are also reduced to alcohols with molecular hydrogen in the presence of catalyst like Pd, Pt or Ni.
9. Aldehydes are oxidized to carboxylic acids. $K_2Cr_2O_7$ in H_2SO_4 or $KMnO_4$, in H_2SO_4 may be used as the oxidising agent. Ketones resist oxidation.
10. Aldehydes form silver mirror with Tollen's reagent. Ketones do not give this test.
11. Aldehydes give a brick red precipitate with Fehling's solution on boiling.

EXERCISE

Q. 1 Fill in the blanks.

1. Aldehydes are the first oxidation product of____________________.
2. Ketones are the first oxidation product of____________________.
3. Aldehydes and ketones undergo________________ addition reactions.
4. Formaldehyde reacts with________________ to give primary alcohol.
5. Acetaldehyde reacts with________________ to give 2-butanol.
6. Aldehydes are strong________________ agents.
7. The oxidation of an________________ always gives a carboxylic acid.
8. The reduction of a________________ always gives a secondary alcohol.
9. Formaldehyde gives________________ test with Tollen's reagent.
10. Acetaldehyde gives a________________ precipitate with Fehling's solution.

Q. 2 Indicate True or False.

1. Formaldehyde is used in the silvering of mirrors.
2. Ketones combine with alcohols in the presence of HCl gas to form acetals
3. Acetaldehyde undergoes Cannizzaro's reaction;
4. Aldol condensation reaction is given by only those aldehydes and ketones which contain an α-hydrogen atom.
5. Cannizzaro's reaction is given by only those aldehydes containing no α-hydrogen atom.
6. Propanal and propanone behave differently with Tollen's reagent.
7. Acetone reacts with sodium bisulphite to give a yellow crystalline product.
8. Acetone on reduction gives a primary alcohol.
9. 40% aqueous solution of formaldehyde is called formalin.

Q. 3 Multiple choice questions. Encircle the correct answer.

i) The carbon atom of a carbonyl group is
(a) sp hybridized (b) sp^2 hybridized
(c) sp^3 hybridized (d) none of these

ii) Formalin is
(a) 10% solution of formaldehyde in water
(b) 20% solution of formaldehyde in water
(c) 40% solution of formaldehyde in water
(d) 60% solution of formaldehyde in water

iii) Which of the following will have the highest boiling point?
(a) Mathanal (b) Ethanal
(c) Propanal (d) 2-Hexanone

(iv) Ketones are prepared by the oxidation of
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) all of these

(v) Acetone reacts with HCN to form a cyanohydrin. It is an example of
(a) Electrophilic addition (b) Electrophilic substitution
(c) Nucleophilic addition (d) Nucleophilic substitution

(vi) Which of the following compounds will not give iodoform test on treatment with I_2/NaOH:
(a) Acetaldehyde (b) Acetone (c) Butanone (d) 3-Pentanone

(vii) Which of the following compounds will react with Tollen's reagent.
(a) $CH_3-\overset{\overset{O}{\|}}{C}-H$ (b) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$
(c) $CH_3-\overset{\overset{O}{\|}}{C}-OH$ (d) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

(viii) Cannizzaro's reaction is not given by
(a) Formaldehyde (b) Acetaldehyde
(c) Benzaldehyde (d) Trimethylacetaldehyde

(ix) Which of the following reagents will react with both aldehydes and ketones?
(a) Grignard reagent (b) Tollen's reagent
(c) Fehling's reagent (d) Benedict's reagent

Q. 4 Give one laboratory and one industrial method for the preparation of formaldehyde.

Q. 5 How does formaldehyde react with the following reagents?
(i) CH_3MgI (ii) HCN (iii) $NaHSO_3$ (iv) conc.NaOH
(v) $NaBH_4/H_2O$ (vi)Tollen's reagent (vii) Fehling's reagent

Q. 6 Give one laboratory and one industrial method for the preparation of acetaldehyde.

Q. 7 How does acetaldehyde react with the following reagents?
(i) C_2H_5MgI (ii) HCN (iii) $NaHSO_3$ (iv) dilute NaOH
(v) $I_2/NaOH$ (vi) $NaBH_4/H_2O$ (vii)NH_2OH (viii) $K_2Cr_2O_7/H_2SO_4$

0 .8 Describe briefly the mechanism of nucleophilic addition to a carbonyl compound.

Q. 9 Explain with mechanism the addition of ethylmagnesium bromide to acetaldehyde. What is the importance of this reaction?

Q. 10 Explain with mechanism the addition of sodium bisulphite to acetone . What is the utility of this reaction?

Q. 11 Describe with mechanism aldol condensation reaction. Why formaldehyde does not give this reaction?

Q. 12 What types of aldehydes give Cannizzaro's reaction? Give its mechanism.

Q. 13 Explain the mechanism of the reaction of phenylhydrazine with acetone.
Q. 14 Using ethyne as a starting material how would you get acetaldehyde, acetone and ethyl alcohol?

Q. 15 Give the mechanism of addition of HCN to acetone.

Q. 16 How would you bring about the following conversions?
(i) Acetone into t-butyl alcohol (ii) Propanal into 1-propanol
(iii) Propanone into 2-propanol (iv) Methanal into ethanal
(v) Ethanal into propanone (vi) Ethanal into 2-propanol
(vii) Ethyne into ethanal (viii) Ethene into ethanal
(ix) Ethanal into ethanol (x) Ethanol into 2-butanone
(xi) Methanol into ethanal (xii) Ethanol into ethanoic acid .

Q. 17 How will you distinguish between:
(i) Methanal and ethanal (ii) Ethanal and propanone
(iii) Ethanal and propanal (iv) Acetone and ethyl alcohol
(v) Butanone and 3-pentanone (vi) Acetaldehyde and benzaldehyde
(vii) 2-Pentanone and 3-pentanone

Q. 18 Discuss oxidation of (a) aldehydes (b) ketones with:
(i) $K_2Cr_2O_7/H_2SO_4$ (ii)Tollen's reagent (iii) Fehling's solution

Q. 19 Discuss reduction of (a) aldehydes (b) ketones with
(i) $NaBH_4/H_2O$ (ii) H_2/Pd

Q. 20 Give three uses for each of formaldehyde and acetaldehyde.

CHAPTER

13

CARBOXYLIC ACIDS

Animaton 13.1: Addition of HCl to a carbonyl group
Source & Credit : Ch.imperial

IN THIS CHAPTER YOU WILL LEARN:

1. How to name carboxylic acids and their derivatives.
2. The commercial method for the preparation of acetic acid.
3. The relationship between the structure of carboxyl group and its reactivity.
4. The effect of hydrogen bonding on the physical properties of carboxylic acids.
5. The ways of preparing four derivaties of carboxylic acids and the conversion of these derivatives back to carboxylic acids.
6. About amino acids and their significance.

13.1 INTRODUCTION

Organic compounds containing $(-\overset{O}{\overset{\|}{C}}-OH)$ as a functional group are called carboxylic acids. The $(-\overset{O}{\overset{\|}{C}}-OH)$ group which itself is made up of a carbonyl group (> C = 0) and a hydroxyl group (-0H) is called a carboxyl group (Carb from carbonyl and oxyl from hydroxyl). Carboxylic acid may be an aliphatic or an aromatic depending upon whether $(-\overset{O}{\overset{\|}{C}}-OH)$ is attached to an alkyl group (or a hydrogen atom) or an aryl group. Their general formulas are:

Aliphatic carboxylicacid

$R-\overset{O}{\overset{\|}{C}}-OH$ where R = H or an alkyl group.

Aromatic carboxylicacid

$Ar-\overset{O}{\overset{\|}{C}}-OH$ where Ar is a phenyl or an aryl group

Carboxylic acids are further classified as mono, di, tri or poly carboxylic acids as they contain one, two, three or many carboxyl groups respectively in their molecules.

Animaton 13.2: Carboxyl
Source & Credit : Phschool

Aliphatic monocarboxylic acids

$H-\overset{O}{\overset{\|}{C}}-OH$ Methanoic acid or Formicacid

$CH_3-\overset{O}{\overset{\|}{C}}-OH$ Ethanoic acid or Acetic acid

Aliphatic dicarboxylic acids

$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

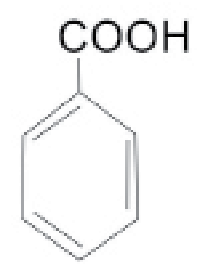
Ethanedioic acid
(Oxalic acid)

$$H_2C\begin{array}{l} \diagup COOH \\ \diagdown COOH \end{array}$$

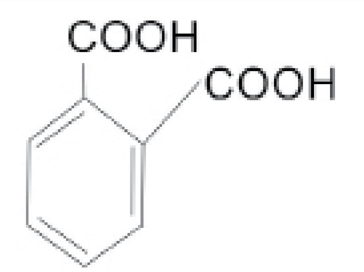
Propanedioic acid
(Malonic acid)

Aromatic monocarboxylic acid

Aromatic dicarboxylic acid:



Benzoic acid



1,2-Benzenedicarboylic acid
or phthalic acid

In this chapter we will discuss, in some detail, the chemistry of monocarboxylic acids only.

13.2 NOMENCLATURE OF CARBOXYLIC ACIDS

The aliphatic monocarboxylic acids are commonly called fatty acids because higher members of this series such as palmitic acid ($C_{15}H_{31}COOH$), stearic acid ($C_{17}H_{35}COOH$), etc. are obtained by the hydrolysis of fats and oils. The aliphatic monocarboxylic acids may be given common names or IUPAC names.

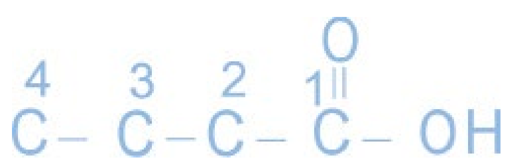
13.2.1 Common or Trivial names

The common names of carboxylic acids were derived from the source from which they are isolated. The irritation caused by an ant bite is due to formic acid (Latin word formica, ant). It was first isolated by the distillation of red ants. Similarly acetic acid was first isolated from vinegar and butyric acid was named after butyrum means butter.

13.2.2 The IUPAC Nomenclature

The IUPAC names of saturated monocarboxylic acids are alkanoic acids. These are derived from the names of the alkanes containing the same number of carbon atoms as the acid. The ending "e" of the alkane name is dropped and suffix-oic acid is added. Thus acetic acid gets the name ethanoicaeid.

The position of substituents are indicated by Arabic numerals with the carboxyl group given number 1 as shown below:



The common and IUPAC names of the some common monocarboxylic acids are given in the table below.

Table(13.1) Common and IUPAC names of some common carboxylic acids.

Structural Formula	Common Name	IUPAC Name
$H - COOH$	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
$CH_3 - CH_2 - COOH$	Propionic acid	Propanoic acid
$CH_3 - CH_2 - CH_2 - COOH$	Butyric acid	Butanoic acid
$CH_3 - CHCOOCH$ | CH_3	Iso-Butyric acid	2-Methylpropanoic acid

13.3 GENERAL METHODS OF PREPARATION

A number of methods for the preparation of carboxylic acids have already been discussed in the previous chapters. However, they are recalled again with different examples.

1. From Primary Alcohols and Aldehydes

Primary alcohols and aldehydes are readily oxidised to corresponding carboxylic acids by oxidising agents such as potassium dichromate in an acidic medium.

Animaton 13.5 : Undergo oxidation
ource & Credit : Biologie.uni-hamburg.de

$$\underset{\text{Primary alcohol}}{R-CH_2-OH} + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{aldehyde}}{R-CHO} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{RCOOH}$$

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} \underset{\text{Ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

Aldehydes are easily oxidised to corresponding carboxylic acids even by mild oxidizing agents such as Tollen's Reagent (Ammoniacal silver nitrate).

$$\underset{\text{Ethanal}}{CH_3-CHO} + [O] \longrightarrow \underset{\text{Ethanoic acid}}{CH_3COOH}$$

2. From Alkanenitriles

Compounds having a cyanide (- C ≡ N) group are called nitriles. Hydrolysis of an alkanenitrile on boiling with mineral acids or alkalis yields corresponding carboxylic acid.

Animaton 13.6 : Nucleophilic substitution
ource & Credit : Wikipedia.org

$$R-C\equiv N + H_2O \xrightarrow{H^+ \text{ or } OH^-} RCOOH + NH_3$$

$$CH_3\,C\equiv N + 2H_2O + HCl \longrightarrow CH_3COOH + NH_4Cl$$

Alkanenitriles can be prepared by treating alkyl halide with alcoholic potassium cyanide.

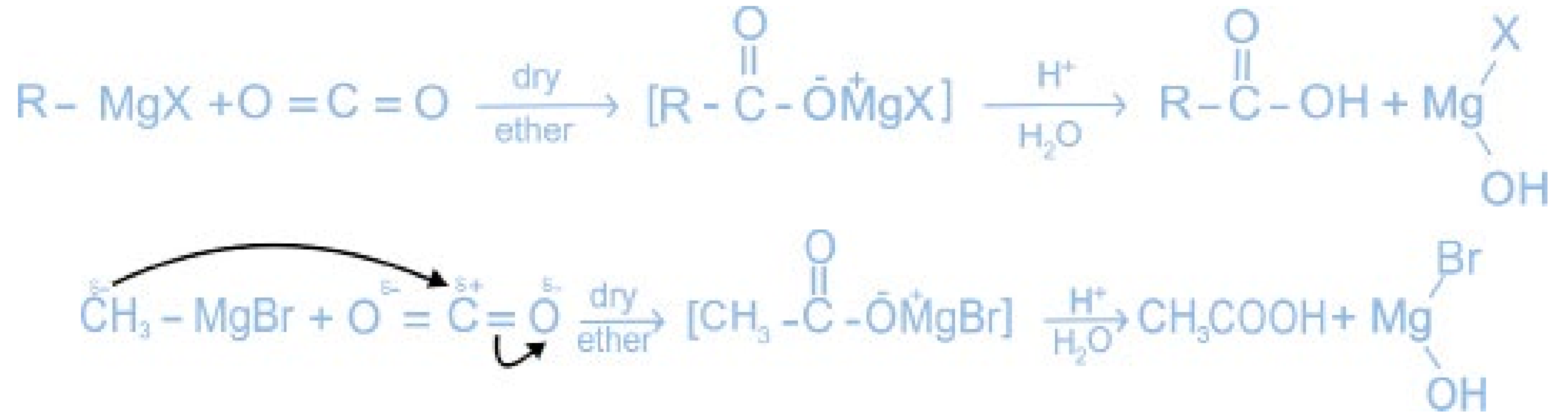
$$R-X + KCN \xrightarrow{\text{Alcohol}} R-CN + KX$$

It may be noted that acid produced has one carbon atom more than the original alkyl halide.

3. From Grignard Reagent

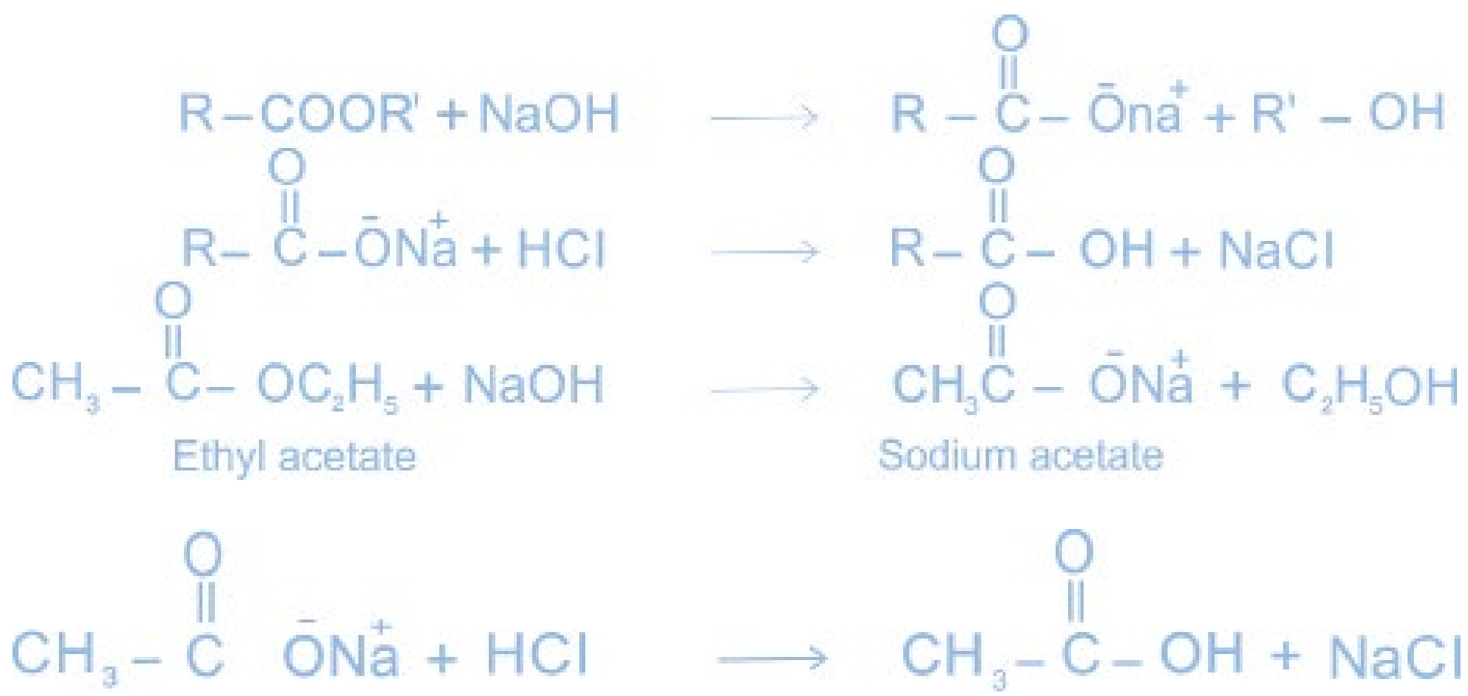
Carboxylic acids can be prepared by the action of Grignard reagent with carbon dioxide. This reaction is either carried out by passing carbon dioxide through the ethereal solution of corresponding Grignard reagent or by adding Grignard reagent to crushed dry ice suspended in ether. The addition product on reaction with a mineral acid produces carboxylic acid.

Animaton 13.7 : Grignard Reagent Attacking a Ketone
ource & Credit : Benettonplay



4. By the Hydrolysis of Esters

The appropriate ester on boiling with concentrated sodium hydroxide yields sodium salt of the acid.This resulting salt when treated with dilute HC1 gives the free carboxylic acid.



5. By the Oxidative Cleavage of Alkenes

Alkenes when heated with alkaline $KMnO_4$ are cleaved at the double bond to form carboxylic acids.

$$\underset{\text{Symmetrical alkene}}{R-CH=CH-R} + 4[O] \xrightarrow[\Delta]{KMnO_4/OH^-} \underset{\text{Carboxylic acid}}{2RCOOH}$$

$$\underset{\text{2-Butene}}{H_3C-CH=CH-CH_3} + 4[O] \xrightarrow{KMnO_4/OH^-} \underset{\text{Ethanoic acid}}{2CH_3COOH}$$

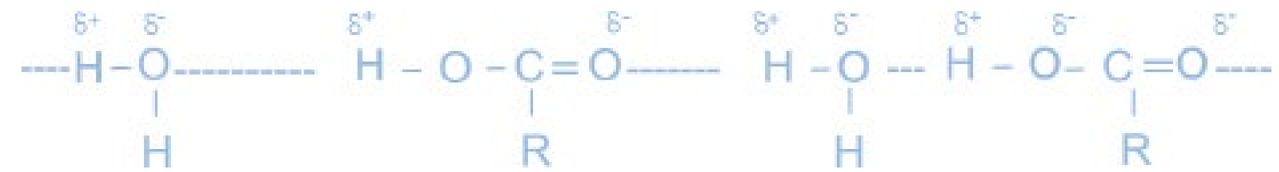
13.4 PHYSICAL CHARACTERISTICS

(i) Smell

The first three aliphatic acids i.e. formic acid, acetic acid and propionic acid are colourless liquids and have pungent smell. The next three acids C_4 to C_6 are colourless liquids with somewhat unpleasant smell.

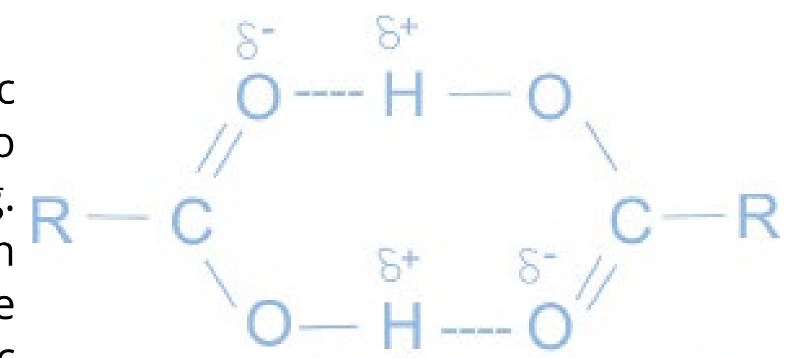
(ii) Solubility

Among the aliphatic acids, the first four members are very soluble in water due to hydrogen bonding.



(iii) Boiling Point

The boiling points of carboxylic acids are relatively high due to intermolecular hydrogen bonding. The molecular mass determination in non-polar solvent like benzene shows that Carboxylic acids exist as cyclic dimers.



dimer of a carboxylic acid

Boiling Points

HCOOH	CH_3COOH	C_2H_5COOH
373K(100°C)	391K(118°C)	424K(141°C)

Melting Points

The melting points of carboxylic acids increase irregularly with the increase in molecular mass. It has been observed that the melting points of carboxylic acids containing even number of carbon atoms are higher than the next lower and higher members containing odd number of carbon atoms e.g.,

CH_3CH_2COOH, $CH_3CH_2CH_2COOH$, $CH_3CH_2CH_2CH_2COOH$

	(3 carbon)	(4 carbon)	(5 carbon)
Melting points	251K(-22°C)	267 K (-6°C)	237 K (-36°C)

13.5 REACTIVITY OF CARBOXYL GROUP ($-\overset{\overset{O}{\|}}{C}-OH$)

The carboxyl group displays the chemistry of both the carbonyl and the hydroxyl groups. In most reactions of carboxylic acids the carboxyl group is retained however, the reactivity of these molecules is a consequence of the presence of the carbonyl group.

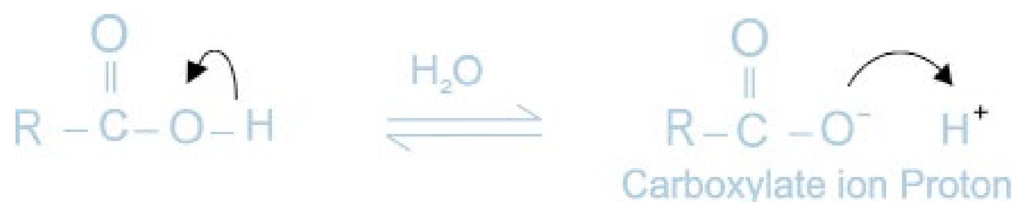
13.6 Reactions of Carboxylic Acids

Carboxylic acids undergo the following type of reactions.

a) The reactions in which hydrogen atom of the carboxyl group is involved (salt formation).
b) The reactions in which OH group is replaced by another group.
c) The reactions involving carboxyl group as a whole.

(a) Reactions Involving H Atom of the Carboxyl Group

Carboxylic acids are weaker acids than mineral acids. They furnish H^+ when dissolved in water.



In the presence of water (H_2O), the proton breaks away as H_3O^+ ion.

1. Reactions with Bases

Carboxylic acids react with bases (NaOH, KOH) to form salts

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

2. Reactions with Carbonates and Bicarbonates

Carboxylic acids decompose carbonates and bicarbonates evolving carbon dioxide gas with effervescence.

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COO^-Na^+ + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COO^-Na^+ + CO_2 + H_2O$$

3. Reactions with Metals

Carboxylic acids react with active metals (Na, K, Ca, Mg etc) to form their salts with the evolution of hydrogen gas.

$$2CH_3COOH + 2Na \rightarrow 2CH_3COO^-Na^+ + CO_2 + H_2$$

(b) Reactions Involving the – OH Group of Carboxylic Acids

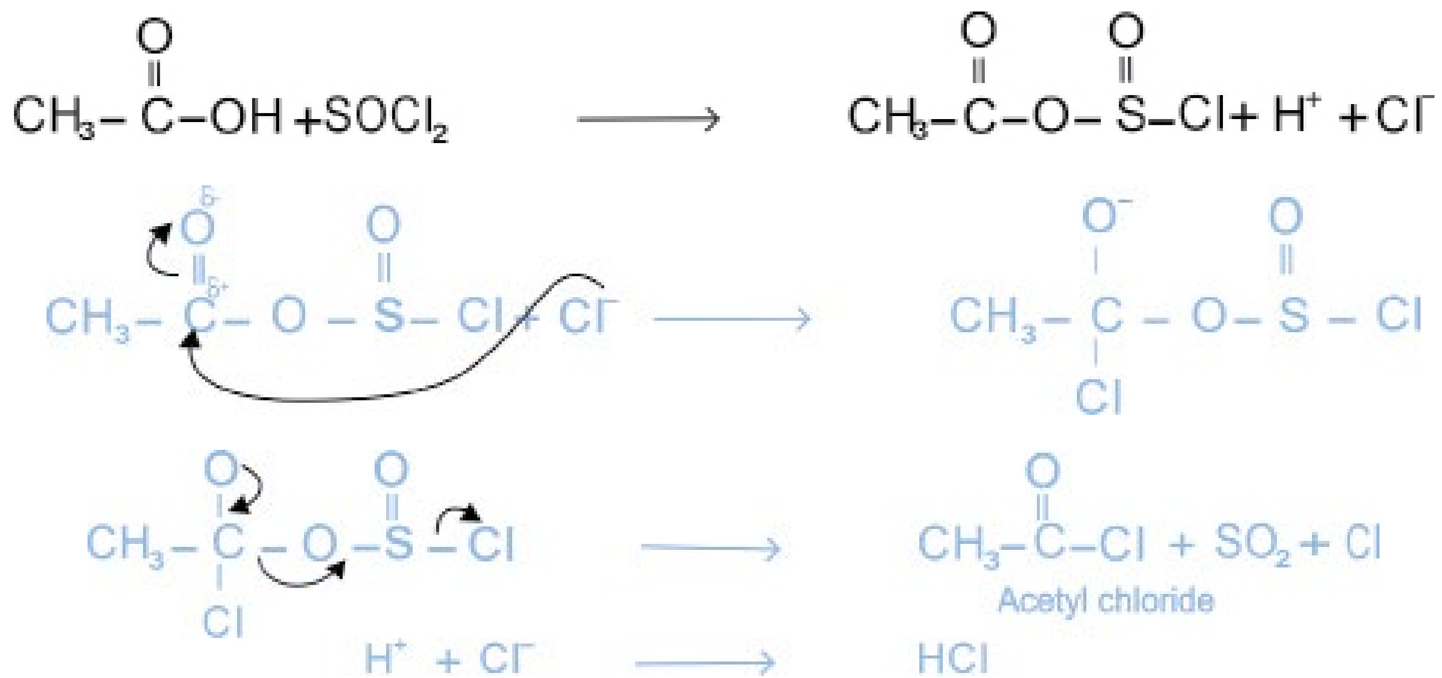
The carboxylic acid contains $-\overset{\overset{O}{\|}}{C}-OH$ functional group, and like the carbonyl group of aldehydes and ketones, is susceptible to attack by a nucleophile. The addition of a nucleophile to the carboxyl group is always followed by the displacement of the –OH group by some other group, producing a carboxylic acid derivative. The –OH group can thus be replaced by X, OR and NH_2 to form halides, esters and amides,respectively.

1 . Reactions with PCl_5 and $SOCl_2$

(a) $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

(b) $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$

Mechanism



2. Formation of an Ester

When carboxylic acids are heated with alcohols in the presence of concentrated H_2SO_4, esters are formed.

$$CH_3COOH + C_2H_5OH \xrightleftharpoons{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

Animaton 13.8 : Ester formation
ource & Credit : Dynamicscience

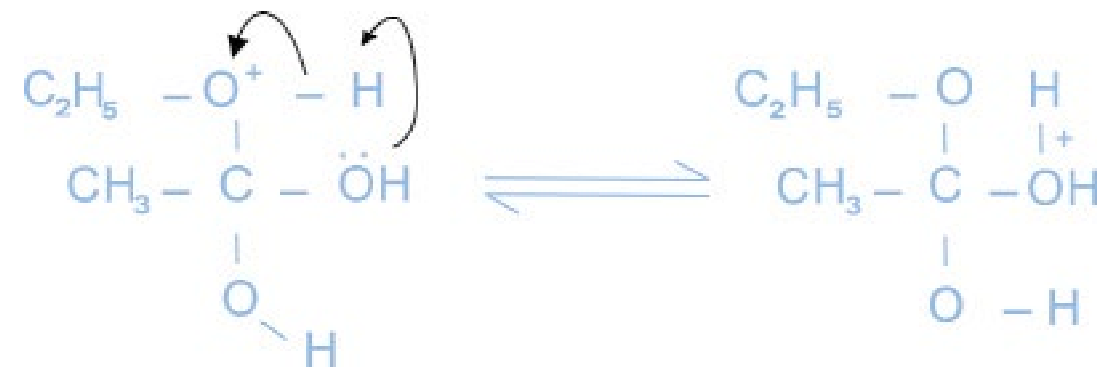
Mechanism

The various steps of the above reactions are as follows:

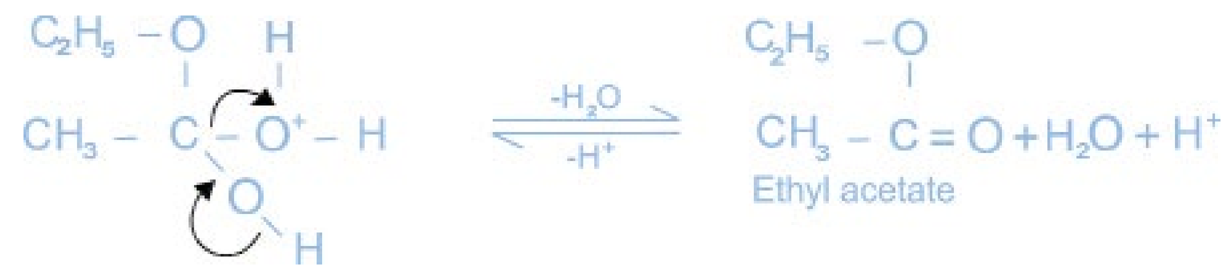
(i) Protonation of Carboxylic Acid

(ii) Attack of $CH_3 - CH_2OH$

(iii) Hydrogen Ion Transfer



(iv) Elimination of Water and H^+



Esters have fruity smell and are used as artificial flavours. Flavours of some estersare listed in the table.

Ester	Flavour
Amylacetate	Banana
Isobutyl formate	Raspberry
Benzylacetate	Jasmine
Ethyl butyrate	Pineapple
Amyl butyrate	Apricot
Octyl acetate	Orange

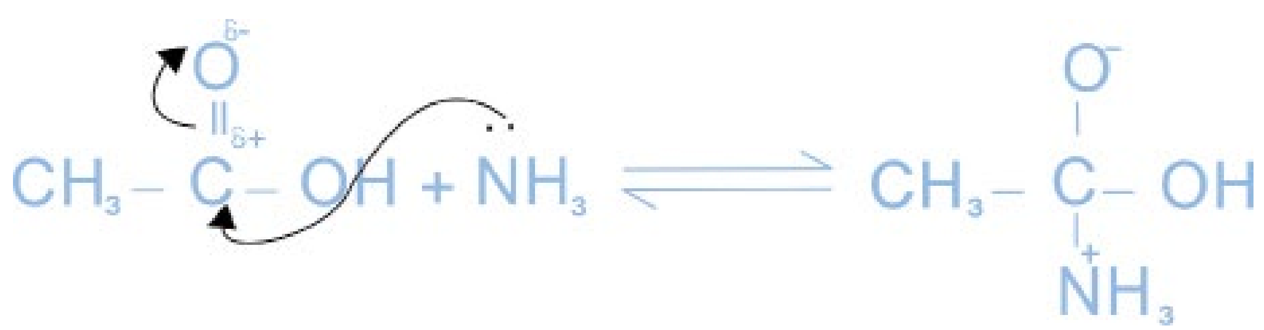
3.Formation of Amide (Reaction with ammonia)

Carboxylic acids react with ammonia to form ammonium salts which on heating produce acid amides.

(i) $$CH_3COOH + NH_3 \rightarrow CH_3COONH_4$$

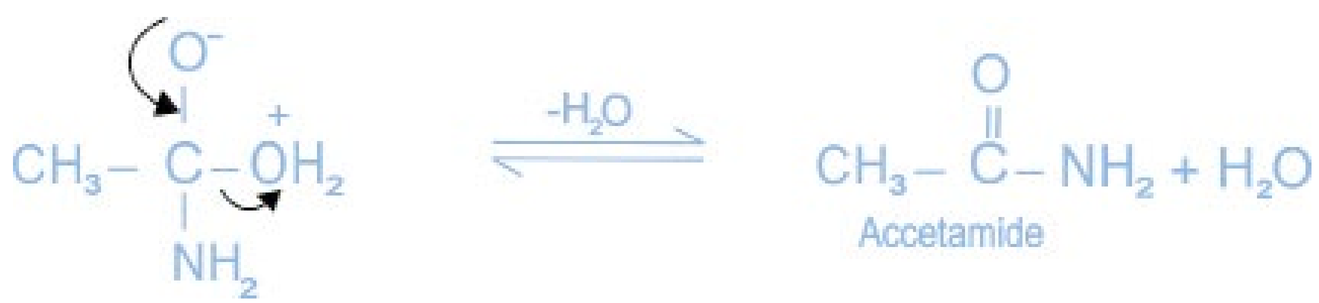
$$CH_3COO^-N^+H_4 \xrightarrow{Heat} CH_3CONH_2 + H_2O$$

Mechanism



(ii)

(iii)



4. Formation of Acid Anhydride

Carboxylic acids are dehydrated on heating strongly in the presence of phosphorus pentoxide.

(c) Reactions Involving Carboxyl Group (—C(=O)—OH)

i. Partial Reduction to Alcohols

Carboxylic acids on reaction with lithium aluminium hydride ($LiAlH_4$) are reduced to alcohols.

ii) Complete Reduction to Alkanes

Carboxylic acids on reduction with HI and red phosphorus give alkanes.

$$CH_3COOH + 6HI \xrightarrow{P} CH_3{-}CH_3 + 2H_2O + 3I_2$$

13.7 ACETIC ACID

It is the most important carboxylic acid. Its dilute solution is known as vinegar. Acetic acid can be prepared by any of the general methods described earlier.

13.7.1 Laboratory Methods

1. By the Oxidation of Ethyl Alcohol or Acetaldehyde

When ethyl alcohol is oxidised with $K_2Cr_2O_7$ and dilute H_2SO_4, acetic acid is produced.

$$CH_3-CH_2OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

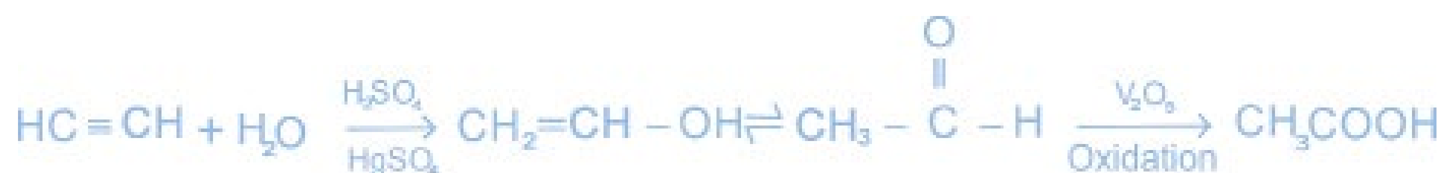
2. By the Hydrolysis of Methyl Cyanide

Ethanenitrile on hydrolysis with dilute HCl, gives acetic acid through acetamide.

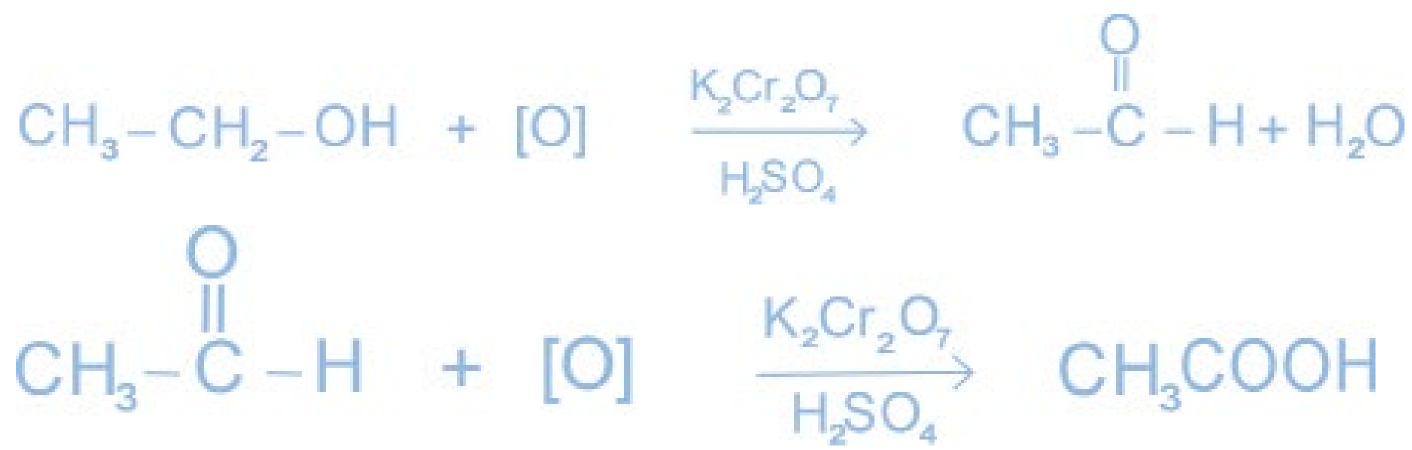
13.7.2 Manufacture of Acetic Acid

1 . From Acetylene

Acetylene is treated with 20% H_2SO_4 and 1.0% $HgSO_4$ at 80°C to give ethanal (acetaldehyde) which is then oxidised using V_2O_5 to give acetic acid.



2. Acetic acid is also prepared commercially by the oxidation of ethyl alcohol.Ethyl alcohol can be commercially prepared from molasses by a process called fermentation.It is oxidized by potassium dichromate in the presence of conc. sulphuric acid to give acetaldehyde which is further oxidized under the same conditions to give acetic acid.



13.7.3 Physical Characteristics

Acetic acid is a colourless liquid with a boiling point 118°C. It has a strong vinegar odour and sour taste. The pure acid freezes to an ice like solid at 17 °C, therefore, it is called glacial acetic acid. It is miscible with water, alcoholand ether in all proportions.

13.7.4 Reactions of Acetic Acid

Chemical reactions of acetic acid have already been discussed in the general properties of the carboxylic acids.

13.7.5 Uses of Acetic Acid

Acetic acid is used:

i) as a coagulant for latex in rubber industry.

ii) in the manufacture of plastics (polyvinyl acetate) rayon (cellulose acetate) and silk.

iii) in medicine as a local irritant.

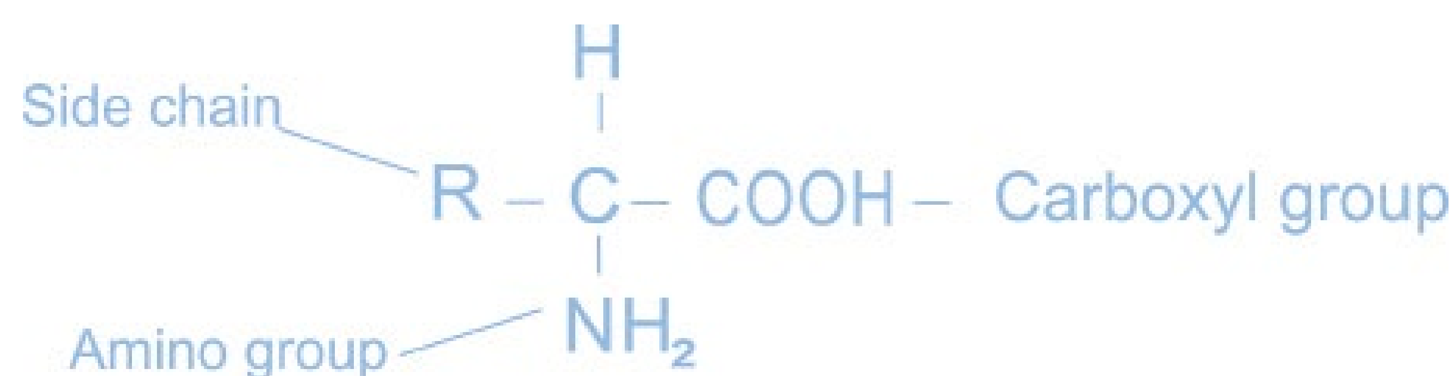
iv) as a solvent in the laboratory for carrying out reactions.

v) in the manufacture of pickles.

vi) in the manufacture of many organic compounds like acetone, acetates and esters.

13.8 AMINO ACIDS

Amino acids are organic compounds containing both amino and carboxyl groups. They are represented by the general formula:



R is different for different amino acids. The amino group may be present at any carbon atom other than that of the carboxyl group (COOH). They are referred to as α, β, γ depending upon whether the amino group is present on the α, β, or γ carbon atom relative to the carboxyl group. Almost all the naturally occurring amino acids are α – amino acids. These amino acids are very important because they are the building blocks of proteins. Proteins are very important for us.

The amino acids which contain two carboxyl groups are called acidic amino acids while those containing two amino groups are called basic amino acids. For example, glutamic acid and aspartic acid are acidic amino acids while lysine is a basic amino acid.

About twenty amino acids have been identified as the constituents of most of the animal and plant proteins.

13.8.1 Essential and Non-essential Amino Acids

Out of twenty amino acids which are required for protein synthesis, the human body can synthesize only ten. The amino acids which body can synthesize are called non-essential amino acids. The remaining ten amino acids which the body is not able to synthesize are called essential amino acids.

The essential amino acids must be supplied to our bodies through our diet because they are required for proper health and growth. The deficiency of essential amino acids may cause diseases.

13.8.2 Nomenclature of Amino Acids

Although amino acids can be named according to IUPAC system, they are generally known by their trivial names. These trivial names usually reflect the origin or an obvious property of the compound.

Glycine, for example is so named, because it has a sweet taste (Greek glykys - sweet) and the tryosine was first isolated from cheese (from Greek tryos-cheese). For the sake of simplicity, each amino acid has been given an abbreviation w'hich generally consists of the first three letters of the common name.

For example, the simplest amino acid is glycine H_2NCH_2 COOH. It may be abbreviated as Gly. Similarly, alanine $CH_3-\underset{NH_2}{\underset{|}{CH}}-COOH$ may be represented as Ala.

Names, structural formulae and other features of some amino acids are given in Table 13.2.

Table 13.2 Names, structural formulae and other features of amino acids

	Name	Nature	Abbreviation	Structural formula
1	Glycine	Neutral	Gly	$\underset{NH_2}{\underset{\vert}{CH_2}}-COOH$
2	Alanine	Neutral	Ala	$CH_3-\underset{NH_2}{\underset{\vert}{CH}}-COOH$
3	Valine	Neutral	Val	$CH_3-\underset{CH_3}{\underset{\vert}{CH}}-\underset{NH_2}{\underset{\vert}{CH}}-COOH$
4	Proline	Neutral	Pro	H_2C-CH_2 $H_2C\ \ \ CHCOOH$ NH (ring)
5	Aspartic acid	Acidic	Asp	$HOOC-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$
6	Glutamic acid	Acidic	Gla	$HOOC-CH_2-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$
7	Lysine	Basic	Lys	$\underset{NH_2}{\underset{\vert}{CH_2}}-(CH_2)_3-\underset{NH_2}{\underset{\vert}{CH}}-COOH$
8	Histidine	Basic	His	$CH=C-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$ N NH CH (ring)

13.8.3 Structure of Amino Acids

The amino acids exist as dipolar ion called Zwitter ion. It has positive as well as negative ends within the same molecule. In the formation of Zwitter ion, the proton goes from the carboxyl group to amino group. The Zwitter ionic structure of an amino acid may be written as:

Animaton 13.9 : Formation of the peptide bond
ource & Credit : Researchpeptides

The dipolar structure is also called internal salt. All α - amino acids exist largely in dipolar ionic forms.

13.8.4 Acidic and Basic Characters of Amino Acids

On the basis of dipolar ion structure, the acidic and basic reactions of amino acids may be represented as :

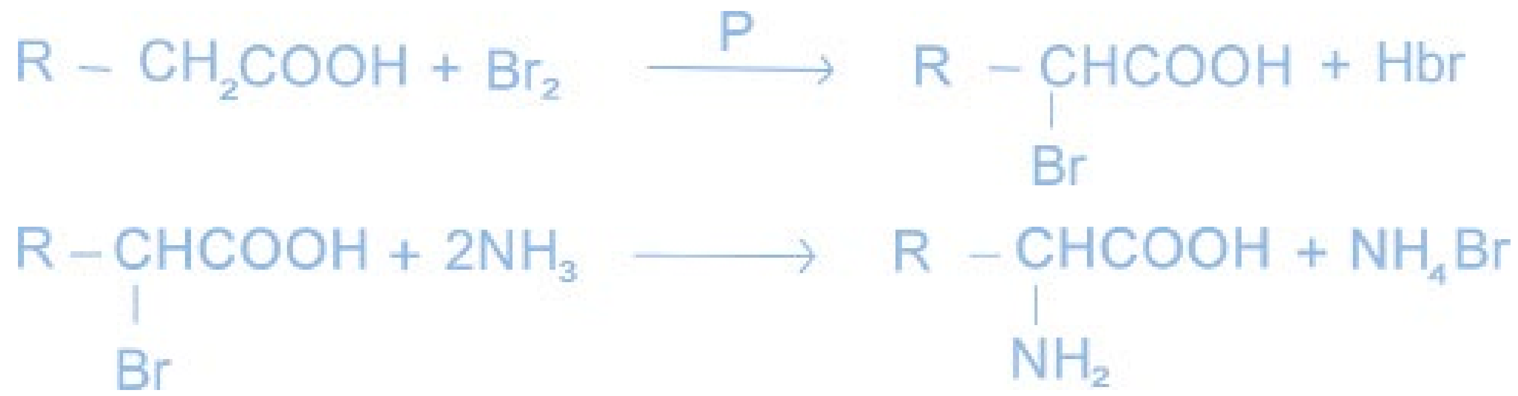
1. When an acid is added to an amino acid the carboxylate ion accepts the proton and, therefore, the basic character is due to this group.

2. When an alkali is added to an amino acid, $-NH_3$ group releases the proton and therefore the acidic character is due to this group.

13.8.5 Synthesis of Amino Acids

Amino acids can be synthesized by the following reactions.

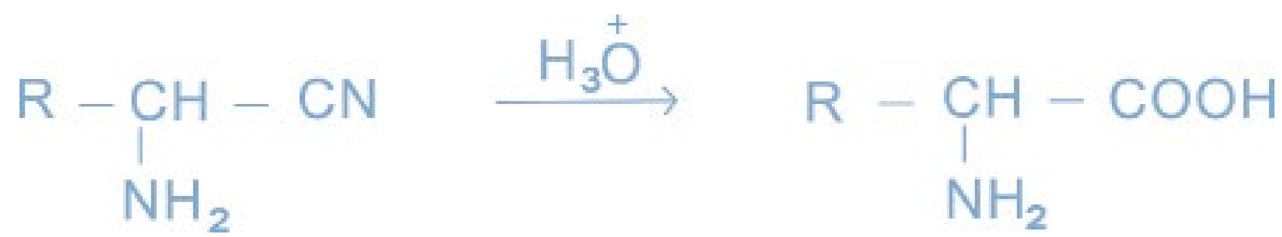
1. By the reaction of α - bromoacid with ammonia.



2. The Strecker Synthesis

When hydrogen cyanide is added to an aldehyde in the presence of ammonia, α - amino acid is obtained.

α - amino nitdle upon acidic hydrolysis yields an α - amino acid:



13.8.6 Reactions of Amino Acids

Amino acids undergo many chemical reactions characteristics of either amino group or carboxyl group.

1. Esterification

Amino acids form aminoester when treated with an alcohol in the presence of catalytic amount of a strong acid.

$$\underset{\displaystyle NH_2}{R-CH}-COOH + R'-OH \xrightleftharpoons{H^-} \underset{\displaystyle NH_2}{R-CH}-COOR' + H_2O$$

2. Reaction with Nitrous Acid

Amino acids react with nitrous acid to produce α - hydroxy carboxylic acid and nitrogen gas.

$$\underset{\displaystyle NH_2}{R-CH}-COOH \xrightarrow[HCl]{NaNO_2} \underset{\displaystyle OH}{R-CH}-COOH + N_2\uparrow + H_2O$$

13.8.7 Test of Amino Acids

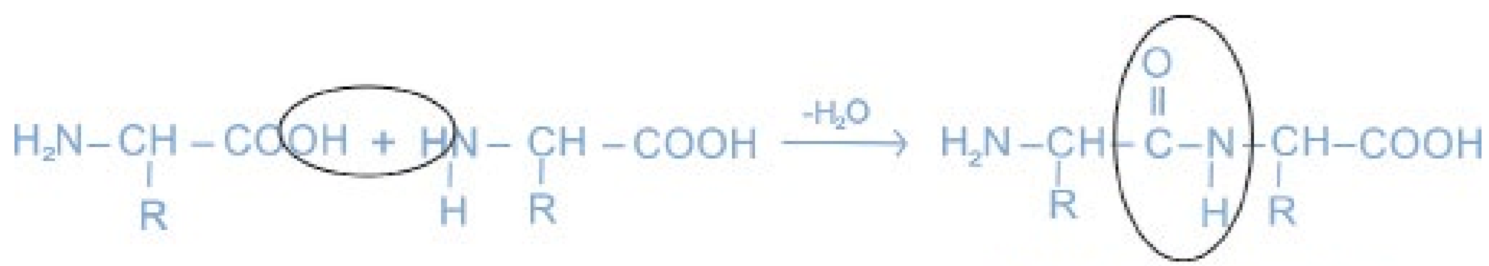
Ninhydrin Test

Ninhydrin reacts with amino acid to form an intensely coloured bluish violet product. The ninhydrin reaction is also widely used to "visualize" amino acids separated by paper chromatography.

13.8.8 Peptidos and Proteins

Peptides are the compounds formed by the condensation of two or more same or different a-amino acids. The condensation occurs between amino acids with the elimination of water. In this case, the carboxyl group of one amino acid and amino group of another amino acid gets condensed with elimination of water. The resulting – CO – NH – linkage is called a peptide linkage.

The formation of peptide is shown below:



Peptide linkage (dipeptide)

If a large number of amino acids (hundreds to thousands) are joined by peptide bonds, the resulting polymide is called a polypeptide.

$$H_2N-\underset{\displaystyle R}{CH}-CO-\left[\underset{\displaystyle H}{N}-\underset{\displaystyle R}{CH}-CO\right]_n NH-\underset{\displaystyle R}{CH}-COOH$$

Depending upon the number of amino acids per molecule, the peptides are dipeptides, tripeptides, polypeptides, etc. The formation of peptide bonds can continue until a molecule containing several hundred thousand amino acids is formed. Such a molecule is called polypeptide or protein. By convention a peptide having molecular mass upto 10,000 is called a polypeptide while a peptide having a molecular mass more than 10,000 is called a protein.

KEYPOINTS

1. Organic compounds containing carboxyl group ($-\overset{O}{\overset{\|}{C}}-OH$) are called carboxylic acids. There are two classes of carboxylic acids i.e., aliphatic and aromatic carboxylic acids. Aliphatic carboxylic acids are also called fatty acids
2. Carboxylic acids can be produced by the oxidation of alcohols and aldehydes and by the hydrolysis of nitriles.
3. Lower members of the series are water soluble and have pungent smell. Solubility decreases with the increase in molecular mass.
4. Carboxylic acids have higher boiling points than the corresponding alcohols. Boiling point increases with the increase in the molar mass.
5. Acid chlorides, acid amides, esters and acid anhydrides are called derivatives of carboxylic acids.
6. Acetic acid is synthesized on commercial scale from acetylene.
7. Carboxylic acids containing amino group in their molecules are called amino acids. They are classified as neutral, basic and acidic amino acids.
8. Amino acids join together to produce peptides. A polypeptide has a molecular mass upto 10,000 whereas the molecular mass of protein is greater than 10,000.

EXERCISE

Q. 1 Fill in the blanks.

(i) Formula of malonic acid is_________________.
(ii) Methyl nitrile upon acidic hydrolysis produces_____________ .
(iii) Melting points of carboxylic acids containing even number of carbon atoms are______________ than the next lower and higher members containing odd number of carbon atoms.
(iv) Acetic acid on heating with___________produces acetic anhydride.
(v) Acid chloride and acid anhydride are called_____________ of acid.
(vi) Pure acetic acid is called ______________ .
(vii) Fox mula of alanine is___________________.
(viii) Proline is a________________ amino acid.
(ix) A peptide having a molecular mass more than 10000 is called_____________.

Q. 2 Indicate True and False.

(i) Acetic acid exists as a dimer in benzene.
(ii) First three aliphatic acids have fruity smells.
(iii) Carboxylic acids on reduction with $LiAlH_4$ produce alkenes.
(iv) Acetic acid on dehydration produces CO and H_2.
(v) Sodium formate on heating with soda lime produces $NaHCO_3$ and hydrogen.
(vi) Amino acids exist as Zwitter ion.
(vii) Histidine is an acidic amino acid.
(viii) A peptide having molecular mass upto 10000 is called protein.
(ix) Phthalic acid is a monocarboxylic acid.
(x) Formula of glycine is CH_2COOH.

Q. 3 Multiple choice questions. Encircle the correct answer.

(i) Acetic acid is manufactured by
(a) distillation (b) fermentation (c) ozonolysis (d) esterification

(ii) A carboxylic acid contains
(a) a hydroxyl group (b) a carboxyl group
(c) a hydroxyl and carboxyl group (d) a carboxyl and an aldehydic group

(iii) Which acid is used in the manufacture of synthetic fibre
(a) formic acid (b) oxalic acid (c) carbonic acid (d) acetic acid

(iv) Which following derivative can not be prepared directly from acetic acid.
(a) acetamide (b) acetyl chloride (c) acetic anyhdride (d) ethyl acetate

(v) Which reagent is used to reduce a carboxylic group to an alcohol.
(a) H_2/Ni (b) H_2/Pt (c) $NaBH_4$ (d) $LiAlH_4$

(vi) The solution of which acid is used for seasoning of food.
(a) formic acid (b) acetic acid (c) benzoic acid d) butanoic acid

(vii) Organic compounds X and Y react together to form organic compound Z. What type of compounds can X, Y and Z be?

	X	Y	Z
(a)	alcohol	ester	acid
(b)	acid	ester	alcohol
(c)	ester	alcohol	acid
(d)	alcohol	acid	ester

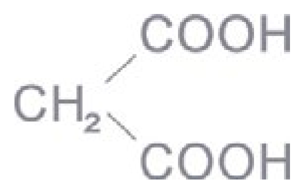
(viii) An aqueous solution of an organic compound reacts with sodium carbonate to produce carbon dioxide gas. Which one of the following could be the organic compound.
(a) $CH_2 = CH - CH_3$ (b) $CH_3 - CHO$
(c) $CH_3COOC_2H_5$ (d) $CH_3 - CH_2 - COOH$

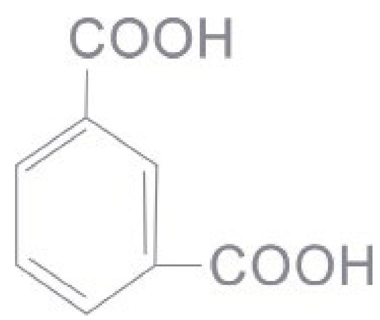
(ix) Which of the following is not a fatty acid?
(a) propanoic acid (b) acetic acid
(c) phthalic acid (d) butanoic acid

(x) Acetamide is prepared by
(a) heating ammonium acetate (b) heating methyl cyanide
(c) heating ethyl acetate (d) the hydrolysis of methyl cyanide

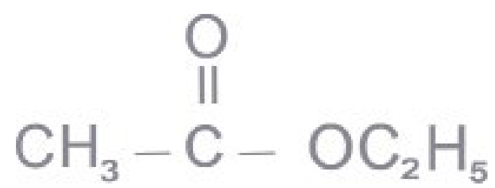
Q. 4 Write down the structural formulae of the followings
(i) Valeric acid (ii) Propionic acid (iii) Oxalic acid
(iv) Benzoic acid (v) Acetic anhydride (vi) Acetyl chloride

Q. 5 Write down the names of the following compounds by IUPAC system.

(i)


(ii)


(iii)


(iv)


(v) CH_2COOH
NH_2

(vi) $HCOOC_3H_7$

Q. 6 (a) How is acetic acid manufactured? What is glacial acetic acid?
(b) How would you convert acetic acid into the following compounds?
(i) Methane (ii) Acetyl chloride (iii) Acetamide
(iv) Acetic anhydride

Q. 7 (a) What are fatty acids ?
(b) What is vinegar? Describe how is vinegar prepared from ethanol?

Q. 8 How would you carry out the following conversions?
(i) Acetic acid into acetamide (ii) Acetic acid into acetone

Q. 9 Write down the mechanisms of the following reactions.
(i) between acetic acid and ethanol (ii) between acetic acid and ammonia
(iii) between acetic acid and thionyl chloride

Q. 10 What happens when the following compounds are heated.
(i) Calcium acetate (ii) Sodium formate and soda lime
(iii) Ammonium acetate

Q. 11 What are amino acids? Explain their different types with one example in each case.

Q. 12 Write a short note on acidic and basic characters of an amino acid.

Q. 13 What is a peptide bond? Write down the formula of a dipeptide.

Q. 14 What are zwitter ions?

Q. 15 What are a amino acids, proteins and peptides? How are they related?

Q. 16 Study the facts given in (a), (b) and (c) below and then answer questions which follow.
(a) A is an organic compound made up of C, H and O. It has a vapour density 15.
[Hint: Molecular mass = 2 x vapour density].
(b) On reduction A gives a compound 'X' which has the following properties.
(i) X is a colourless liquid miscibie with water.
(ii) X is neutral to litmus.
(iii) When X is warmed with a few drops of conc. H_2SO_4 followed by a little salicylic acid a characteristic smell is produced.
(c) When X is subjected to strong oxidation, it gives compound B, which has the following properties.
(i) B is a pungent smelling mobile liquid.
(ii) It is miscible with water, alcohol or ether.
(iii) It is corrosive and produces blisters on contact with skin.
(iv) B can be obtained by passing the vapours of A with air over platinum black catalyst.
(v) B liberates H, with sodium.
(vi) It givesCO_2 with $NaHCO_3$.
1. What is the molecular mass of A?
2. Identify A, X and B.
3. Give five appropriate reactions to confirm the identities of A, X and B.
4. State one large-scale use of either A, X or B.

CHAPTER

14

MACROMOLECULES

In This Chapter You Will Learn

1. The concepts of polymerization and macromolecules.
2. Types of polymerization and products of these polymerizations e.g., polyvinyl chloride, polystyrene, polyvinyl acetate, polyamides, polyester and epoxy resins.
3. About life molecules, for example, carbohydrates, lipids, proteins, enzymes and nucleic acids.

14.1 INTRODUCTION

Acceptance of the macromolecular hypothesis came about in 1920's largely because of the efforts of Staudinger. He proposed long chain formulas for polystyrene, rubber and polyoxymethylene. Macromolecules or polymers are described as large molecules built up from small repeating units called monomers.

The development of the process of polymerization is, perhaps, one of the most significant things chemists have done, where it has had the major effect on every day life. The world would be a totally different place without artificial fibres, plastics, etc. One of the most significant changes has been the gradual replacement of natural materials such as wood and cotton with man made synthetic polymers. For better or worse we are living in a "plastic" society.

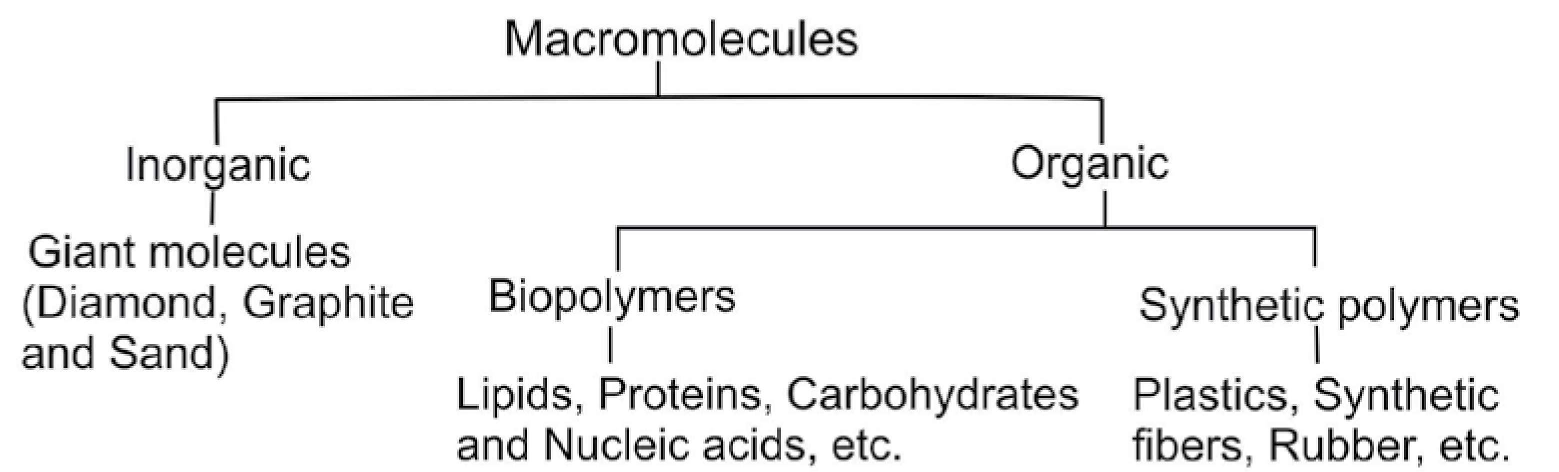


Fig. 14.1 Classification of macromolecules

The word polymer is derived from Greek, poly means 'many' and mer means 'parts'. Macromolecules can be classified into the following types, Fig 14.1.

14.2 STRUCTURE OF POLYMERS

A polymer is a large molecule build up by the repetition of small and simple chemical units known as monomers. In some cases the repetition is linear while in others, it is branched or interconnected to form three dimensional network Fig 14.2.

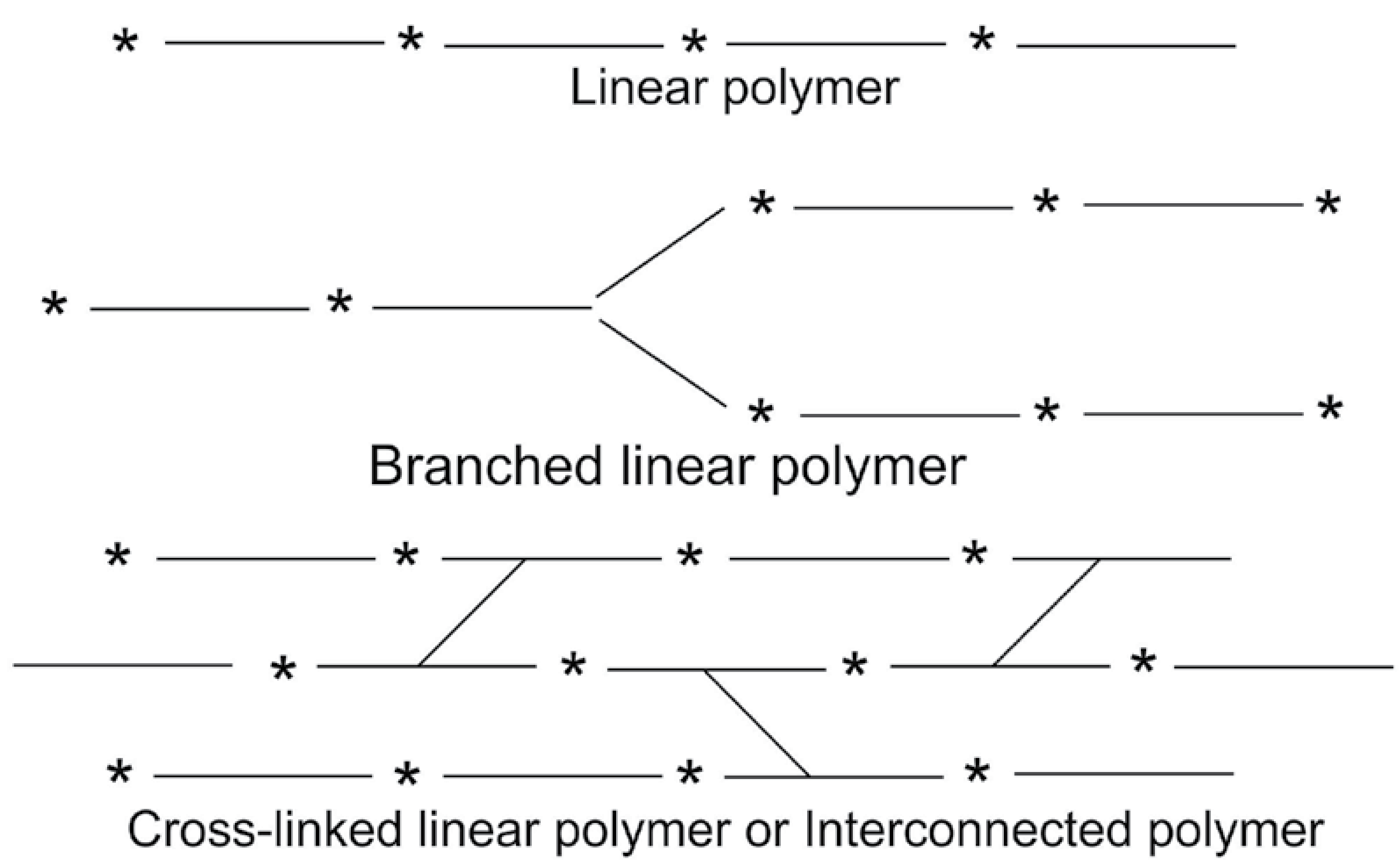


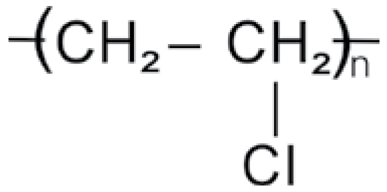
Fig. 14.2 Three ways of polymerization

The length of the polymer chain is specialized by the number of repeating units in the chain known as the degree of polymerization (DP), for example, in linear polythene.

$$—CH_2 – CH_2 – CH_2 – CH_2 – CH_2—$$

The repeating unit is $\left(CH_2 – CH_2\right)_n$ where n is a large number.
The molecular mass of the polymer is the product of the molecular mass of the repeating unit and the DP For example, polyvinyl chloride, a polymer of DP 1000, has a molecular mass

Mol. mass = Mol. mass of the repeat unit x DP



= 63.5 x 1000 = 63500

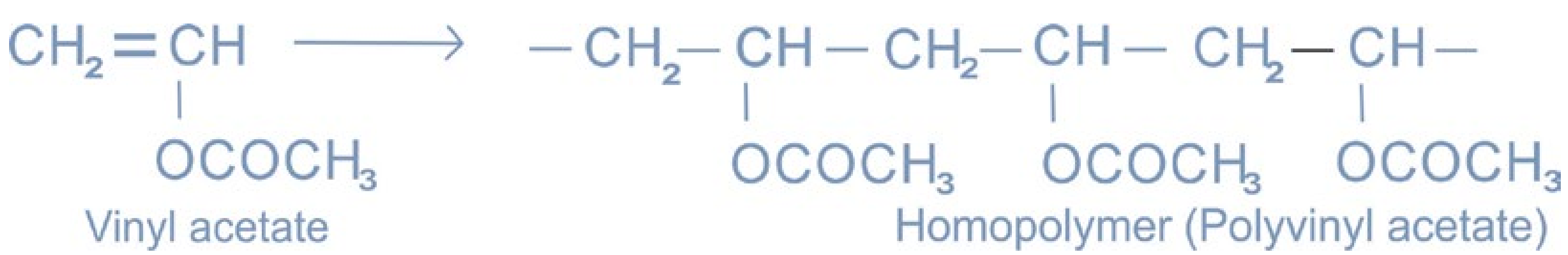
Most high molecular mass polymers are useful for making plastics, rubbers or fibres, etc. and have molecular masses between 10,000 to 1,000, 000. The properties of polymeric materials vary widely depending upon the chemical composition and structure of the macromolecule.

14.3 TYPES OF POLYMERS

The polymers formed are of the following types:

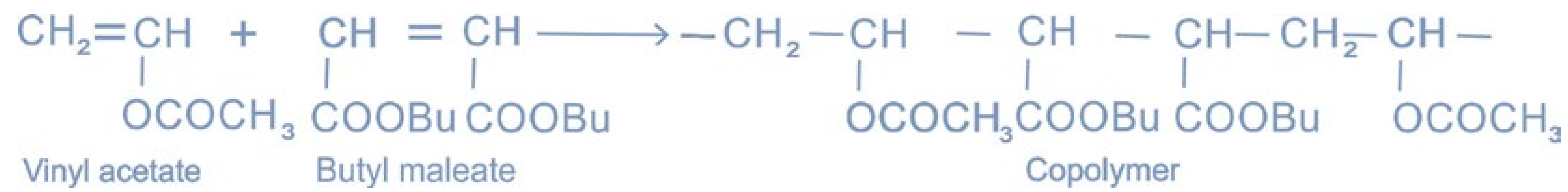
1) Homopolymer

A homopolymer is formed by the polymerization of a single type of monomer.
For example, the polymerization of vinyl acetate.



2) Copolymer

A copolymer is formed by the polymerization of two monomers together, e.g; vinyl acetate reacts with butyl maleate to give a copolymer.



3) Terpolymer

In terpolymer three different monomers are polymerized and the polymerization reaction is carefully controlled. For example, combination of butyl acrylate, methacrylate and acrylic acid monomers gives a highly tough polymer which serves as a weather-resistant paint. Based on the thermal properties of polymers, they can be divided into two types.

i) Thermoplastic Polymer

A thermoplastic polymer is one which can be softened repeatedly when heated and hardened when cooled with a little change in properties. For example; PVC pipes, plastic toys, etc.

ii) Thermosetting Polymer

The polymers which become hard on heating and cannot be softened again are called thermosetting polymers. A thermosetting polymer, on heating, decomposes instead of melting. For example, synthetic varnish, epoxy resins, etc.

14.4 POLYMERIZATION PROCESS

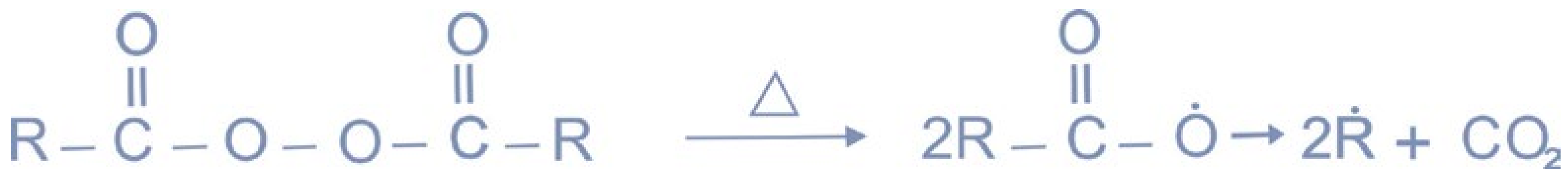
In 1929, W.H. Carothers suggested a classification of the polymerization process into two types depending upon the way the polymers are formed.

1. Addition polymerization
2. Condensation polymerization

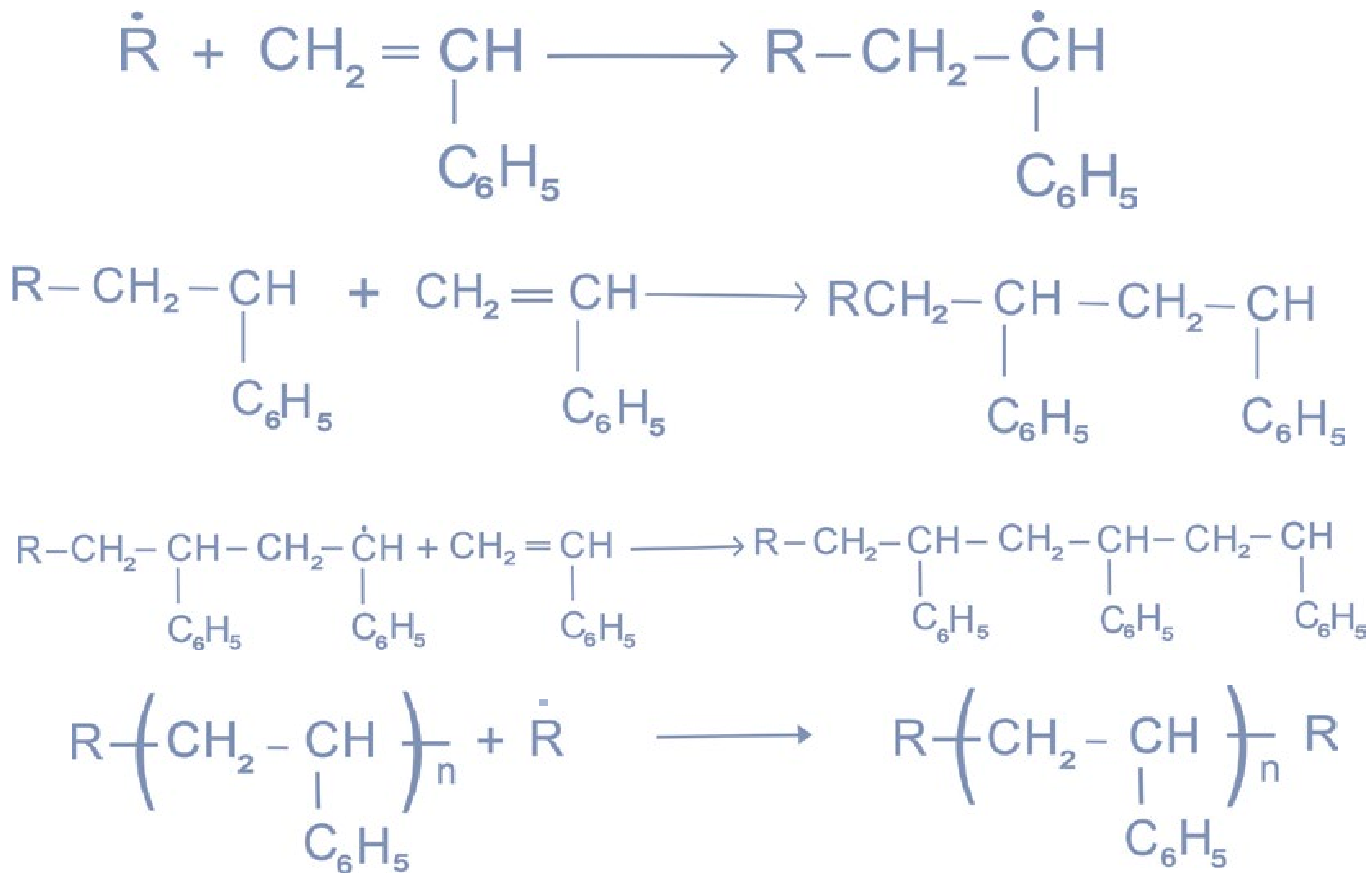
1) Addition Polymerization

It is a free-radical addition reaction which involves initiation, propagation and termination steps. For example, polymerization of styrene. Addition of polymerization is catalyzed by thermal or photochemical decomposition of organic peroxides to give free radicals.

Initiation

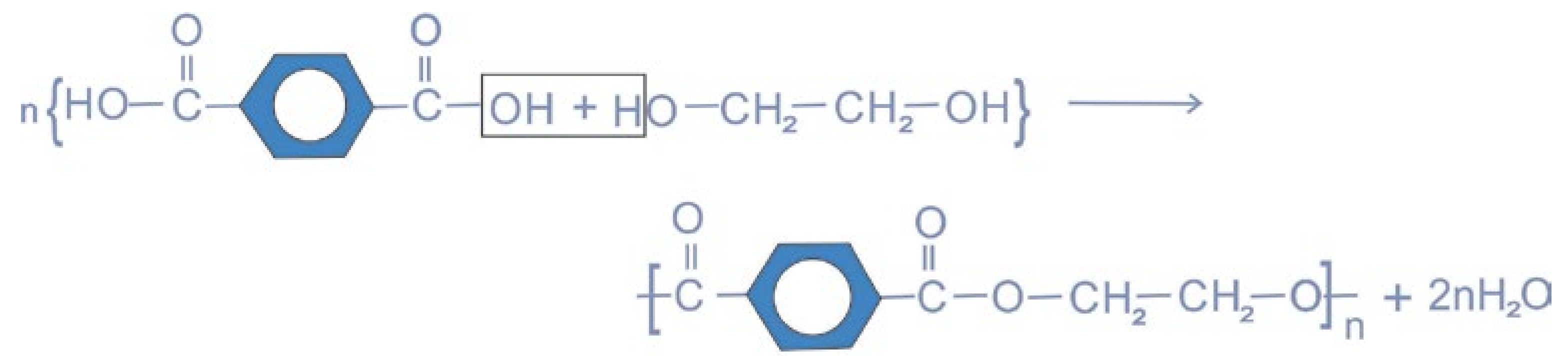


Propagation



2. Condensation Polymerization

This type of polymerization results from the mutual reaction of two functional groups. The reaction usually involves the removal of a water molecule or a methanol molecule. It takes place at both ends of the growing chain. For example; dicarboxylic acids or esters combine with diols to get the desired polymer like nylon and polyester fibre. Such polymerizations are generally ionic in nature.

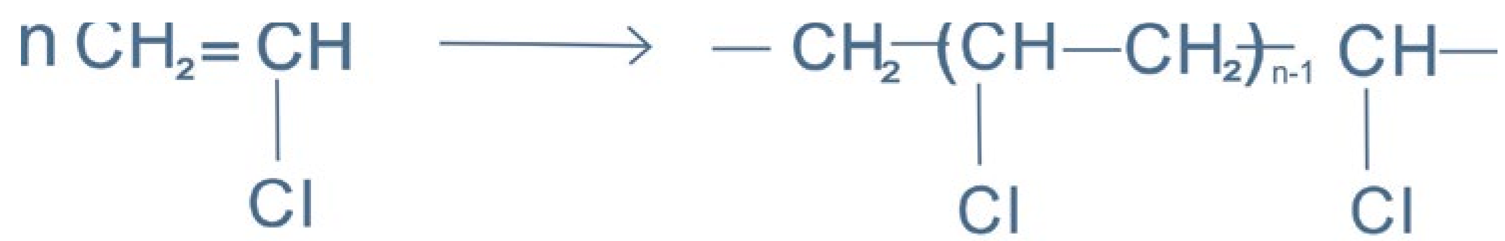


Polyester

14.5 BRIEF DESCRIPTION OF SYNTHETIC POLYMERS

1. Polyvinyl Chloride (PVC)

It is an addition polymer obtained by polymerizing vinyl chloride at 52°C and 9 atmospheric pressure.



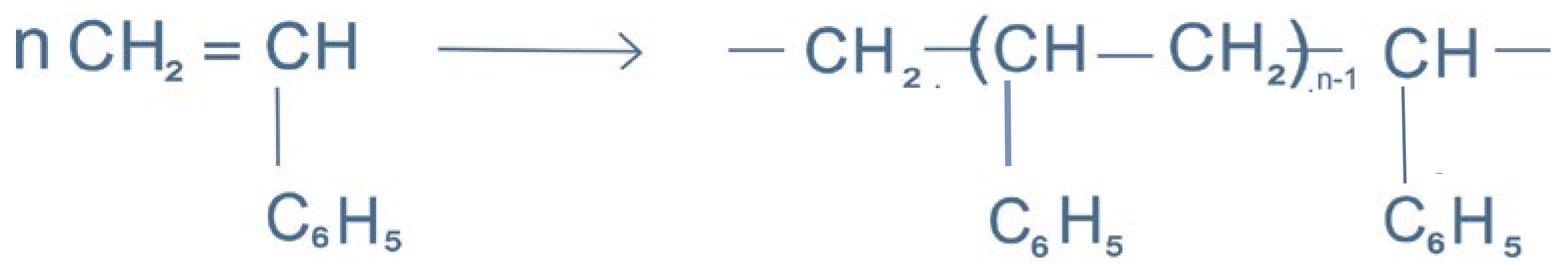
Vinyl chloride Polyvinyl chloride (PVC)

Addition of a plasticizer improves the flexibility of the polymer.It is widely used in floor coverings, in pipes, in gramophone recorders, etc.

2) Polystyrene

It is also an addition polymer and is obtained by the polymerization of styrene in the presence of a catalyst.

Polystyrene is used in the manufacture of food containers, cosmetic bottles, toys and packing material, etc.



Styrene Polystyrene

3. Polyvinyl Acetate (PVA)

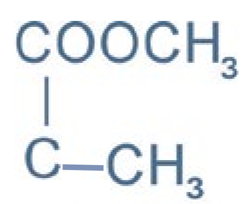
PVA is a colourless, non-toxic resin. It is supplied in a number of grades differing in the degree of polymerization.The resin has a characteristics odour. It is mostly used as an adhesive material and as a binder for emulsion paints.

4. Acrylic Resins

These are closely related to the vinyl resins. The most important monomers of acrylic resins are methylmethacrylate, acrylic acid and butyl acrylate. The acrylic fibres are based largely on acrylonitrile.Acrylic resins are used in the manufacture of plastics, paints for car industry and water based weather resistant paints.

$CH_2{=}CHCOOH$

Acrylic acid



Methylmethacrylate

$CH_2{=}CH{-}CN$

Acrylonitrile

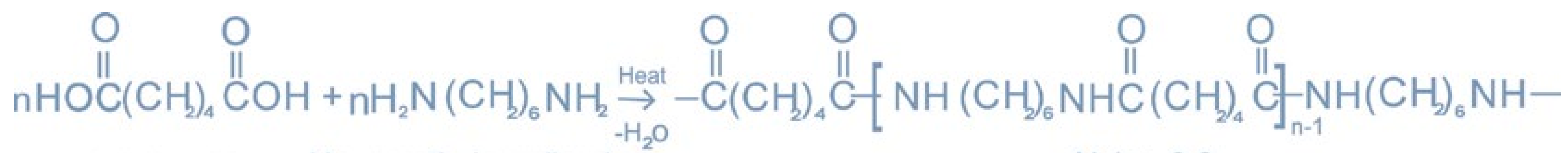
5. Polyester Resins

Polyester resins are the product of the reaction of an alcohol (ethane 1, 2 diol) and aromatic bi-functional acids (benzene 1,4 dicarboxylic acid). This product has a large number of uses in clothing. Polyester is often blended with cotton or wool for summer and winter clothing. Polyester resins are also used for making water tanks, etc. (For a chemical equation please see under condensation polymerization).

6) Polyamide Resins

These resins are formed by the condensation of polyamines with aliphatic dicarboxylic acids.One of the most famous condensation polymers discovered is Nylon.

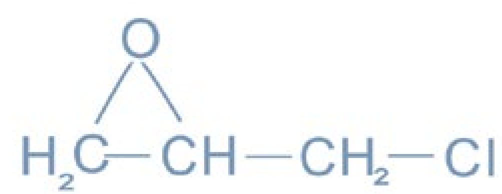
The word Nylon has been accepted as a generic name for synthetic polyamides. Nylon 6, 6 is the most important polyamide. It is obtained by heating adipic acid (hexanedioic acid) with hexamethylene diamine. Nylon 6,6 derives its name from its starting materials adipic acid and hexamethylene diamine,both of which have six carbon atoms. Nylon is mainly used as a textile fibre. It has a combination of high strength, elasticity, toughness and abrasion resistance.



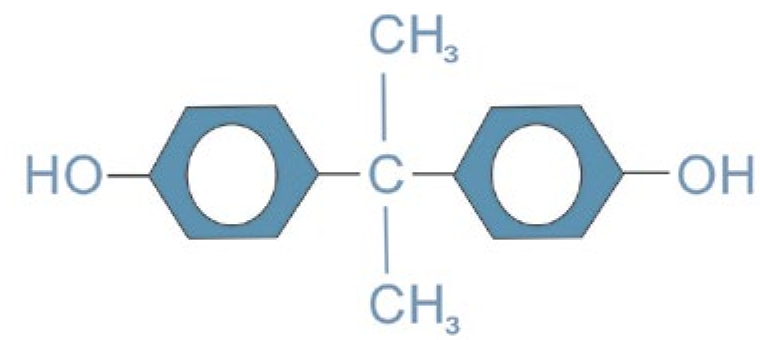
Adipic acid Hexamethylenediamine Nylon-6,6

7. Epoxy Resins

The epoxy resins are fundamentally polyethers but retain their name on the basis of their starting materials and the presence of epoxide group in the polymer.The epoxy resin is made by condensing epichlorohydrin with diphenylol propane.



Epichlorohydrin



Diphenylolpropane

The major use of epoxy resins is in coating materials which give toughness, flexibility, adhesion and chemical resistance. Industrial materials, thermal power stations, packing materials are coated with epoxy paints. Dams, bridges, floors, etc. are painted with epoxy resins.

14.6 BIOPOLYMERS

Most biologically important substances are organic compounds built up from skeleton of carbon atoms. Many of them are very large molecules and most of these are polymers. The four major classes of organic compounds in living cells are carbohydrates, lipids, proteins and nucleic acids.

14.6.1 Carbohydrates

The term carbohydrate is applied to a large number of relatively heterogeneous compounds. They are the most abundant biomolecules on earth. The name carbohydrate (hydrate of carbon) is derived from the fact that the first compound of this group which was studied had an empirical formula $C_x(H_2O)_y$. They are commonly called 'sugars' and are 'polyhydroxy compounds' of aldelydes and ketones.

14.6.2 Classification of Carbohydrates

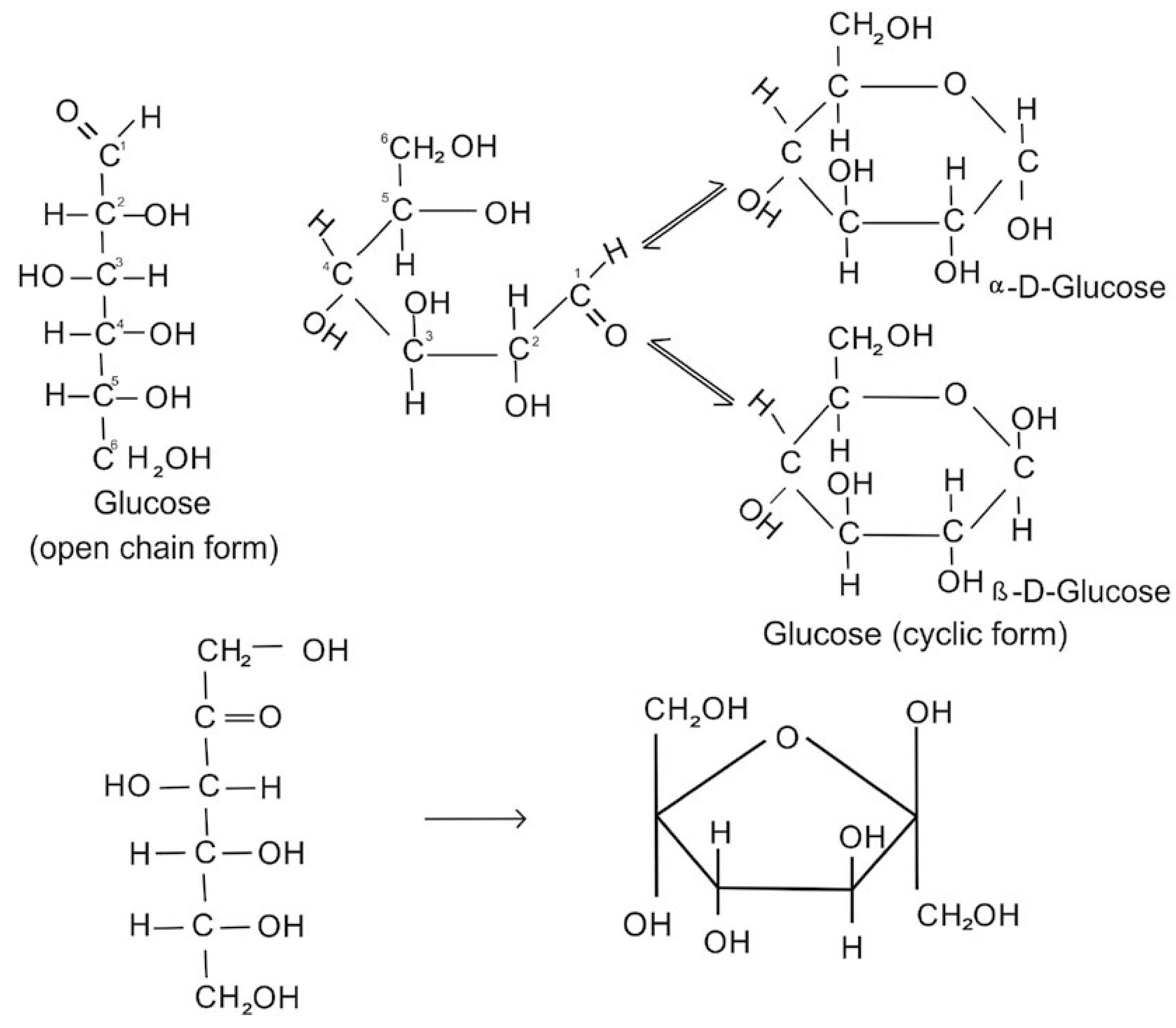
The commonly described classification is given below.

1. Monosaccharides

These are simple sugars which cannot be hydrolyzed. They have an empirical formula $(CH_2O)_n$ where n = 3 or some large number. Monosaccharides are either aldoses (aldehydic group) or ketoses (ketonic group). Common examples are glyceraldehyde, glucose, fructose, etc.

14. Macromolecules
eLearn.Punjab

Sugars with five carbon atoms (pentoses) or six carbon atoms (hexoses) are more stable as cyclic structures than as open chain structures. Glucose and fructose are very common examples of hexoses, both of which have molecular formula, $C_6H_{12}O_6$.



Glucose (open chain form)

Glucose (cyclic form)

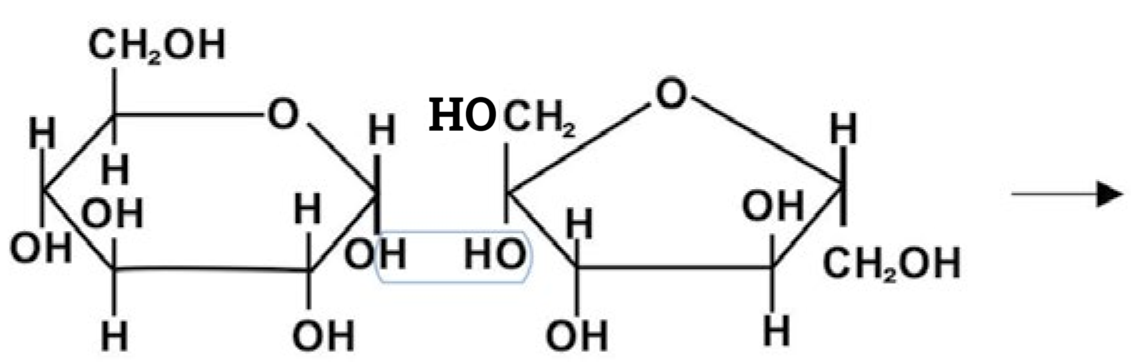
Fructose (open chain form)

Fructose (cyclic form)

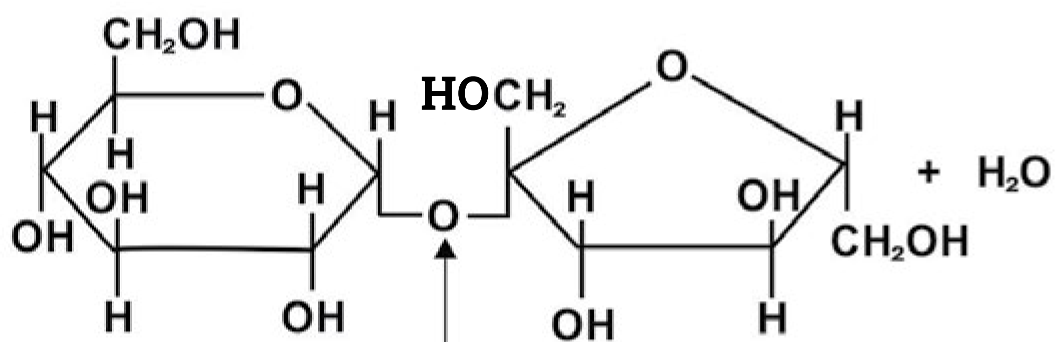
Glucose also called dextrose, grape sugar or blood sugar, occurs naturally in both combined and free states. In the free state, it is present in most sweet fruits and in honey. Small quantities of glucose are also present in human blood and urine. In the combined state it forms a major component of many disaccharides and polysaccharides.It is the source of energy in our body. Fructose is also found in combined and free states.It is used as a sweetening agent in confectionery and as a substitute of cane sugar. Other examples of monosaccarides are galactose and mannose.

2. Disaccharides or Oligosaccharides

The oligosaccharides are formed when two to nine monosaccharide units combine by the loss of water molecules. This results in the formation of a glycosidic linkage. For example; sucrose which is a common table sugar, is a disaccharide of glucose and fructose.



α-D-Glucose Fructose



Glycosidic linkage

Sucrose

Conversely, hydrolysis of an oligosaccharide by water in the presence of an acid or by enzymes yields two or more monosaccharide units. Among the most common disaccharides are sucrose, lactose and maltose. Of these, sucrose occurs in sugar cane, sugar beet, pineapple, apricot, mango, almond, coffee and honey. Lactose (milk sugar) occurs in the milk of all animals. It does not occur in plants.

Trisaccharides, which yield three monosaccharide molecules on hydrolysis, have molecular formula, $C_{18}H_{32}O_{16}$, for example, raffinose. In general, the mono-saccharides and oligosaccharides are crystalline solids soluble in water and sweet to taste. They are collectively known as 'sugars'.

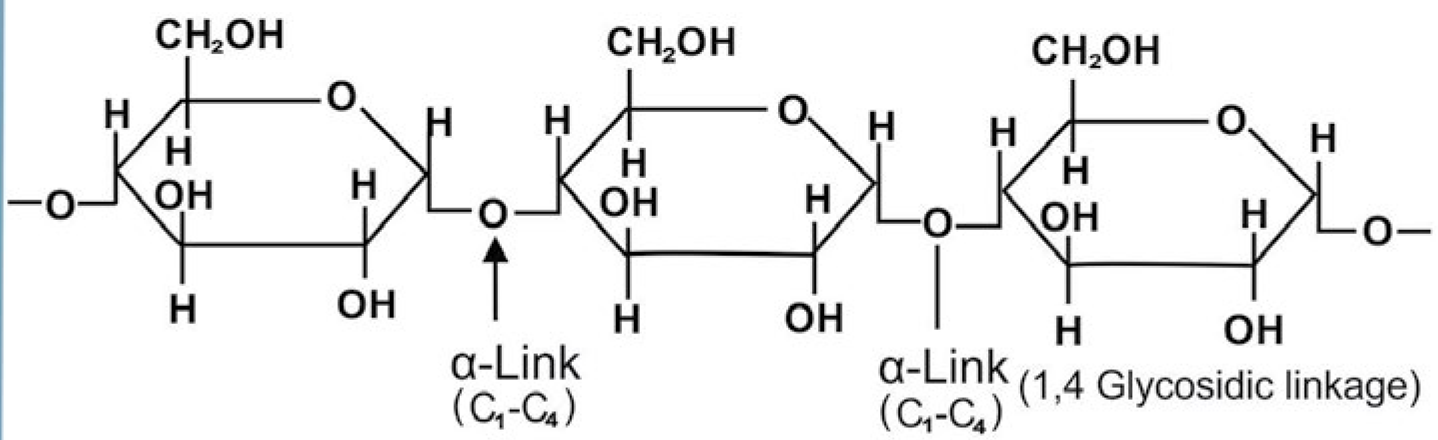
3. Polysaccharides

The polysaccharides are carbohydrates of high molecular mass which yield many monosaccharide molecules on hydrolysis. Examples are, starch and cellulose, both of which have molecular formula, $(C_6H_{10}O_5)_n$.The polysaccharides are amorphous solids, insoluble in water and tasteless and are called 'non-sugars'. Polysaccharides perform two principal functions in animals and plants. They are used as energy storage compounds and for building structural elements of cells. Plants store glucose as starch and animals store glucose in the form of a highly branched polymer known as glycogen. Glycogen is stored in the liver and muscles.

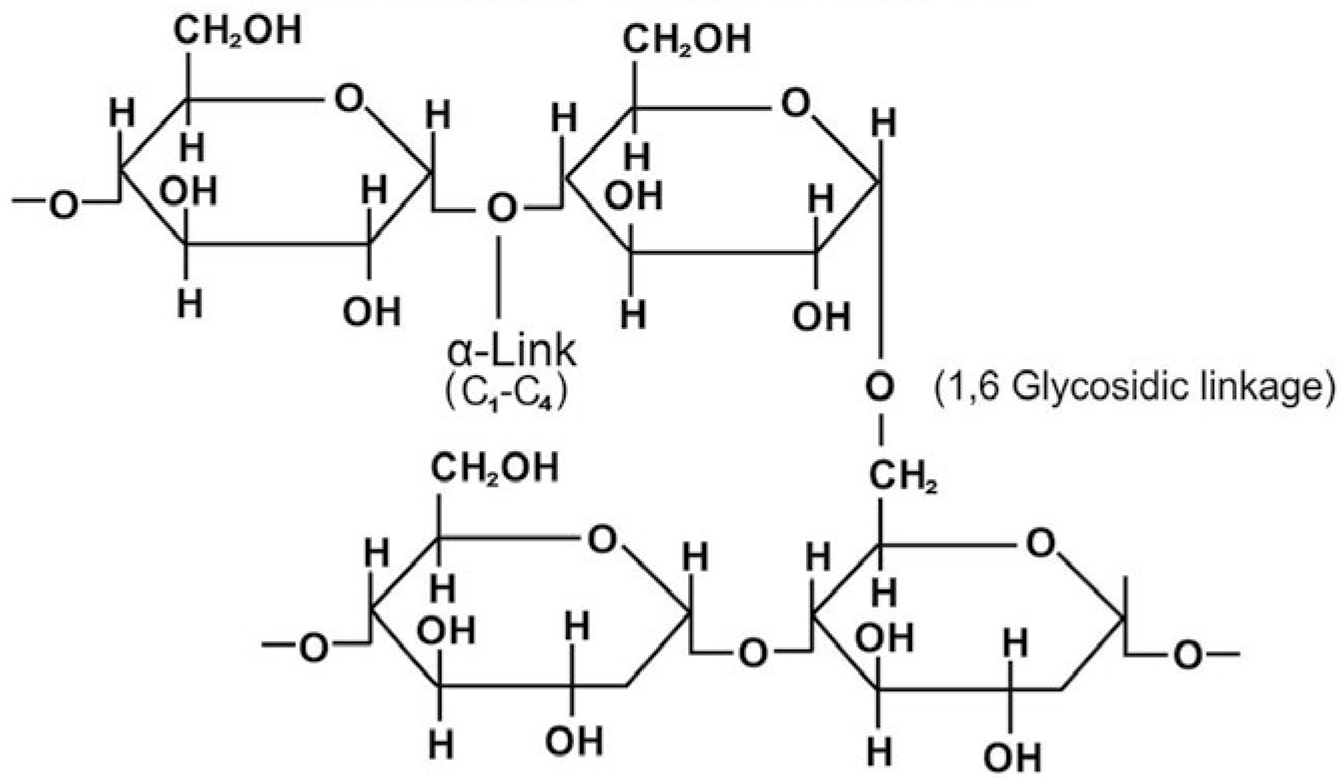
i) Starch

Starch is the most important source of carbohydrates in human diet. The chief commercial sources of starch are wheat, rice, maize, potatoes and barley. Starch is a polymer of α-D-glucose.

Starch is not a pure compound. It is a mixture of two polysaccharides, amylose and amylopectin which can be separated from one another. Amylose is soluble in water and gives a deep blue colour with iodine while amylopectin is insoluble and gives no colour. Natural starch consists of 10 to 20% amylose and 80 to 90% amylopectin. It is used in coating and sizing of paper to improve the writing qualities. It is also used in laundering and in the manufacture of glucose and ethyl alcohol.



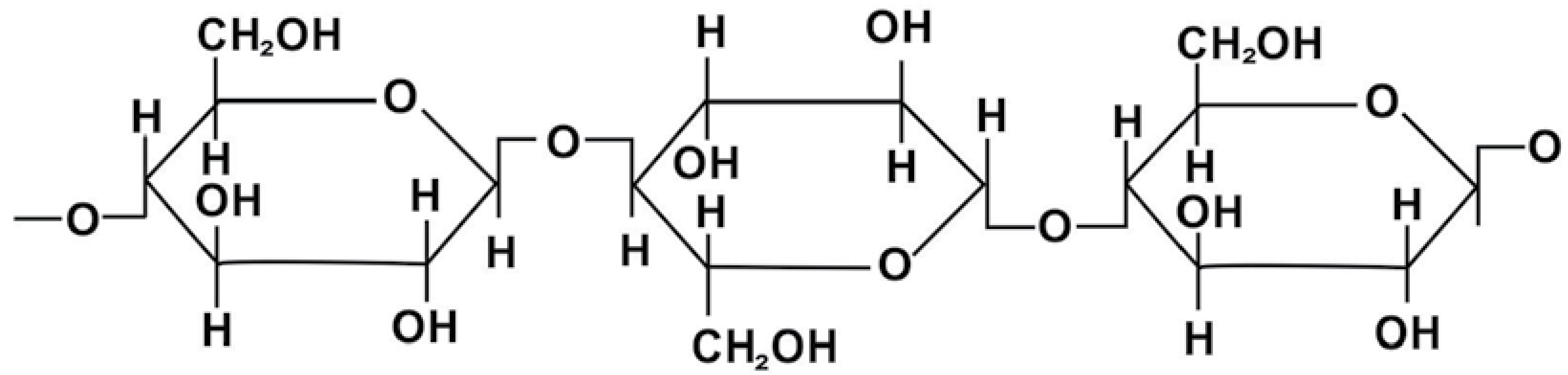
Structure of Amylose (Polymer of α-D-glucose)



Structure of Amylopectin

ii) Cellulose

By far, the most abundant structural polysaccharide is cellulose. Some 100 billion tons of cellulose are produced each year by plants. For example, cotton is 99% cellulose and the woody parts of trees are generally more than 50% cellulose. It is a polymer of β-D-glucose. It is present mainly in the plant kindom but also occurs in some marine animals. It is an unbranched polymer consisting of a large number (up to 2500) of glucose residues joined to each other through β -1—>4 linkages.



Cellulose (Polymer of β-D-glucose)

iii) Glycogen

It occurs mainly in the liver and muscles where it represents the main storage polysaccharide in the same way as starch functions in plant cells. Glycogen is therefore also called 'animal starch'. Its structure closely resembles with that of amylopectin having 1 → 4 and 1→6 glycosidic linkages. Human glycogen is a much more branched molecule than amylopectin. On hydrolysis it yields glucose units.

14.6.3 Proteins

Proteins are extremely complicated molecules of living things. They are the nitrogeneous compounds made up of a variable number of amino acids. The human body probably contains at least 10,000 different kinds of proteins. The name protein is derived from the Greek word proteios meaning of prime importance.

Proteins are present in all living organisms and without proteins life would not be possible. They are present in muscles, skin, hair and other tissues that make up the bulk of the body's non-bony structure.

All proteins contain the elements carbon, hydrogen, oxygen and nitrogen. They may also contain phosphorus and traces of other elements like iron, copper, iodine, manganese, sulphur and zinc. Proteins are very high molecular weight macromolecules.All proteins yield amino acids upon complete hydrolysis.
Thus proteins may be defined as the high molecular weight organic materials, which upon complete hydrolysis, yield amino acids.

14.6.4 Classfication of Proteins

Based on the physico-chemical properties, proteins may be classified into three types.

1. Simple protiens
2. Compound or Conjugated proteins
3. Derived proteins

1. Simple Proteins

These proteins on hydrolysis yield only amino acids or their derivatives. For example, albumins, globulins, legumin, collagen, etc. Globulins are insoluble in water but soluble in dilute salt solutions. They are found in animals, e.g; lactoglobulin is found in muscles and also in plants. Legumin and collagen proteins are present in the connective tissues throughout the body . They are the most abundant proteins in the animal kingdom forming some 25 to 35% of body protein.

2. Compound or Conjugated Proteins

In these molecules the protein is attached or conjugated to some non- protein groups which are called prosthetic groups. For example; phospho-proteins are conjugated with phosphoric acid, lipoproteins are conjugated with lipid substances like lecithin, cholesterol and fatty acids.

3. Derived Proteins

This class of protein includes substances which are derived form simple and conjugated proteins.For example, proteoses enzymes, peptones, oligopeptides, polypeptides, etc.

Based on their functions, proteins may also be classified as regulatory or hormonal proteins, structural proteins, transport proteins, genetic proteins, etc.

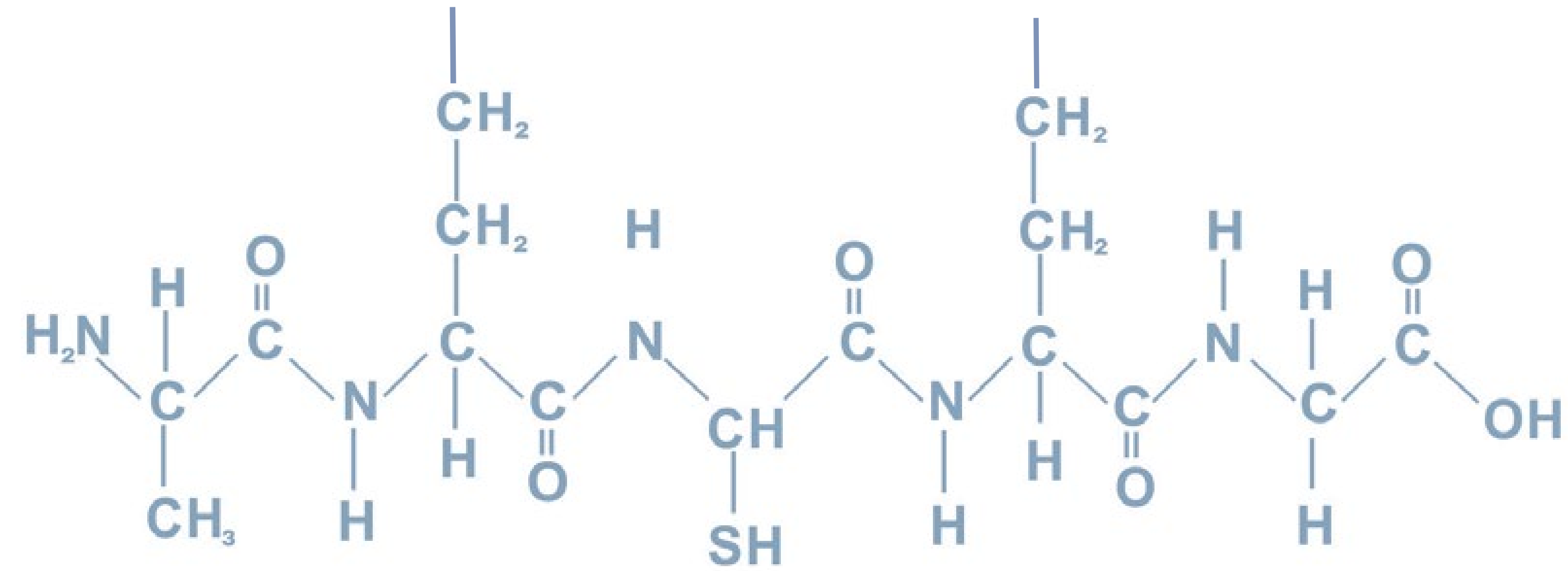
14.6.5 Structure of Proteins

The majority of proteins are compact, highly convoluted molecules with the position of each atom relative to the others determined with great precision. To describe the structure of a protein in an organism it is necessary to specify the three- dimensional shape that the polypeptide chain assumes. Proteins assume at least three levels of structural organization.

(i) Primary structure
(ii) Secondary structure
(iii) Tertiary structures

Some proteins also possesses a fourth structure called the quaternary structure.

The sequence of the amino acids combined in a peptide chain is referred to as the primary structure.



The secondary structure of a protein is a regular coiling or zigzagging of polypeptide chains caused by hydrogen bonding between NH and C = 0 groups of amino acids near each other in the chains. The three dimensional twisting and folding of the polypeptide chain results in the tertiary structure of proteins.

14.6.6 Denaturation of Proteins

The structure of proteins can be disrupted easily by heat, change in pH and under strongly oxidizing or reducing conditions. Under such conditions the proteins undergo denaturation. The most familiar example of denaturation is the change that takes place in albumin, the principal component of egg white, when it is cooked. In this particular case the change is irreversible.

14.6.7 Importance of Proteins

1. Proteins take an essential part in the formation of protoplasm which is the essence of all forms of life.
2. Nucleoproteins which are complexes of proteins with nucleic acids serve as carriers of heredity from one generation to the other.
3. Enzymes which are biological catalysts are protein in nature. Without them life is not possible.
4. Many proteins have specialized functions. Haemoglobin acts as a carrier of O_2. Some proteins act as hormones which have regulatory functions, for example; insulin, thyroxine etc.

Industrially proteins have great importance. We are familiar with the use of leather made by tanning of hides. This is essentially a precipitation of the proteins with tannic acid. Gelatin is obtained by heating bones, skin and tendons in water. It is used in bakery goods. Caesein is another protein used in the manufacture of buttons and buckles.

14.6.8 Lipids

Lipids (Greek, lipos means fat) are naturally occurring organic compounds of animals and plants origin which are soluble in organic solvents and belong to a very heterogeneous group of substances.

Lipids have the following characteristics:

1. They are insoluble in water and soluble in non-polar solvents e.g. ether, chloroform and benzene, etc.
2. Their primary building blocks are fatty acids, glycerol and sterols.
3. They are utilized by the living organisms.

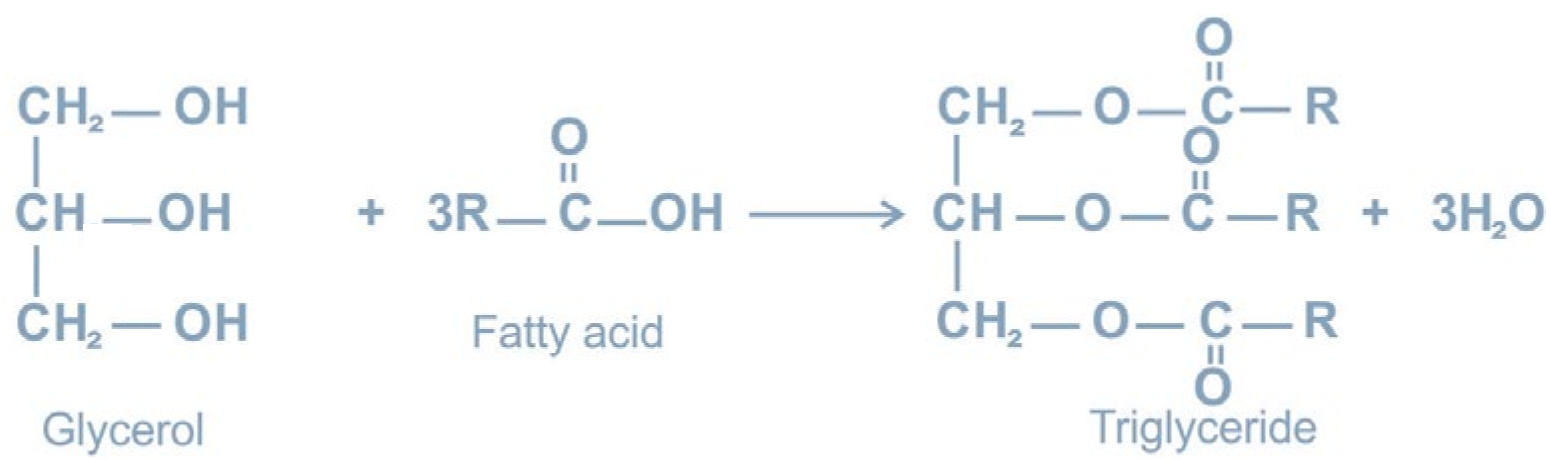
Fats and oils are the most important lipids found in nature. They are one of the three major "food factors" needed for human body, the other two being proteins and carbohydrates. Fats and oils are widely distributed in various type of foods and are of great nutritional value. Not only the edible fats and oils occupy a place of pride in human diet but they also find use as raw materials for the manufacture of soaps and detergents, paints, varnishes, polishes, cosmetics, printing inks and pharmaceuticals.

14.6.9 Sources of Fats and Oils

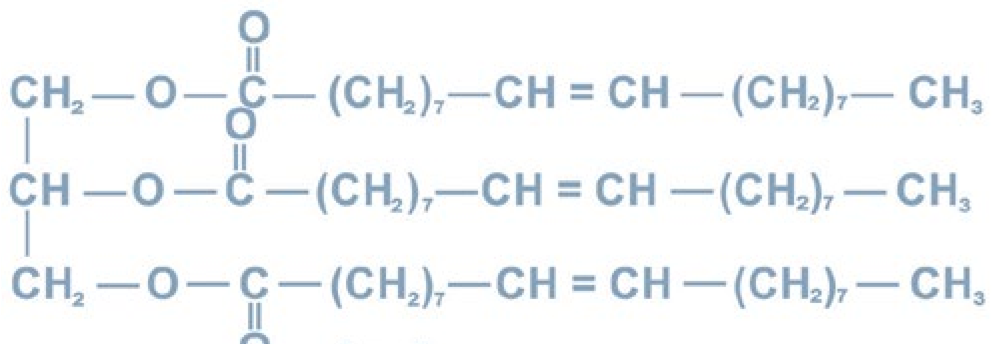
Fats and oils come from a variety of natural sources like animals, plants and marine organisms. Animal fats are located particularly in adipose tissue cells. Butter and ghee are a special type of animal fats which are made form milk. Vegetable oils are chiefly present in seeds and nuts of plants. Marine oils are obtained form sea animals like salmons and whales etc.

14.6.10 Structure and Composition of Fats and Oils

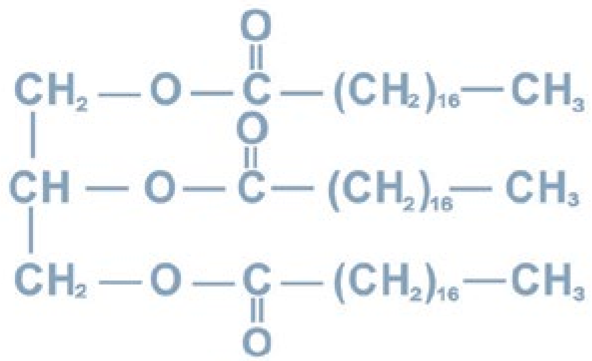
Animal and vegetable fats and oils have similar chemical structures. They are triesters formed from glycerol and long chain acids called fatty acids.



A triester of glycerol is called a triglyceride or glyceride.The degree of unsaturation of the constituent fatty acid determines whether a triglyceride will be a solid or a liquid. The glycerides in which long- chain saturated acid components predominate tend to be solid or semi-solid and are termed as fats.On the other hand, oils are glycerol esters which contain higher proportion of unsaturated fatty acid components.



An oil



A fat

The melting points of mixed glycerides would depend on the extent of unsaturated fatty acid components in the molecule. The poly unsaturated glycerides therefore have very low meting points and are liquids (oils). Chemically common oils and fats are the mixture of saturated and unsaturated triglycerides, present in various ratios.

14.6.11 Classification

Lipids are classified as:

1. Simple Lipids

These are esters of fatty acids with glycerol. For example, common fats and oils.

2. Compound Lipids

These contain radicals in addition to fatty acids and alcohol and include glycerol phospholipids, sphingolipids, lipoproteins and lipopolysaccharides.

3. Derived or Associated Lipids

They are the hydrolytic products of the above mentioned compounds. Sterols, vitamin D and terpenes belong to this class of lipids.

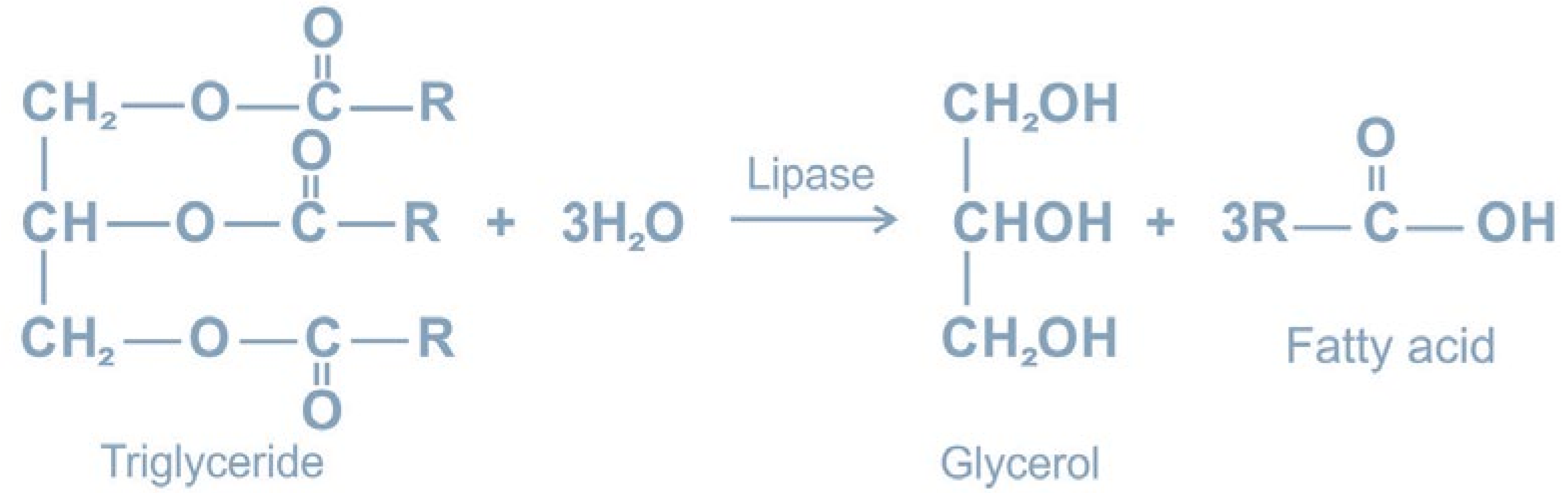
14.6.12 Physical Properties

1. Oils and fats may either be liquid or non-crystalline solids at room temperature.
2. When pure they are colourless, odourless and tasteless.
3. They are insoluble in water and readily soluble in organic solvents like diethyl ether, acetone, carbon tetrachloride and carbon disulphide.
4. They readily form emulsions when agitated with H_20 in the presence of soap or other emulsifiers.
5. They are poor conductor of heat and electricity and therefore serve as excellent insulator for the animal body.

14.6.13 Chemical Properties

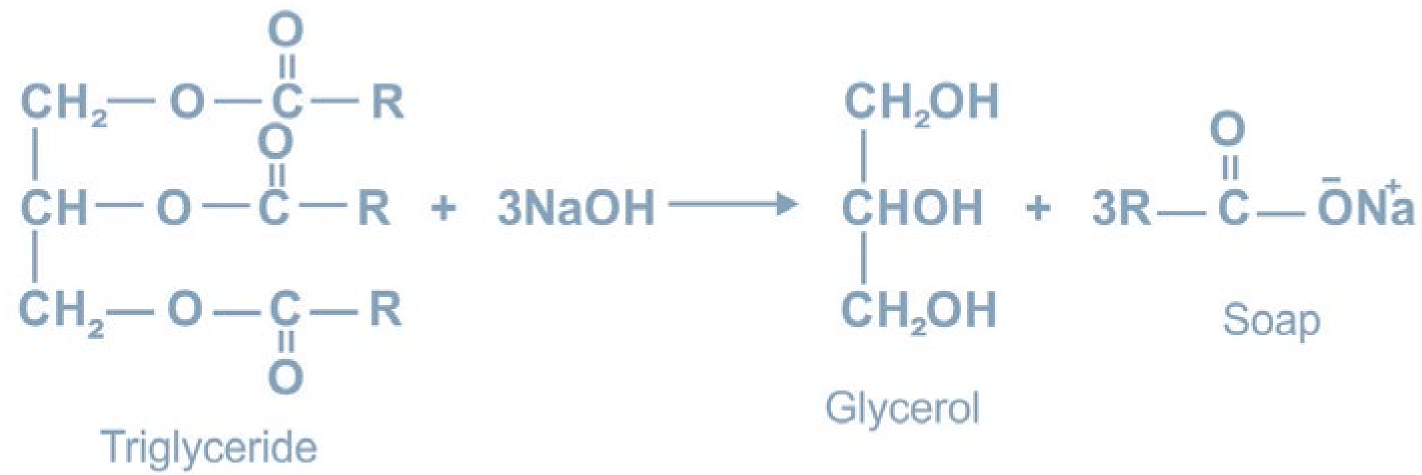
1. Hydrolysis

Triglycerides are easily hydrolyzed by enzymes called lipases to fatty acids and glycerol.



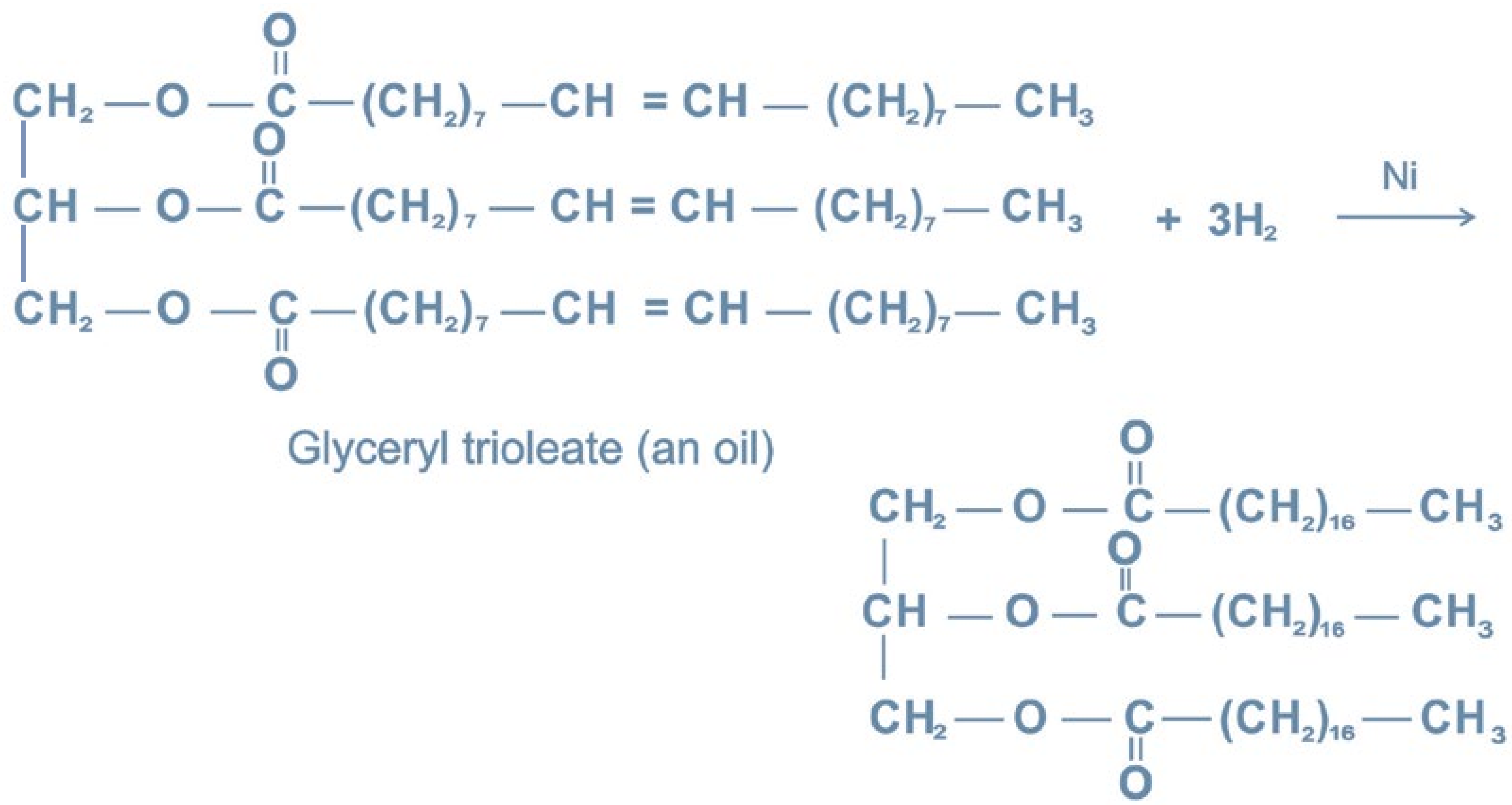
2. Saponification

It is the hydrolysis of a fat or an oil with an alkali to form soap (salt of fatty acid) and glycerol.



3. Hardening of Oils

Unsaturated glycerides react with hydrogen in the presence of a metal catalyst to give saturated glycerides. The result is the conversion of a liquid glyceride (an oil) into a semi-solid glyceride (a fat).



Glyceryl trioleate (an oil)

Glyceryl tristearate (a fat)

This reaction is used commercially to harden vegetable oils for the production of vegetable ghee or margarine. Hardened oils are also extensively used for making soaps and candles.

14.6.14 Saponification Number

It is defined as the number of milligrams of potassium hydroxide or sodium hydroxide required to saponify one gram of the fat or oil. For example, one mole of glycerol tripalmitate (mol. wt = 807) requires 168,000 mg of KOH for saponification. Therefore, one gram of fat will require 168000/807 mg of KOH. Hence the saponification number of glycerol tripalmitate is 208.

14.6.15 Rancidity of Fats or Oils

Fats or oils are liable to spoilage and give off an odour known as rancidity. It is mainly caused by the hydrolytic or oxidative reactions which release foul smelling aldelydes and fatty acids. Oils from sea animals which contain a relatively high proportion of unsaturated acid chains deteriorate rapidly.

14.6.16 Iodine Number

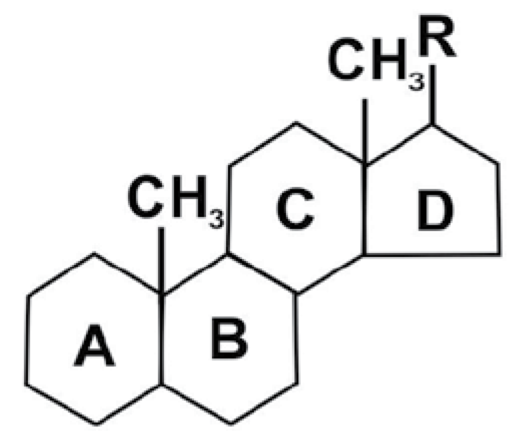
The extent of unsaturation in a fat or an oil is expressed in terms of its iodine number. It is defined as the number of grams of iodine which will add to 100 grams of a fat or an oil The value of iodine number depends on the number of double bonds present in the acid component of the glycerides. The glycerides with no double bonds have zero iodine number.

14.6.17 Acid Number

The acid number of a fat or an oil tells the amount of free fatty acids present in it. It is expressed as the number of milligrams of potassium hydroxide required to neutralize one gram of fat.

14.6.18 Steroids

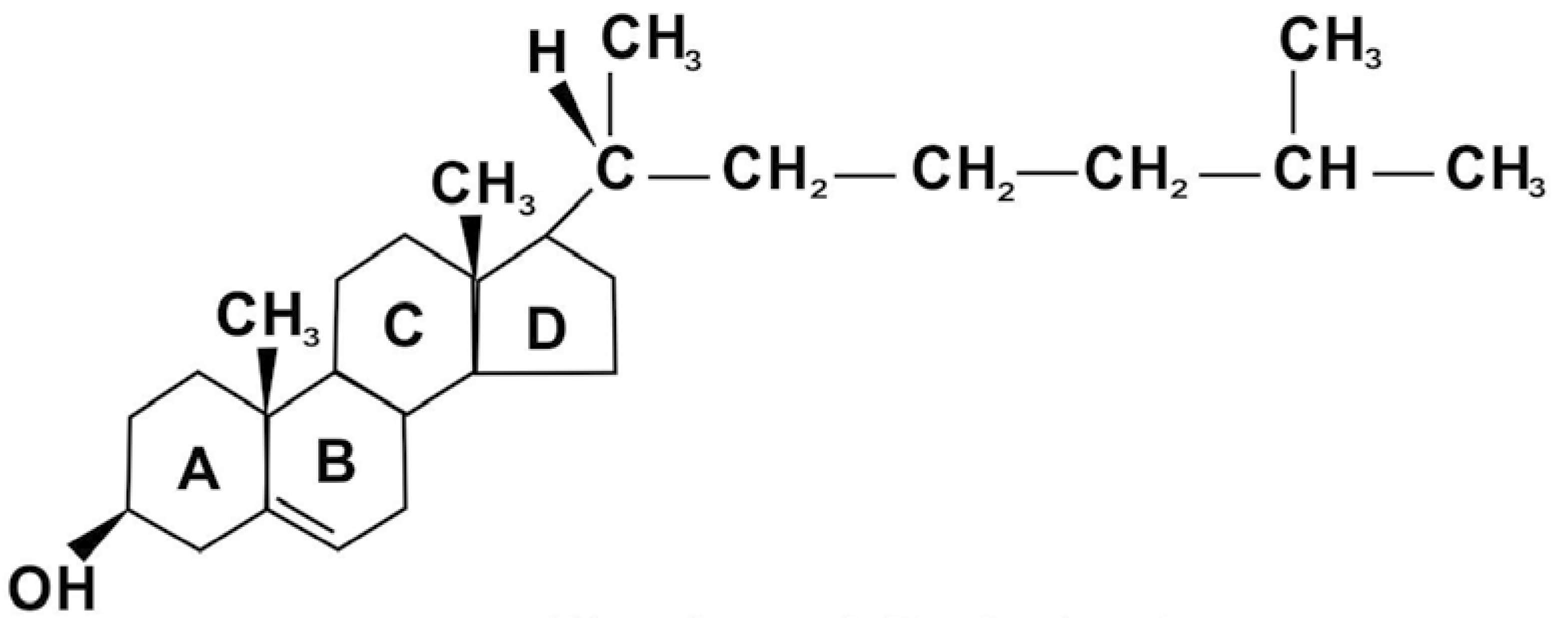
Steroids are naturally occurring lipids. Their parent nucleus has perhydrocyclopentanophenanthrene component which consists of three six- membered rings (A, B and C) and one five-membered ring (D). These rings are joined or fused to each other and have a total of 17-C atoms Very small variations in the bonding of atoms in the ring and in the groups attached to them give rise to compounds that are remarkably diverse in their biological functions. Some of the natural occurring compounds belonging to steroids are cholesterol, ergosterol, male and female sex hormones and the hormones of the adrenal cortex.



Structure of Steroid Nucleus

1. Cholesterol

It is the most abundant animal sterol and occurs in all animal tissues but only in a few higher plants. Cholesterol is present both in the free as well as esterified form in the blood, animal tissues, egg, yolk, various oils and fats and nerve tissues. Its increased quantities in blood makes plaque like deposits in the arteries causing blood pressure and other heart diseases.



Structure of Cholesterol

2. Ergosterol

It is the sterol of fungi and yeasts. When irradiated with ultraviolet rays, it is converted into ergocalciferol or vitamin D_2.

3. Phospholipids

Phospholipids are molecules of enormous biological importance. In the compounds, two of the hydroxyl groups are esterified with fatty acids and third forms a link with phosphoric acid or a derivative of phosphoric acid.

14.6.19 Importance of lipids

1. They are good source of energy and make the food more palatable.
2. They exert an insulating effect on the nervous tissues.
3. They are good energy reservoirs in the body.
4. Lipids are an integral part of cell protoplasm and cell membranes.
5. Some lipids act as precursors of very important physiological compounds. For example, cholesterol is the precursor of steroid hormones.

14.6.20 Enzymes

Enzymes can be defined as the reaction catalysts of biological systems produced by living cells and are capable of catalyzing chemical reactions. Typically enzymes are macromolecules with molecular masses ranging into millions. Two remarkable properties of enzymes are their extraordinary specificity – each enzyme catalyzes only one reaction or one group of closely related reactions – and their amazing efficiency – they may speed up reactions by factors of upto 10^{20}. Each enzyme molecule possesses a region known as the active site and the substrate binds itself with this active site.

Enzymes are either pure proteins or contain proteins as essential components and in addition require non-protein components which are also essential for their activity.

The protein component of the enzyme is called apoenzyme and the non-protein component is called the co-factor or co-enzyme.The co-factors include inorganic ions and complex organic or metallo-organic molecules. Important inorganic co-factors alongwith their respective enzymes include Fe^{2+}(chrome oxidase) Zn^{2+}(carbonic anhydrase) and Mg^{2+}(-glucose 6- phosphatase), etc. Many enzymes contain vitamins as their co-factors, for example; nicotinamide adenine dinucleotide contains nicotinamide vitamin and thiamine pyrophosphatase contains vitamin B_1.

While naming the enzymes, suffix-"ase" is added to the name of the substrate on which the enzyme acts, for example, urease, sucrase, cellulase are the enzymes, which act upon the substrates urea, sucrose and cellulose respectively.

14.6.21 Classification of Enzyme

The commission on enzyme, appointed by the International Union of Bio-Chemistry (IUB) classified enzymes into six main types.

1. Oxidoreductases

These enzymes catalyze oxidation-reduction reactions. Common examples are oxidase, dehydrogenase and peroxydase.

2. Transferases

These enzymes bring about an exchange of functional group such as phosphate or acyl between two compounds,For example; phospho-transferases, etc.

3. Hydrolases

These enzymes catalyze hydrolysis.They include proteases called protolytic enzymes.

4. Lyases

These enzymes catalyze the addition of ammonia, water or carbon dioxide to double bonds or removal of these to form double bonds, for example phospho-glyceromutases.

5. Isomerases

These enzymes catalyze the transfer of groups within molecules to yield isomeric forms of the substrate . An example is the conversion of fumaric acid to maleic acid in' the presence of fumarase enzyme.

6. Ligases

These enzymes link two molecules together through the breaking of high energy bonds, for example; acetyl S COH, a carboxylase and succinic thiokinase.

14.6.22 Properties of Enzymes

1. Specificity

Enzymes are specific in their action which means that an enzyme will act on only one substrate or a group of closely related substrates. For example, hexokinase catalyses the conversion of hexoses like glucose, fructose and mannose to their 6-phosphate derivatives but glucokinase is specific for glucose only.

2. Protein Nature

Enzymes with few exceptions are protein in nature. They are produced by living cells but act in vivo as well as in vitro.

3. The Direction of Enzym e Reactions

Most enzymatic reactions are reversible i.e. the same enzyme can catalyze reactions in both directions.

4. Isoenzymes

These are the enzymes from the same organisms which catalyze the same reaction but are chemically and physically distinct from each other.

14.6.23 Factors Affecting Enzyme Activity

1. Enzyme Concentration

The rate of an enzymatic reaction is directly proportional to the concentration of the substrate. The rate of reaction is also directly proportional to the square root of the concentration of enzyme. It means that the rate of reaction also increases with the increasing concentration of enzyme

2. Temperature

The enzymatic reaction occurs best at or around 37°C which is the average normalbody temperature. The rate of chemical reactions is increased by a rise in temperature but this is true only over a limited range of temperature. The enzymes usually destroy at high temperature. The activity of enzymes is reduced at low temperature. The temperature at which an enzyme reaction occurs the fastest, is called its optimum temperature.

3. Effect of pH

Just like temperature, there is also an optimum pH at which an enzyme will catalyze the reaction at the maximum rate. For example, the optimum pH of salivary amylase is 6.4 to 6.9.

4. Other Substances

The enzyme action is also increased or decreased in the presence of some other substances such as co-enzymes, activators and inhibitors. For example, some enzymes consist of simple proteins only such as insulin. Most of the enzymes are, however, the combination of a co-enzyme and an apo-enzyme. Activators are the inorganic substances which increase the enzyme activity. For example; Mg^{2+} and Zn^{2+} ions are the activators of phosphatase and carbonic anhydrase enzymes respectively. Inhibitors are the substances which reduce the enzyme activity.

5. Radiation

Generally enzymes are readily inactivated by exposure to ultraviolet light, beta rays, gamma rays and X-rays.

14.6.24 Importance of Enzymes

Enzymes are of great biological importance and are of great help in the diagnosis of certain diseases. Some examples are, alkaline phosphatase is raised in rickets and obstructive jaundice, lactic dehydrogenase or LDH-1 is raised in heart diseases. Many enzymes have proved very useful as drugs. For example; thrombin is used locally to stop bleeding. Many enzymes are used for cancer treatment, for example, L-asparaginase has proved very useful in the treatment of blood cancer in children.

14.6.25 Nucleic Acids

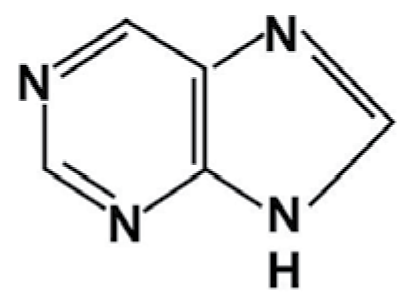
Nucleic acids were first demonstrated in the nuclei of pus cells in 1868 and in sperm heads in 1872 by Friedrik Miescher. They are present in every living cell as well as in viruses and have been found to be the essential components of the genes. They contain in their structure the blue-prints for the normal growth and development of each and every living organism.

The nucleic acids are responsible for the two fundamental functions which are common to all living organisms, these are (a) their ability to reproduce, store and transmit genetic information and (b) to undergo mutation.

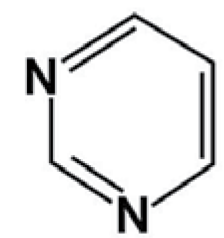
Two types of nucleic acids have been discovered, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). In the body nucleic acids occur as part of the conjugated proteins called nucleoproteins. The nucleic acids direct the synthesis of proteins. Cancer research involves an extensive study of nucleic acids.

14.6.26 Components of Nucleic Acids

Both DNA and RNA are formed by joining together a large number of nucleotide units or mononucleotides units, each of which is a nitrogenous base sugar phosphoric acid complex.



Purine



Pyrimidine

Nitrogenous bases are either purine or pyrimidine derivatives. Purines include adenine and guanine whereas pyrimidines include, cytosine, uracil and thymine. A nucleoside is a combination of nitrogenous base (purine or a pyramidine) with a sugar (ribo or deoxyribose). Depending upon the presence of ribo or a deoxyribo, nucleoside can either be a ribonucleoside or deoxyribonucleoside. Dexoyribonucleic acid (DNA) carries the genetic information and ribonucleic acid (RNA) is involved in putting this information to work in the cell. They differ in three ways.

1. The sugar in RNA is ribose while the sugar in DNA is 2-deoxyribose.
2. Four different bases are found in DNA cytosine (C), thymine (T), adenine (A) and guanine (G). In RNA, .thy mine does not occur and its place is taken by uracil (U).
3. DNA is nearly always double stranded, while RNA is usually single stranded.

The key to the ability of DNA to preserve genetic information and to pass it on from generation to generation is its double-stranded structure, first deducted by James Watson and Francis Crick in 1953. This was the discovery that initiated the field of molecular biology. Watson and Crick noticed that the double stranded structure provides a mechanism whereby the genetic information can be duplicated. This process is called replication. The synthesis of a polypeptide (protein) involves a series of events which occur in accordance with the information contained in the DNA.

KEY POINTS

1. Macromolecules are large molecules built up from small units called monomers.
2. The organic macromolecules are biological and non- biological in nature.
3. Biological macromolecules are called life molecules and non-biological are man made synthetic polymers.
4. The polymer chains may be linear, branched or cross-linked.
5. A thermoplastic polymer is the one which can be softened and hardened by heating and cooling respectively.
6. A thermosetting polymer is one which becomes permanently hard on heating.
7. The polymerization process involves addition and condensation reactions.
8. The formation of polyethene is an example of addition polymerization.
9. Nylon, a polyamide and terylene, a polyester, are examples of condens- -ation polymers.
10. Carbohydrates, proteins, fats, and nuclei acids are naturalmacromolecules.
11. Carbohydrates are the most abundant biomolecules on earth.They are classified into monosaccharides, oligosaccharides and polysaccharides.
12. Proteins are the essential components of all living organisms. They are the polymers of amino acids.
13. Lipids are naturally occuring organic compounds of animal and plant origin and they are soluble in organic solvents. Fats and oils are the most important lipids found in nature.
14. Enzymes are proteins that catalyze chemical reactions in living organisms. They are very specific in their action.

EXERCISE

Q. 1 Fill in the blanks

1. Macromolecules are built up from small units called______
2. Nylon is a polyamide and terylene is a _________
3. Nylon is prepared by the reaction of _________ and hexamethylenediamine.
4. Based on their thermal properties, plastics are divided into _________ main classes.
5. Polyvinyl chloride is a ________ plastic.
6. Glucose is stored as________ in the liver.
7. Glucose and fructose are water_________ carbohydrates.
8. Protein after digestion changes to _______
9. Purine and pyrimidine are_________ of nucleic acids.
10. Addit ion of a plasticizer _________ the flexibility of the polymer.

Q. 2 Indicate True or False.

1. Nylon 6,6 and terylene are condensation polymers.
2. The disposal of plastics does not cause any pollution problem.
3. Fructose is a polysaccharide carbohydrate.
4. Human beings get no food nutrient from cellulose.
5. The most abundant and the most important steroid in the human body is vitamin D.
6. Enzymes are the compounds containing C, H and O only.
7. The degree of unsaturation of fats is measured by their iodine number.
8. Activity of an enzyme varies with temperature and pH.
9. Nucleic acids are biological catalysts.
10. The nucleic acids are responsible for protein synthesis in the human body.

Q. 3. Multiple choice questions. Encircle the correct answer.

(i) In which of these processes are small organic molecules made into macromolecules
(a) the cracking of petroleum fractions
(b) the fractional distillation of crude oil
(c) the polymerization of ethene
(d) the hydrolysis of proteins

(ii) Which of these polymers is an addition polymer?
(a) nylon-6,6 (b) polystyrene (c) terylene (d) epoxy resin

(iii) Which of these polymers is a synthetic polymer?
(a) animal fat (b) starch (c) cellulose (d) polyester

(iv) Plastics are a pollution problem because many plastics
(a) are made from petroleum
(b) are very inflammable
(c) burn to produce toxic fumes
(d) decompose to produce toxic products

(v) The fibre which is made from acrylonitrile as monomer:
(a) PVC (b) rayon fibre (c) acrylic fibre (d) polyester fibre

(vi) A polymeric substance that is formed in the liquid state and then hardened to a rigid solid is called a

(a) fibre (b) plastic (c) varnish (d) polyamide resin

(vii) Vegetable oils are
(a) unsaturated fatty acids (b)glycerides of unsaturated fatty acids
(c) glycerides of saturated fatty acids (d)essential oils obtained from plants

(viii) Which one of the following elements is not present in all proteins?
(a) carbon (b) hydrogen (c) nitrogen (d) sulphur

(ix) Which one o f the following nitrogeneous bases is not present in RNA
(a) cytosine (b) adenine (c) thiamine (d) uracil

(x) Which one of the following enzymes brings about the hydrolysis of fats?
(a) urease (b)maltase (c) zymase (d) lipase

(xi) The reaction between fat and NaOH is called
(a) esterification (b) hydrogenolysis
(c) fermentation (d) saponification

(xii) Which one of the following statements about glucose and sucrose is incorrect?
(a) both are soluble in water (b) both are naturally occurring
(c) both are carbohydrates (d) both are disaccharides

Q. 4 Explain the following terms:
(a) Addition polymer (b) Condensation polymer
(c) Thermoplastic (d) Thermosetting plastic

Q. 5 Write notes on
(a) Polyester resins (b) Polyamide resins (c) Epoxy resins

Q. 6 What is the repeating unit in each of the following polymers?
(a) polystyrene (b) nylon 6,6 (c) teflon (d) orlon

Q. 7 What are carbohydrates and how are they classified?

Q. 8 Point out one difference between the compounds in each of the following pairs.
(a) Glucose and fructose
(b) Sucrose and maltose
(c) Cellulose and starch

Q. 9 What are lipids? In what way fats and oils are different?
Q. 10 Define saponification number and iodine number. Discuss the term rancidity.
Q. 11 What is the difference between a glycoside linkage and a peptide linkage?
Q.12 What is the chemical nature of enzymes? Discuss the classification of enzymes.
Q. 13 What are nucleic acids? Write down the role of DNA and RNA in life.

CHAPTER

15

COMMON CHEMICAL INDUSTRIES IN PAKISTAN

In This Chapter You Will Learn:

A brief description of the processes alongwith flow sheet diagrams and the reactions involved in the important industries like fertilizers, cement and paper.

15.1 INTRODUCTION

Pakistan had an almost negligible industrial base at the time of its creation in l947. For the past 55 years the country has undergone a structural change from a purely agrarian economy to a semi-chemical industrial state. Pakistan has developed most of the consumer goods industries. Heavy industries like iron, fertilizer, cement and paper are also on the road to development.

The natural resources are being exhausted with growing population and increase in the standard of living all over the world. To meet this situation the scientists and technologists are busy in the development of the substitute materials from cheaper and reusable sources, e.g. the natural fibres like cotton, silk, wool cannot meet the clothing requirements of the world, therefore, scientists have developed the artificial fibres.

Similarly, crop yield has been increased by the development of the fertilizers, pesticides and herbicides to meet the world food requirements. All these materials require their chemical preparation on industrial scales. In fact the magnitude of chemical industry of a country is a measure of its economic development and progress. Different chemical industries such as fertilizer, cement and paper are developing very fast in Pakistan.

15.2 FERTILIZERS

15.2.1 Early History

Agriculture has been one of the oldest industry known to man. The use of manure as a fertilizer dates back to the beginning of agriculture. Since 5000 B.C, the Chinese have been using animal manure in their fields. A manure is an organic material used to fertilize land and it usually consists of faeces and urine of domestic livestock.

The first prerequisite to the use of fertilizers was an understanding of the function of plant nutrients in plant growth. Compounds of these elements namely nitrogen, phosphorus and potassium are considered to be the most important nutrients essential for plant growth.The elements, like sulphur, magnesium and calcium are considered of secondary importantance

15.2.2 What are Fertilizers

Fertilizers are the substances added to the soil to make up the deficiency of essential elements like nitrogen, phosphorus and potassium (NPK) required for the proper growth of plants. Fertilizers enhance the natural fertility of the soil or replenish the chemical elements taken up from soil by the previous crops.

15.3 ELEMENTS ESSENTIAL FOR PLANT GROWTH

Plants need nutrients from the soil for a healthy growth.The elements essential for the plant growth can be classified as micro-nutrients and macro-nutrients.

15.3.1 Micro-nutrients (Trace elements)

The nutrients which are required in a very small amount for the growth of plant, are called micro-nutrients. These include Boron, Copper, Iron, Manganese, Zinc, Molybdenum and Chlorine.

Only minute amounts of these elements are needed for healthy plant growth and it may be dangerous to add too much quantity because they are poisonous in larger quantities. These are generally required in quantities ranging from 6 grams to 200 grams per acre.

15.3.2 Macro-nutrients

The nutrients which are required in a large amount for the growth of plants, are called macro-nutrients. These include Nitrogen, Phosphorus, Potassium, Calcium, Magnesium, Sulphur, Carbon, Hydrogen and Oxygen.These are generally required in quantities ranging from 5 kg to 200 kg per acre.

15.3.3 Requirement of a Fertilizer

Every compound of the desired elements cannot be a fertilizer. The desired elements should be present in the compound in a water soluble form (so that the plant can take it up) readily available to the plants.The compound employed as fertilizer should be stable in soil as well as in storage e.g., it should not be deliquescent or set to hard stony materials with time. Above all it should be cheap to manufacture.

15.3.4 Essential Qualities of a Good Fertilizer

The essential requisites of a good fertilizer are:

1. The nutrient elements present in it must be readily available to the plant.
2. It must be fairly soluble in water so that it thoroughly mixes with the soil.
3. It should not be injurious to plant.
4. It should be cheap.
5. It must be stable so that it is available for a longer time to the growing plant.
6. It should not alter the pH of the soil.
7. By rain or water, it should be converted into a form, which the plant can assimilate easily.

15.4 CLASSIFICATION OF FERTILIZERS

Fertilizers are classified according to the nature of the elements like nitrogen, phosphorus and potassium which they provide to the soil. This classification gives the following types of fertilizers.

i) Nitrogeneous fertilizers ii) Phosphatic fertilizers
iii) Potassium fertilizers

15.4.1 Nitrogeneous Fertilizers

These fertilizers supply nitrogen to the plants or soil. Nitrogen is required during the early stage of plant growth for the development of stems and leaves. It is the main constituent of protein, imparts green colour to the leaves and enhance the yield and quality of the plants. Some of the examples of nitrogen fertilizers are: - ammonium sulphate, calcium ammonium nitrate, basic calcium nitrate, calcium cyanamide, ammonia, ammonium nitrate, ammonium phosphate, ammonium chloride and urea.

(i) Ammonia (NH_3) as a Fertilizer

Ammonia is used in liquid state while all the other fertilizers are used in the solid form. All the nitrogen fertilizers except calcium nitrate, sodium nitrate and potassium nitrate make the soil acidic but this acidity can easily be controlled through liming of the soil (by the addition of lime) at regular intervals.

liquid ammonia has become an important fertilizer for direct application to soil. It contains 82% nitrogen and it is injected about 6 inches under the surface of soil to avoid it from seeping out.

(ii) Urea (NH_2- CO - NH_2)

Urea is a high quality nitrogeneous fertilizer.It contains about 46% nitrogen and is the most concentrated solid nitrogen fertilizer.It is the most widely used nitrogen fertilizer in Pakistan.

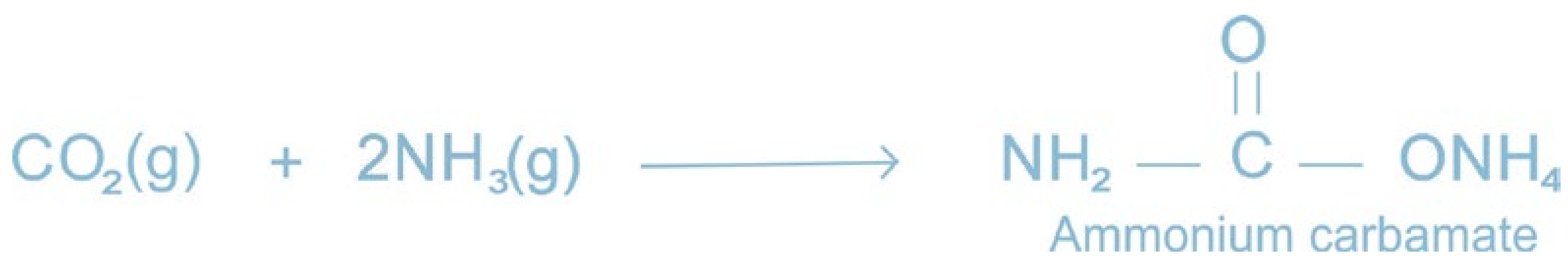
Manufacturing Process

Urea is produced by the reaction of liquid ammonia with gaseous carbon dioxide. Following steps are involved in the manufacture of urea.

i) Preparation of Hydrogen and Carbon dioxide
ii) Preparation of Ammonia
iii) Preparation of Ammonium Carbamate
iv) Preparation of Urea
v) Concentration of Urea.
vi) Prilling

Preparation of Ammonium Carbamate

Gaseous CO_2 is mixed with ammonia in the volume ratio of 1:2 in a reactor to produce ammonium carbamate.



Preparation of Urea

Dehydration of ammonium carbamate gives urea.

Concentration of Urea Solution

The urea solution is concentrated in an evaporation section where water is evaporated by heating with steam under vacuum in two evaporation stages whereby 99.7% urea melt is obtained. It is then pumped to prilling tower.

Prilling

The molten urea is sprayed at the prilling tower by means of prilling bucket where it is cooled by the air rising upward. Molten droplets solidify into the form of prills. Urea prills thus produced are either sent to the bagging section or to the bulk storage, Fig. 15.1.

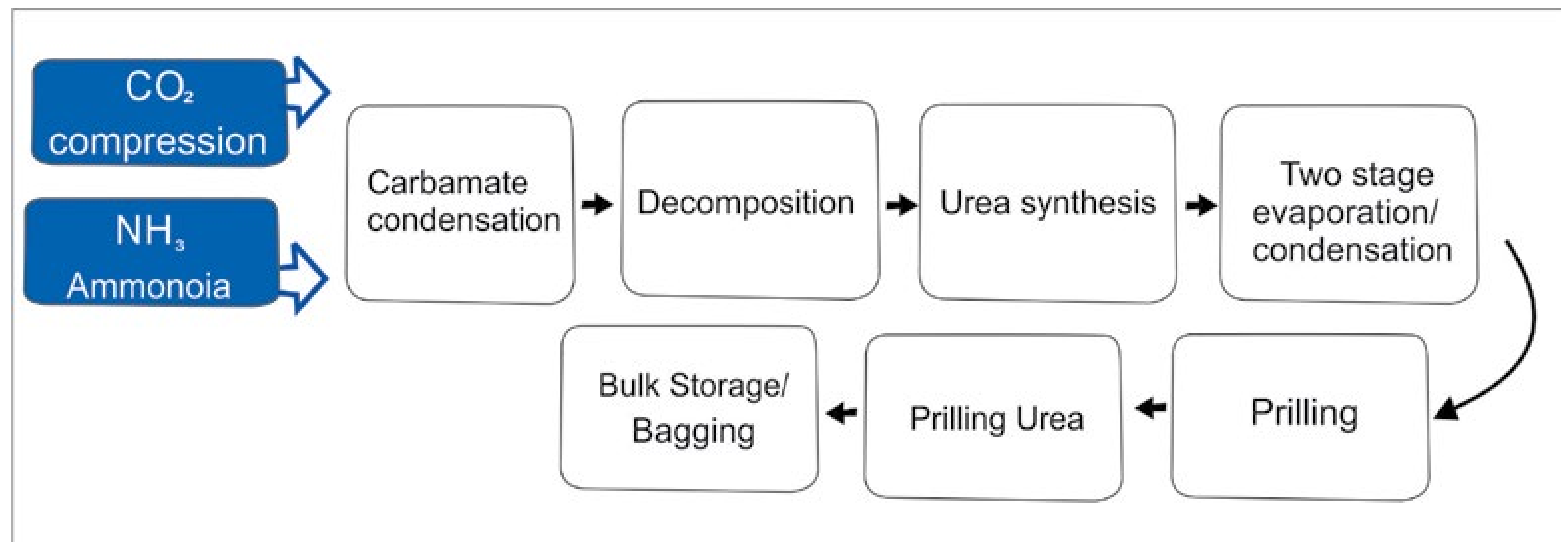


Fig. 15.1 Flow sheet diagram for manufacture of urea

(iii) Ammonium Nitrate (NH_4NO_3)

It is manufactured by the neutralization reaction between ammonia and nitiic acid as given below.

$$NH_3(g) + HNO_3(g) \rightarrow NH_4NO_3(s)$$

After neutralization, the water is evaporated. The solid ammonium nitrate is melted and then sprayed down from a tall tower. The falling droplets are dried by an upward current of air. The fertilizer solidifies as tiny, hard pellets called prills. Prills of fertilizers are free of dust, easy to handle and easy to spread on the field.Ammonium nitrate contains 33 33.5% nitrogen.

It is a useful fertilizer for many crops except paddy rice because the microbial bacteria in flooded fields decomposes it to nitrogen gas. It is also used in combination with limestone. It is hygroscopic in nature.

15.4.2 Phosphatic Fertilizers

These fertilizers provide phosphorus to the plants or soil. Phosphorus is required to stimulate early growth to accelerate the seed and fruit formation during the later stages of growth. It also increases resistance to diseases. The various phosphatic fertilizers have different compositions, due to which they have different solubilities. The two most important water soluble fertilizers are super phosphate (calcium super phosphate) $Ca(H_2PO_4)_2$and triple phosphate (diammonium- phosphate $(NH_4)_2HPO_4$).

(i) Diammonium Phosphate $(NH_4)_2HPO_4$

This compound of fairly high purity is prepared by continuous process that consists of reacting anhydrous ammonia gas and pure phosphoric acid at 60 - 70 °C and pH 5.8 - 6.0.

$$2NH_3(g) + H_3PO_4(l) \rightarrow (NH_4)_2HPO_4 + heat$$

It is an exothermic reaction. The heat of reaction vaporizes water from the liquor and the crystals of diammonium phosphate are taken out, centrifuged, washed and dried. It contains 16% nitrogen and 48% P_2O_5. This product contains about 75% plant nutrients and is deemed suitable for use either alone or in mixed with other fertilizers.

15.4.3 Potassium Fertilizers

These fertilizers provide potassium to the plant or soil. Potassium is required for the formation of starch, sugar and the fibrous material of the plant. They increase resistance to diseases and make the plants strong by helping in healthy root development. They also help in ripening of seeds, fruits and cereals. Potassium fertilizers are especially useful for tobacco, coffee, potato and corn.

(i) Potassium Nitrate (KNO_3)

On industrial scale it is prepared by the double decomposition reaction between sodium nitrate and potassium chloride.

$$NaNO_3(aq) + KCl(aq) \rightarrow NaCl(aq) + KNO_3(aq)$$

A concentrated hot solution of sodium nitrate is prepared and solid potassium chloride is added into it. On heating, the potassium chloride crystals change into sodium chloride crystals, and the hot potassium nitrate is run through the sodium chloride crystals at the bottom of the kettle. A little water is added to prevent further deposition of sodium chloride as the solution is cooled, which results into a good yield of pale yellow solid potassium nitrate.It contains 13% nitrogen and 44% potash.

15.4.4 Fertilizer Industry in Pakistan

Pakistan is essentially an agricultural country. In order to keep up the production of agricultural commodities and to compensate for the depletion of nutrients which get exhausted by repeated cultivation, the urea fertilizer has gained importance.

For a developing country like Pakistan, there is an ever-growing demand for urea fertilizer. Government of Pakistan is trying its utmost to narrow the gap between supply and demand of fertilizers. Consistant efforts have been made to instal fertilizer manufacturing plants. At present, there are about 14 fertilizer plants in private as well as public sectors in the country which are manufacturing different types of fertilizers.

The total production of urea fertilizer in 2002 in Pakistan is about 56,30,100 metric tons/annum

15.5 CEMENT

15.5.1 Early History

Cement is a very important building material which was first introduced by an English Mason Joseph Aspdin. He found it when strongly heated mixture of limestone and clay was mixed with water and allowed to stand, it hardened to a stone like mass which resembled Portland rock; a famous building stone of England. Since then the name of **Portland Cement** is given to the mixture of lime (obtained from limestone), silica, iron oxide and alumina.

This was the start of Portland cement industry, as we know today. The cement is now low in cost, as it is applied everywhere in the construction of houses, public buildings, roads, industrial plants, dams, bridges and many other structures.

15.5.2 Definition

Cement is the material obtained by burning an intimate mixture of calcarious and argillaceous materials at sufficiently high temperature to produce clinkers. These clinkers are then ground to a fine powder.

The essential constituents are lime (obtained from limestone) silica and alumina (present in clay).

15.5.3 Raw Materials

The important raw materials used for the manufacture of cement are:

1. Calcarious material (limestone, marble, chalks, marine shell) as source of CaO.
2. Argillaceous material (clay, shale, slate, blast furnace slag) They provide acidic components such as aluminates and silicates,
3. Other raw material being used is gypsum.

An average composition of a good sample of Portland cement is as follows:

Compound	%age
Lime (CaO)	62
Silica (SiO_2)	22
Alumina (Al_2O_3)	7.5
Magnesia (MgO)	2.5
Iron oxide (Fe_2O_3)	2.5
Sulphur trioxide (SO_3)	1.5
Sodium oxide (Na_2O)	1.0
Potassium oxide (K_2O)	1.0

15.5.4 .Manufacturing Process of Cement

The manufacturing process of cement involves either a dry process or a wet process. The choice of dry or wet process depends on the following factors.

1. Physical condition of the raw materials.
2. Local climatic conditions of the factory.
3. The price of the fuel.

In Pakistan most of the factories use wet process for the production of cement. Dry process needs excessive fine grinding and it is more suited for the hard material, Wet process, on the other hand, is free from dust, grinding is easier and the composition of the cement can easily be controlled.

15.5.5 Wet Process

In this process grinding is done in the presence of water. There are five stages in the manufacture of Portland cement Fig. 15.2.

1. Crushing and grinding of the raw material.
2. Mixing the material in correct proportion.
3. Heating the prepared mixture in a rotary kiln.
4. Grinding the heated product known as clinker.
5. Mixing and grinding of cement clinker with gypsum.

1. Crushing and Grinding

Soft raw materials are first crushed into a suitable size, often in two stages, and then ground in the presence of water, usually in rotating cylindrical ball or tube mills containing a charge of steel balls.

2. Mixing of Raw Material

The powdered limestone is then mixed with the clay paste in proper proportion (limestone 75%, clay 25%); the mixture is finely ground and made homogeneous by means of compressed air mixing arrangement. The resulting material is known as slurry. The slurry, which contains 35 to 45% water, is sometimes filtered to reduce the water content from 20 to 30% and the filler cakes are stored in storage bins. This reduces the fuel consumption for heating stage.

3. Heating the Slurry in a Rotary Kiln

Raw meal or slurry prepared as above is introduced into the rotary kiln with the help of a conveyer. The rotary kiln consists of a large cylinder 8 to 15 feet in diameter and 300-500 feet in length. It is made of steel and is lined inside with firebricks. The kiln rotates horizontally on its axis at the rate of 1-2 revolution per minute and it is inclined a few degree. As the kiln rotates,the charge slowly moves downward due to the rotary motion.

Now the charge is heated by burning coal, oil or natural gas. In the rotary kiln the charge passes through the different zones of temperature where different reactions take place. The charge takes 2-3 hours to complete the journey in the kiln.

(a) Drying or Pre-heating Zone (Minimum temperature zone)

In this zone the temperature is kept at 500°C, whereby the moisture is removed and the clay is broken into Al_2O_3, SiO_2, and Fe_2O_3.

(b) Decomposition Zone (Moderate temperature zone)

Here the temperature goes upto 900°C In this zone the limestone ($CaCO_3$) decomposes into lime (CaO) and CO_2.

$$CaCO_3(s) \xrightarrow[900°C]{} CaO(s) + CO_2(g)$$

(c) Burning Zone (Maximum tem perature zone)

In this zone, the temperature goes up to 1500°C and the oxides, e.g. CaO, SiO_2, Al_2O_3 and Fe_2O_3combine together and form calcium silicate, calcium aluminate and calcium ferrite.

(d) Cooling Zone

This is the last stage in the kiln where the charge is cooled up to 150-200°C

(iv) Clinker Formation

The resulting product obtained from the kiln is known as cement clinker. This has the appearance of greenish black or grey coloured balls varying in size from small nuts to peas.

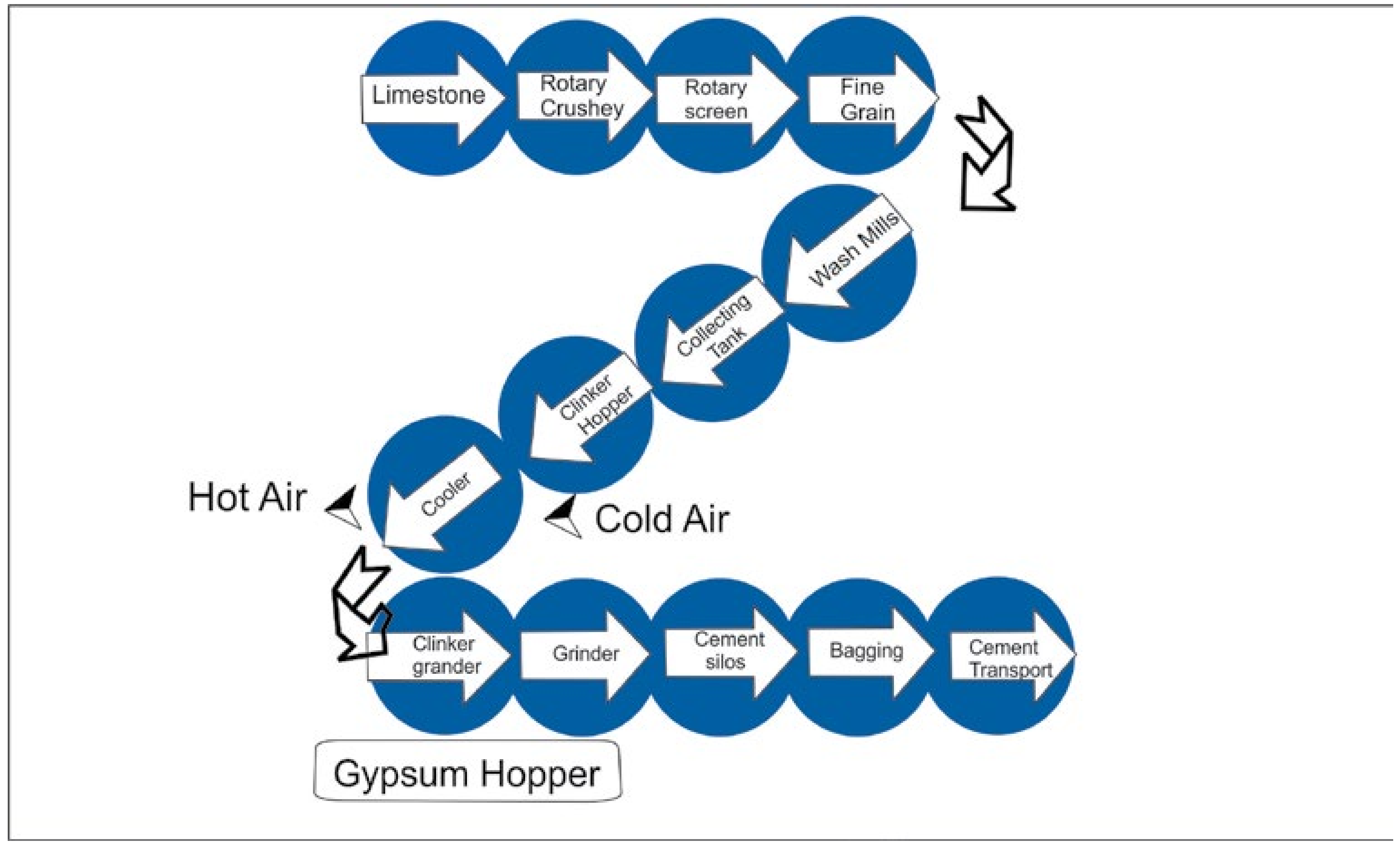


Fig. 15.2 Flow sheet diagram for the manufacture of cement

(v) Grinding the Clinkers with Gypsum

The cement clinkers are then air-cooled. The required amount of gypsum (2.0%) is first ground to a fine powder and then mixed with clinkers. At this stage finished cement is pumped pneumatically to storage silos from where it is drawn for packing in paper bags or for dispatch in bulk containers.

15.5.6 Setting of Cement

The use of cement in the construction of building is based on its property of setting to a hard mass when its paste with water is allowed to stand for sometime. The reactions involved in the setting of cement are described as follows:

(i) Reactions Taking Place in First 24 Hours.

A short time after the cement is mixed with water, tri-calcium aluminate absorbs water (hydration) and forms a colloidal gel of the composition, 3 Ca. Al_2O_3. $6H_2O$, (hydrated tricalcium aluminate).

This gel starts crystallizing slowly, reacts with gypsum ($CaSO_4$. 2 H_2O) to form the crystals of calcium sulpho-aluminate ($3CaO.Al_2O_3.3CaSO_4.2H_2O$).

(ii) Reactions Taking Place Between 1 to 7 Days

Tricalcium silicate (3CaO. SiO_2) and tri-calcium aluminate (3CaO . Al_2O_3) get hydrolyzed to produce calcium hydroxide and aluminium hydroxide. The calcium hydroxide, thus formed, starts changing into needle-shaped crystals, which get studded in the colloidal gel and impart strength to it. Aluminium hydroxide, on the other hand, fills the interstices resulting in hardening the mass. The gel formed starts losing water partly by evaporation and sets to a hard mass.

15.5.7 Cement industry in Pakistan

At the time of partition in 1947, there were four cement plants in West Pakistan, which produced about 330,000 tons of cement every year. However, in 1954 the production of cement went up to 660,000 tons. In 1956 two more cement factories were set up at Daud Khel and Hyderabad, but even then the production of cement was not enough to meet the increasing demand of the construction industry in the country.

For a developing country like Pakistan there is always an increasing need of cement for development projects. Efforts were thus made to build more factories. At present there are about 22 cement factories in private as well as in public sectors, which are manufacturing cement both by dry and wet processes. The total production of these 22 cement plants is 9,578,802 metric tons/annum.

15.6 PAPER INDUSTRY

15.6.1 Early History

The word paper is derived from the name of a reedy plant Papyrus, which grew abundantly along the marshy delta of the River Nile in Egypt around 3000B.C.

The invention of modern paper is credited to Ts'ai Lun of China, who, in 105 A.D, was an official attached to the Imperial Court of China. He prepared a sheet of paper using the bark of mulberry tree that was treated with lime and mixed with bamboo and other fibres to get the paper of desired properties.

15.6.2 Definition

Paper is defined in term of its method of production, that is a sheet material made up of a network of natural cellulosic fibres which have been deposited from an aqueous suspension.The product obtained is a network of interwinning fibres.

15.6.3 Brief Description of the Process.

Raw Material.
The main raw materials used in the production of pulp and paper in Pakistan is of two types, that is non-woody and woody raw materials.

Nonwoody Raw Materials		Woody Raw Materials
(i) Wheat straw	(vi)Cotton stalk	(i)Poplar (hard wood)
(ii) Rice straw	(vii)Cotton linter	(ii)Eucalyptus (hard wood)
(iii)Bagasse	(viii)Kahi grass	(iii) Douglas fir (soft wood)
(iv)Bamboo	(ix)Grasses	
(v)Rag		

15.6.4 Pulping Processes

The following are three principal methods of chemical pulping and are used for the production of paper pulps.

1. Kraft process (Alkaline)
2. Sulphite process (Acidic)
3. Neutral sulphite semi-chemical process (NSSC)

The neutral sulphite semi chemical process has come to occupy the dominant position because of the advantages in chemical recovery and pulp strength. In this section, we will discuss only the neutral sulphite semi chemical process, which is mostly used in pulp and paper industry in Pakistan.

15.6.5 Neutral Sulphite Semi Chemical Process

Process Description

This process utilizes sodium sulphite cooking liquor which is buffered with sodium carbonate or NaOH to neutralize the organic acid liberated from the raw materials.

The non-woody raw materials which are used in this process are wheat straw, rice straw, bagasse, cotton linter and rags. Wheat straw may be used alone or combined with other materials in different proportions. The essential steps in the process are as follows Fig. 15.3.

i. Cutting of the raw materials
ii. Dry cleaning
iii. Wet cleaning
iv. Screening
v. Digestion
vi. Blow tank
vii. Pulp washing
viii. Bleaching
ix. Paper making machine
x. Stock preparation plant

(i) Cutting of Raw Materials

The non-woody raw materials come in the precut state and are processed as such. But in the case of wood based raw materials, big logs are cut into small chips before further processing.

(ii) Dry Cleaning

Wheat straw is collected from the storage and is then sent for dry cleaning. For this purpose air is blown into the raw material, which removes unwanted particles.

(iii) Wet Cleaning

Dry wheat straw is then subjected to wet cleaning, which not only removes the remaining dust particles, but the soluble materials also get dissolved in water.

(iv) Screening

In most pulp and paper processes some type of screening operation is required to remove the over sized troublesome and unwanted particles. Magnetic separator removes iron pieces like nails and bolts, etc. Stones and other oversized pieces are removed by centricleaners. The major types of chest screens are vibratory, gravity, and centrifugal. The material is then sent to wet silo.

(v) Digestion

From wet silo, the material is sent to digester. The digester is usually 10 meters in length and 2 meters in diameter. It is made of steel and wrought iron. This is the main unit of the process. The digestion process can be either batch or continuous. In our country batch process is mostly used.

As the raw material enters into the digester, steam is introduced at the bottom and a liquor containing sodium sulphite is injected simultaneously to cover the raw material. Sodium sulphite used is buffered with sodium carbonate or sodium hydroxide to maintain its pH 7-9. The digester is closed carefully. It is revolved at 2.5 RPM and a temperature of 160- 180°C is maintained. The digester takes 45 minutes to attain the desired temperature after which it gets switched off automatically and pressure is released.

(vi) Blow Tank

The cooked material from the digester is blown into a blow tank and then pumped to a centrifugal screen for the separation of cooked from uncooked materials.

(vii) Pulp Washing

The cooked material from the blow tank is washed thoroughly with water using 80- mesh sieve to remove the black liquor that would contaminate the pulp during subsequent processing steps. The pulp is washed with required amount of water to remove soluble lignin and coloured compounds. Lignin is an aromatic polymer and causes paper to become brittle. It is then thickened and finally stored in high-density storage tower.

(viii) Bleaching

The pulps obtained from chemical pulping are brown in colour and are unsuitable for printing and writing papers which require a bright white pulp. The colour of these pulps is mainly due to residual lignin. These pulps are then sent to bleaching unit.

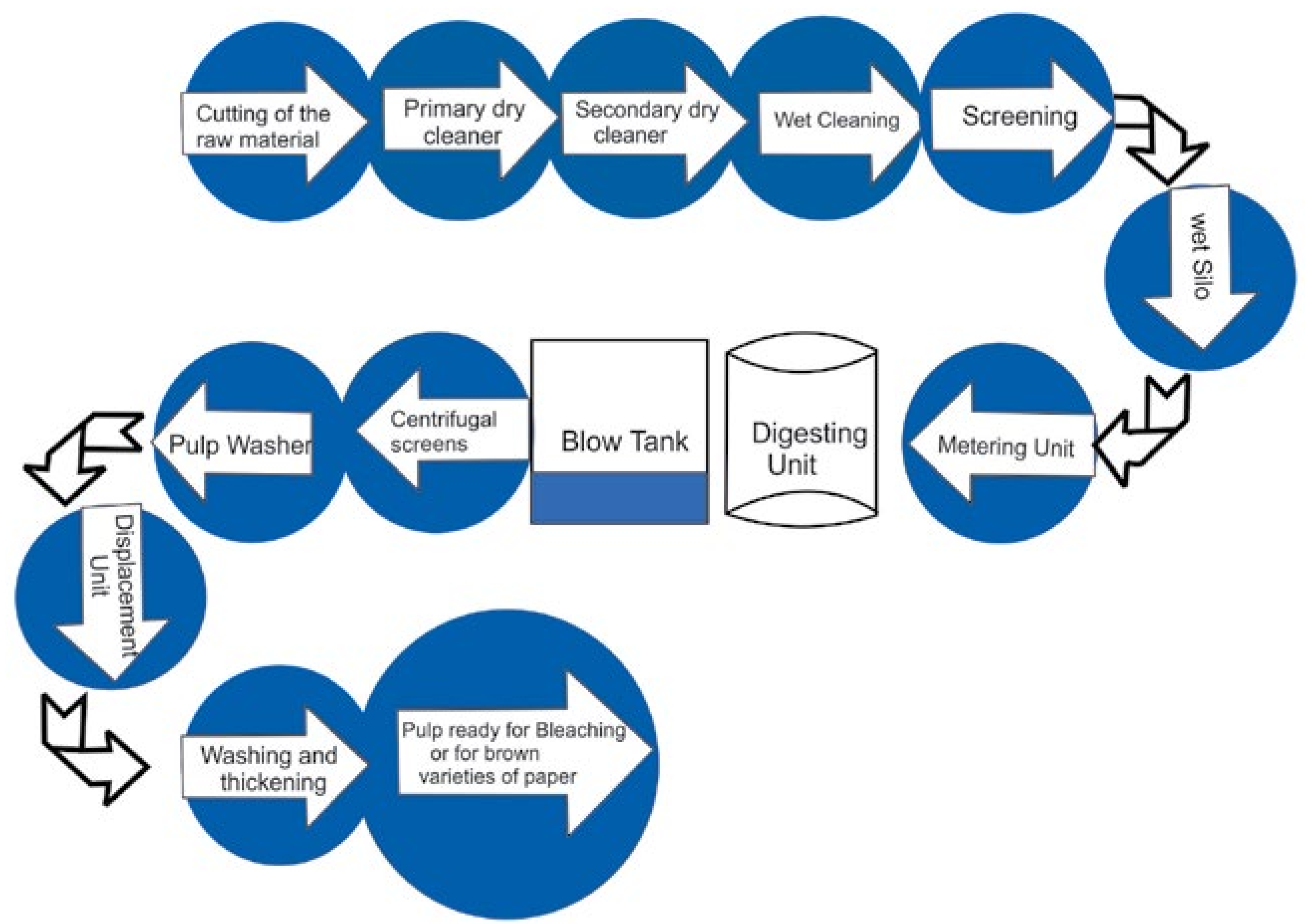


Fig. 15.3 Flow sheet diagram for neutral sulphite semi-chemical process

In Pakistan, bleaching is done with chlorine or sodium hypochlorite and hydrogen peroxide. After washing, the unbleached pulp is sent to the chlorinator where chlorine at 4 - 5 bar pressure is injected from chlorine tank. The chlorine react with unbleached pulp at about 45°C for 45-60 minutes to give the good results. The residual chlorine is neutralized with water which act as antichlor. The correct dosage is important and calculated amount of chlorine is needed to achieve the required brightness. After chlorination pulp is washed with hot water at 60°C and is then sent to the storage tank. Pulp is dried with hot air supply. After drying the pulp is ready for manufacturing of paper.

(ix) Stock Preparation Plant

There are three important stages in the treatment of the pulp prior to its delivery to the paper making machine.The first is the dispersion of the pulp as a slurry in water, the second is the mechanical refining or beating of the fibres to develop appropriate physical and mechanical properties for the product being made and the third is the addition of chemical additives end recycled fibres from the waste paper plant. Wet end chemistry of paper start from here,

(x) Paper Making Machine

A basic Fourdrinier type machine is used for paper making and a brief description of its major components is given below Fig. 15.4.

(a) Flow Spreader

The flow of spreader takes the plup and distributes it evenly across the machine from back to front. Consistency of the stock is below 1%.

(b) Head Box

The pressurized head box discharges a uniform jet of pulp suspension on a fabric where special suction devices work for the removal of water.

(c) Fourdrinier Table

The endless, moving fourdrinier fabric forms the fibre into a continuous matted web while the fourdrinier table drains the water by suction forces.

(d) Press Section

The paper sheet is conveyed through a series of roll presses where additional water is removed and the web structure is consolidated (i.e the fibres are forced into intimate contact).

(e) Dryer Section

Wet sheet of paper so formed is dried in the dryer section of the machine with the help of rotary drum. Water is separated from the fibre either by gravity, by suction or by pressing and by heating.

(f) Calendar Stock

The sheet is calendered through a series of roll nips to reduce thickness and smooth the surface.

(g) Reel

The dried paper is wound in the form of a reel having final moisture of about 6-8%.

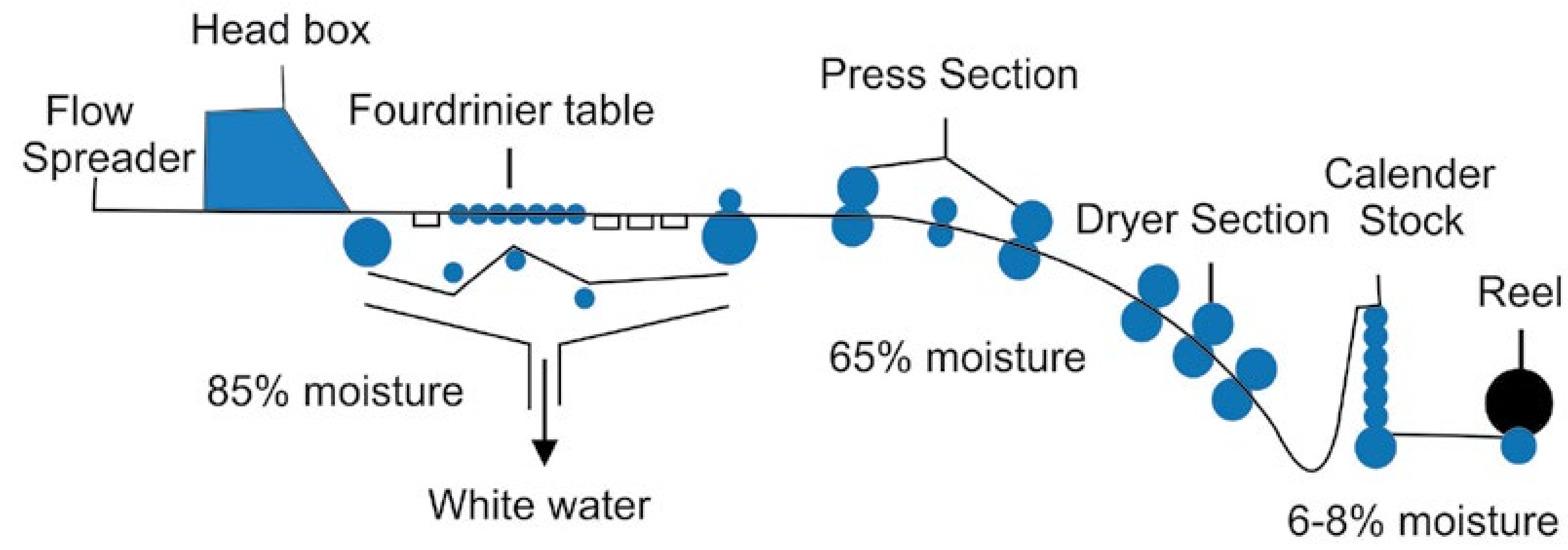


Fig. 15.4 Fourdrinier paper making machine.

15.6.6 Paper Industry in Pakistan

Paper plays such an important role in the present day economic development that its consumption is taken as an index of a country's progress and prosperity. There was no pulp and paper industry in Pakistan at the time of independence in 1947.The country consumed about 25000 tons of pulp and paper products per year and all of these were imported from abroad at a cost of 25 million rupees. The start of the paper industry in our country was very slow because of various reasons, amongst the major ones being the non-availability of suitable fibrous raw material.

Due to high prices of paper in Pakistan its per head consumption is among the lowest in the world. Paper consumption in Pakistan is around 5 kg per person per year.

To make our country self-sufficient in this important commodity, we must utilize every source of raw material like non-woody and woody. Fortunately, Pakistan has enough source of non-woody material, which in future can meet the requirements of our pulp and paper industry. The efforts are being made to install more pulp and paper industries in the country.

At present there are more than 30 pulp and paper industries in private as well as in public sectors, which are manufacturing pulp and paperboard.

KEY POINTS

1. Agriculture has been one of the oldest industry known to man. Since 5000 B.C Chinese have been using animal manure in their fields.
2. Fertilizer is the natural or artificial substance containing the chemical elements that improve growth and productiveness of plants.
3. Natural fertilizers are materials derived from plants and animals whereas artificial fertilizers consist of manufactured material like urea, super phosphate and ammonium nitrate, etc.
4. Synthetic fertilizers are mainly used for making up the immediate deficiency of essential nutrient elements needed in relatively large amount.
5. The nutrients required in a very small amount for growth of plants are called micro-nutrients and the nutrients which are required in a very large amount are called macro-nutrients.
6. Urea and ammonium nitrate are the major nitrogeneous fertilizers whereas super phosphate and triple phosphate are important phosphatic fertilizers.
7. Cement is a very important building material which was first introduced in 1824 by an English mason Joseph Aspdin.
8. Cement is the material obtained by burning an intimate mixture of calcarious and argillaceous materials at sufficiently high temperature to produce clinkers which are subsequently ground to a fine powder. Wet process is generally used in the production of cement.
9. The use of cement for construction purposes is based on its property of setting to a hard mass when mixed with water.
10. Paper is a sheet material made up of a network of natural cellulosic fibres.
11. The neutral sulphite semi-chemical process is often used for the manufacturing of paper because of the advantages in the chemical recovery and pulp strength.
12. The prime objective of all pulp making steps is to separate fibres present in the straw from cementing material called lignin, which is a natural binder.

EXERCISE

Q. 1 Fill in the blanks with suitable words.

1. Fertilizers enhance the natural__________ of the soil.
2. Micro-nutrients are required in quantity ranging from_________ per acre.
3. Ammonia contains__________ % nitrogen.
4. Manure is an__________ material used to fertilize land.
5. Cement was first introduced by an English mason__________.
6. Phosphorus is required to stimulate_______ of plant.
7. In Pakistan, bleaching of pulp is carried out with_________ .
8. Cement is generally manufactured using__________ process.
9. The use of cement in the construction of building is based on its property of__________ when its paste with water is allowed to stand for sometime.
10. Lignin is an_________ polymer and causes paper to become brittle.

Q. 2 Indicate True or False.

1. Potassium fertilizers are especially used for tobacco and corn.
2. Ammonia is used in gaseous state while all other fertilizers are used in the solid form.
3. In wet process for the manufacture of cement, grinding of raw material is done in the presence of water.
4. The total production of cement in Pakistan is 56,30,100 metric tons/annum.
5. In neutral sulphite semi-chemical process, sodium sulphite is used buffered with sodium carbonate.
6. Lignin is an inorganic binder.
7. Paper consumption in Pakistan is around 5kg per person per year.
8. Urea contains 90% nitrogen.
9. The temperature of the digester in paper industry should be around 160-180°C.
10. Potassium fertilizers increase the capability of plants to resist diseases.

Q. 3 Multiple choice questions. Encircle the correct answer.

(i) Which three elements are needed for the healthy growth of plants.
(a) N,S, P (b) N, Ca, P (c)N ,P K (d)N ,K,C

(ii) Which woody raw material is used for the manufacture of paper pulp?
(a) Cotton (b) Bagasse (c) Poplar (d) Rice straw

(iii) The nitrogen present in some fertilizers helps plants
(a) to fight against diseases (b) to produce fat
(c) to undergo photosynthesis (d) to produce protein

(iv) Phosphorus helps the growth of
(a) root (b) leave (c) stem (d) seed

(v) Micro-nutrients are required in quantity ranging from
(a) 4-40g (b) 6-200g (c) 6-200kg (d) 4-40kg

(vi) During the manufacturing process of cement the temperature of the decomposition zone goes up to
(a) 600°C (b) 800°C (c) 1000°C (d) 1200°C

(vii) The word paper is derived from the name of which reedy plant
(a) Rose (b) Sun flower (c) Papyrus (d) Water Hyacinth

(viii) Which is not a calcarious material?
(a) lime (b)clay (c) marble (d) marine shell

(ix) How many zones through which the charge passes in a rotary kiln?
(a) 4 (b) 3 (c) 2 (d) 5

(x) Ammonium nitrate fertilizer is not used for which crop.
(a) Cotton (b) Wheat (c) Sugar cane (d) Paddy rice

Q. 4 What are phosphatic fertilizers. How are they prepared? Mention the role of phosphorus in the growth of plants.

Q. 5 (a) What are fertilizers? Why are they needed?
(b) Discuss the classification of fertilizers and their uses.
(c) How is urea manufactured in Pakistan? Describe in detail the process used.

Q. 6 (a) What are the prospects of fertilizer industry in Pakistan?
(b) What are essential nutrient elements and why these are needed for plant growth?
(c) Write down the essential qualities of a good fertilizer?

Q. 7 (a) Describe the composition of a good portland cement.
(b) Discuss the wet process for the manufacturing of cement with the help of flow sheet diagram.
(c) What do you understand by the term "setting of cement". Also discuss the reactions taking place in first 24 hours?

Q. 8 What are the essential non-woody raw materials used in the production of pulp and paper in Pakistan?

Q. 9 (a) What are the principal methods of chemical pulping used for the production of paper?
(b) Describe the neutral sulphite sem i-chem ical process for the manufacturing of pulp and paper.

Q. 10 (a) What are the common bleaching agents used in paper industry in Pakistan? Briefly describe the bleaching process.
(b) What are the prospects of paper industry in Pakistan?

CHAPTER

16 ENVIRONMENTAL CHEMISTRY

Animation 16.1 : Water Pollution
Source and Credit : rohma24

IN THIS CHAPTER YOU WILL LEARN:

1. The meaning of environmental pollution.
2. The sources of air pollutants like CO, SO_2, oxides of nitrogen, etc.
3. Effects of polluted air on environment.
4. The causes of water pollution.
5. The preparation of potable water.
6. About the solid waste and its management like dumping and incineration, treatment of industrial waste and recycling of solid waste.

16.1 INTRODUCTION

Environmental chemistry deals with the chemicals and other pollutants in the environment. In this we study the sources, reactions, transportation of the chemicals and other toxic substances especially created by human activity in the environment and their adverse effects on human beings. This branch of chemistry is interrelated with all other branches of science, i.e. biology, physics, medicine, agriculture, public health and sanitary engineering, etc.

16.1.1 Components of the Environment

The environment consists of the following components:

(i) Atmosphere (ii) Hydrosphere
(iii) Lithosphere (iv) Biosphere

(i) Atmosphere

The layer of gases surrounding the earth is called atmosphere. It consists of various gases in different proportions i.e., N_2 (78%), O_2 (21%), Ar (0.9 %), CO_2 (0.03 %) and trace amounts of H_2, O_3, CH_4, CO, He, Ne, Kr and Xe. It also contains varying amounts of water vapours.

Its thickness is about 1000 km above the surface of the earth and half of its mass is concentrated in the lower 5.6 km. The gases in the atmosphere absorb most of the cosmic rays and the major portion of the harmful electromagnetic radiation coming from the sun. The absorption of these harmful radiation protects the life on the earth.

The gases present in the atmosphere are essential for sustaining life on earth i.e., O_2 is required for breathing, CO_2 is required for plant photosynthesis, N_2 is used by nitrogen fixing bacteria and water vapours are responsible for sustaining various forms of life on the earth. Atmosphere also maintains the heat balance of the earth.

(ii) Hydrosphere

The hydrosphere includes all water bodies, mainly oceans, rivers, streams, lakes, polar ice caps, glaciers and ground water reservoirs (water below earth surface). Oceans contain 97% of earth's water but because of high salt contents this water cannot be used for human consumption. The polar ice caps and glaciers consist of 2% of the earth's total water supply. Only 1% of the total earth's water resources are available as fresh water i.e., surface water; river, lake, stream and ground water. The fresh water is being used by agriculture (69%), industry (23%) and for domestic purposes (8%).

(iii) Lithosphere

It consists of rigid rocky crust of earth and extends to the depth of 100 km. The mantle and core are the heavy interior of the earth, making up most of the earth's mass. The 99.5 % mass of the lithosphere is made of 11 elements, which are oxygen (~ 46.60 %), Si (~27.72 %), Al (8.13 %), Fe (5.0 %), Ca (3.63 %), Na (2.83 %), K (2.59 %), Mg (2.09 %) and Ti, H_2 and P (total less than 1 %). The elements present in trace amounts (0.1 to 0.02 %) are C, Mn, S, Ba, Cl, Cr, F, Zr, Ni, Sr and V. These elements mostly occur in the form of minerals.

(iv) Biosphere/Ecosphere

Biosphere is the region of earth capable of supporting life. It includes lower atmosphere, the oceans, rivers, lakes, soils and solid sediments that actively interchange materials with all types of living organisms i.e., human beings, animals and plants. Ecosystem is a smaller unit of biosphere which consists of community of organisms and their interaction with environment i.e., animals, plants and microorganisms which lie in a definite zone and depend on the physical factors such as soil, water, and air. Any substance in the environment which adversely affects the human health, quality of life and the natural functioning of ecosystem, is known as **environmental pollutant**. With continuous rapid growth in population, urbanization, industrialization and transportation, environmental pollution is spreading in almost every city of the world. The quantity of pollutants affecting the environments have increased rapidly in the last half-century and they have adversely affected human health and eco-system.

16.2 TYPES OF POLLUTION

16.2.1 Air Pollution

The atmosphere is polluted when harmful substances which damage the environment, human health and quality of life are mixed in it. The main sources of air pollution are:

The waste products given out from chimneys of industrial units and exhaust of automobiles may contain gases such as sulphur dioxide, sulphur trioxide, nitrogen oxides, carbon monoxide, hydrocarbons, ammonia, compounds of fluorine and radioactive materials. These waste products are called primary pollutants.

The primary pollutants in the atmosphere through various reactions produce **secondary pollutants such as sulphuric acid, carbonic acid, hydrofluoric** acid, peroxyacetyl-nitrate (PAN), ozone, aldehydes, ketones and peroxybenzol. All these compounds are toxic and their concentration in the atmosphere must be controlled. The sources for some of the main primary air pollutants are described below:

1. Carbon Monoxide

It is a colourless, odourless and highly toxic gas. It is three times lighter than air. It is soluble in water.

Sources

(a) Natural

Natural sources of carbon monoxide emission are volcanic eruption, natural gas emission and oxidation of methane in the atmosphere.

(b) Human Activities

Fuel burning in various types ot transportation i.e., motor vehicles, railways and aircraft is the major source (75%) of carbon monoxide in the atmosphere. Other sources of carbon monoxide emission are forest fires, combustion of fossil fuel and agricultural products. Carbon monoxide is also emitted from industries in which any type of fuel is burnt in air.

These industries include iron and steel, petroleum, cement, brick kilns, paper and pulp, etc.Incomplete combustion and dissociation of CO_2 at high temperature also produces CO.

Carbon monoxide is highly poisonous gas and causes suffocation if inhaled. It binds blood haemoglobin more strongly than oxygen thus excluding oxygen from normal respiration. The CO poisoning can be reversed by giving high pressure oxygen. Exposure to high concentration of CO results in headache, fatigue, unconsciousness and eventually death (if such exposure is sustained for longer period).

2. Nitrogen Oxides (NO_x)

The gases nitric oxide, NO and nitrogen dioxid, NO_2 are represented by NO_x.

Sources:

(a) Natural

Bacterial action produces NO_x mainly NO

(b) Human Activities

Nitrogen oxides are generally produced by combustion of coal, oil, natural gas and gasoline. Both oxides result from the oxidation of nitrogeneous compounds present in fossil fuel. The burning of fuel in the presence of air in internal combustion engine also produces NO.

$$N_2 + O_2 \xrightarrow{\text{high temperature}} 2NO$$

Nitrogen dioxide is produced when nitric oxide reacts with oxygen.

$$2NO + O_2 \rightarrow 2NO_2$$

The residence time of NO and NO_2 in the atmosphere are 4 and 3 days respectively. Due to photochemical reactions, NO_x are converted to HNO_3 which is carried down in either rain fall or as dust.

3. Sulphur Oxides, SO_2

Sources:

(a) Natural

On global scale most of sulphur dioxide is produced by volcanoes (67%) and by oxidation of sulphur containing gases produced by decomposition of organic matter.

(b) Human Activities

Air is polluted with SO_2 due to combustion of coal (containing 1-9%S), crude oil and other fossil fuel in power plants and petroleum industry, etc.

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

These gases (SO_2 and SO_3) because of their pungent odour are very irritant and suffocating. Through various reactions in the atmosphere they form sulphate aerosols. These aerosols cause severe respiratory troubles particularly among older people. Sulphur dioxide is the major source of acid deposition in the atmosphere.

4. Hydrocarbons

Sources

(a) Natural:

Large quantities of hydrocarbons are emitted by different trees and plants in the atmosphere. Paddy fields produce a significant amount of methane in the atmosphere.

Another natural source of methane is the anaerobic decomposition of organic matter by bacteria in water sediments and in soils. Methane has a mean residence time of about 3 -7 years in the atmosphere.

$$2CH_2O \xrightarrow{\text{Bacteria}} CO_2 + CH_4$$

(b) Human Activities

Automobiles are the major source of hydrocarbons emission. In addition to this, petroleum, coal, wood, incinerators, refuse burning and solvent evaporator also contribute towards the emission of hydrocarbons into the atmosphere.

16.2.2 The Effects of Polluted Air on Environment

1. Acid Rain

Acid rain which now-a-days is termed as acid deposition, was discovered by Angus Smith in Great Britain in the mid seventeenth century but this phenomenon gained importance as a serious environmental problem in 1950's. Initially it was referred to the precipitation which was more acidic than natural rain.

Due to the presence of CO_2 in the atmosphere the natural rain itself forms carbonic acid:

$$CO_2(g) + H_2O(aq) \rightarrow H_2CO_3(aq)$$

Animation 16.2 : Acid rain
Source and Credit : kidsgen

The pH of unpolluted rain water should be 5.6.The rain water has pH less than 5 is considered truly acidic. In the atmosphere SO_z and NO_x are transformed by reactions with oxygen and water into H_2SO_4 and HNO_3 respectively. These acids get mixed with rain. The acid deposition includes both wet (rain, snow, fog) and dry acidic deposition.

$$SO_2 + 1/2O_2 + H_2O \xrightarrow{\text{(hydrocarbon,smoke,metal oxides)}} H_2SO_4$$

In some countries due to release of HCI by volcanic eruption there is temporary acid rain.
Acidification of the soil and rocks can leach metals like aluminium, mercury, lead and calcium and discharges them into water bodies. These heavy metals are accumulated in the fishes and are health hazards for humans and birds as they eat these fishes. The elevated concentration of aluminium is harmful for fish as it clogs the gills thus causing suffocation. Acidification of the soil can also leach nutrients thus damaging leaves and plants and growth of forest. It also damages building materials such as steel, paint, plastic, cement, masonry work and sculptural materials especially of marble and limestone.

Animation 16.3 : Acid rain 1
Source and Credit : s-cool

2. Smog

The word smog is a combination of smoke and fog. If it contains high contents of SO_2 it is chemically reducing in nature and is known as 'reducing smog'. The main cause of reducing smog is combustion of coal. Photochemical smog consists of higher concentrations of oxidants like ozone and is also termed as oxidizing smog, it is a yellowish brownish grey haze which is formed in the presence of water droplets and chemical reactions of pollutants in the air.

It has unpleasant odour because of its gaseous components. The main reactants of photochemical smog are nitric oxide NO and unburnt hydrocarbons. Nitric oxide is oxidized to nitrogen dioxide within minutes to hours depending upon the concentration of pollutant gas.

The yellow colour in photochemical smog is due to the presence of nitrogen dioxide.The following conditions are required for the formation of smog:

Animation 16.4 : Smog
Source and Credit : citylab

1. There must be sufficient NO ,hydrocarbons and volatile organic compounds (VOC) emitted by the vehicular traffic.
2. Sunlight, so that some of the chemical reactions may occur at a rapid rate.
3. The movement of air mass must be little so that reactions are not disturbed.

The overall result of photochemical smog in afternoon is the built up of oxidizing agents such as H_2O_2, HNO_3, peroxyacetyl nitrate (PAN) and ozone in the air. PAN is an eye irritant and is also toxic to plants.

3. Ozone

Ozone, O_3, is a gas having low boiling point. It is present in small concentrations throughout the atmosphere.The amount of ozone in the atmosphere is expressed in Dobson units (DU). The normal amount of overhead ozone is about 350 DU.

The ozone layer, 25 - 28 km high, in the stratosphere surrounds the globe and filters most of the harmful ultraviolet (UV) rays in the sunlight before they could reach on the earth. Therefore, if there is substantial reduction in the ozone layer the life on earth would be threatened. In 1980's a large hole in the ozone layer over Antarctic was discovered which represented a major environmental crisis.

Ozone is produced in most of the tropical regions by the photochemical reactions of oxygen, from where it is transported to polar regions. It acts as a pollutant and causes various health problems i.e., damages eyes and aggravates asthma, decreases the elasticity of lung tissues, coughing, chest discomfort, etc. It is harmful to the plants and other materials i.e., attacks rubber, reduces durability and appearance of paint and causes fabric dyes to fade.

The amount of ozone is less in the regions closer to the equator.

Animation 16.5 : Ozone concentration
Source and Credit : wikipedia

The thickness of the ozone layer has been decreasing over Antarctic during the spring time since the mid 1970's. By the mid 1980's loss in ozone at some altitudes over Antarctica resulted in about 50% depletion of the total overhead amount. The region in which ozone depletes substantially in every year during Sep-Nov is now termed as "ozone hole".

The concentration of ozone in the stratosphere is being depleted through various chemical reactions not only above Antarctica but worldwide. The stratosphere where the ozone layer exists in the atmosphere is approximately at 15 to 40 kilometer altitudes and is just above the troposphere which extends to an altitude of 0-15 kilometer from the earth. The temperature in troposphere decreases with the increasing altitude from 15 to - 56°C, it is because the air near the earth is heated by radiation reemitted from the earth.

Whereas the temperature in stratosphere increases with increase of altitude i.e., -56 to-2 °C. The ozone is the main chemical species present in stratosphere which absorbs the ultraviolet radiation and increases the temperature in the upper part of the ozone layer.

Role of Chlorofluorocarbons (CFCs) in Destroying Ozone

Chlorofluorocarbons used as refrigerants in air conditioning and in aerosol sprays are inert in the troposphere but slowly diffuse into stratosphere, where they are subjected to ultraviolet radiation generating Cl^0 free radicals. Chlorofluorocarbons (CFCs) play an effective role in removing O_3 in the stratosphere due to following reactions.

$$CFCl_3 \rightarrow CFCl_2 + Cl$$

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

A single chloride free radical can destroy upto 100,000 ozone molecules.

16.2.3 Water Pollution

Water is essential for life on earth. All living organisms contain water in them. To sustain life every human being drinks several litres of water daily. Marine life is also impossible without water.

Surface and ground water which are vital resources of fresh water are vulnerable to contamination. The human activities such as livestock waste, landfills, agriculture, pesticides, oil leaks and spills, disposal of industrial effluents on open land, water bodies, septic tanks, detergents, mining, petroleum and natural gas production may result in the contamination of the surface and ground waters.

Animation 16.6 : Water Pollution1
Source and Credit : masters

1. Livestock Waste

Mostly the livestock waste is either being dumped on the open land or is discharged into sewage, canals or rivers. This practice pollutes the surface and ground water posing serious health problems to the population. Chemical and bacterial contents in livestock waste can contaminate surface and ground water causing such infectious diseases as dysentery, typhoid and hepatitis.

2. Oil Spillage

Petroleum or crude oil is a complex mixture of many compounds mainly hydrocarbons. The petroleum products are used as fuel, lubricant, for manufacturing petrochemicals, plastics, electrical appliances, synthetic rubber and detergents, etc.

Sea water gets polluted by accidental oil spills and leakage from cargo oil tankers in sea, tanker trucks, pipelines leakage during off shore exploration and leakage of underground storage tanks. Many petroleum products are poisonous and pose serious health problems to humans, animals and aquatic life. Hydrocarbons particularly polycyclic aromatics are known to be carcinogenic even at very low concentrations. The marine organisms are severely affected by soluble aromatic fractions of oil (C-10 or less). The spilled oil damages the marine life often causing death. The light transmission through surface of water is affected by oily layer on it thus photosynthesis of the plants and dissolved oxygen in water is decreased.

3. Detergents

Detergents are excessively used in industries and household as cleaning agents. The amount of disposed detergents in waste water is increasing day-by-day. This waste water when discharged in rivers or sea, greatly affects the aquatic life. Detergent contents of waste water mobilize the bound toxic ions of heavy metals such as Pb, Cd and Hg from sediments into water.

4. Pesticides

Pests harm crops and transmit diseases both to human beings and animals. Pesticides are the substances that can directly kill an unwanted organism or otherwise control by interfering with its reproduction process.

The current ability to produce large amounts of food on relatively small amount of land has been made possible around the world by the use of pesticides. At present more than ten thousand different types of synthetic organic pesticides have been formulated. They are broadly classified into several principal types according to their general chemical nature.

The most important and widely used pesticides are insecticides (which kill insects), herbicides (which kill undesired plants) and fungicides (which control the growth of fungus on the plant).

The use of various pesticides also helped in the eradication of diseases such as malaria, yellow fever, bubonic plague and sleeping sickness.

Wide spread use of pesticides for getting greater crop yields if not properly checked and controlled has associated risks of contaminating the soil, plants and the water. The drainage water from the agricultural land (where the pesticides are being used) mostly contains pesticides.

Therefore if the use of any type of pesticide is not properly controlled it enters through various roots i.e., agricultural food products and drinking water into the food chain and thus pose serious health problems to both human beings and animals.

Organic chemicals in drinking water do not have any healthy effects on human or animal health. At best, some organic chemicals may have no detrimental effects at low concentrations. But many compounds once thought safe, especially the synthetic organic chemicals, can have serious and substantial heath risks, even at very low concentrations. At even higher concentrations, most of the compounds are tasteless and odourless. It is now known that many of the light molecular weight chlorinated hydrocarbons in drinking water are carcinogens and they have no safe levels. That is they cannot be consumed through air, food, or water without the risk of adverse health effects.

When synthetic organic chemicals are ingested through food or drinking water, they can cause health problems. At high concentrations they can cause nausea, dizziness, tremors, and blindness. At lower concentrations, at which these compounds become tasteless and odourless, humans may develop skin eruptions or central nervous system impairment. At still lower concentrations when ingested over months or years, the compounds can cause health problems. With human or animal carcinogens, there is often a long period of time between exposure and manifestation of the disease.

5. Industrial Waste Effluents

The finished products in any chemical related manufacturing industries i.e., leather tanneries, fertilizers, oil refining, petrochemical, textiles, paper pulp and paper board, rubber products, agrochemicals, leather goods, etc. are always accompanied by some byproducts and waste effluents. The waste products may be in the form of waste heat, smoke, solid or waste water effluents.

The industrial waste pollutants may contain organic chemicals including highly toxic synthetic organic compounds and heavy metals i.e., Pb, Cd, Cr, Hg, As, Sb etc. oils and greases, mineral acids, etc.

The toxic organic compounds and heavy metals and metalloids results in contamination of both surface and ground water used for irrigation and potable water supply. This also causes irreversible degradation of the environment causing serious health problems for public and marine life.

It must be mentioned here that heavy metals such as Pb, Cd, Cr, As, Hg, etc. are highly toxic and do not have any safe limits; they have accumulation effects when ingested through food or water and cause various health problems like anemia, kidney diseases, nervous disorder, high blood pressure, etc.

6. Leather Tanneries

Many leather tanning units, varying from the cottage scale to big industrial units, are working in and around many big cities of Pakistan. They use large quantities of chromium (VI) salts for leather tanning. They are producing good variety of exportable leather, but only some units have the facility of waste water treatment by reducing Cr (VI) into trivalent state followed by alkaline precipitation of $Cr(OH)_3$.

The effluents are discharged onto the open land or put into the sewage system. These industries are the big source of chromium (VI) pollution in the environment. Chromium (VI) is highly toxic and is known to cause cancer.

16.3 FACTORS AFFECTING THE QUALITY OF WATER

The terms dissolved oxygen, biochemical oxygen demand and chemical oxygen demand are frequently used in measuring the quality of water. These terms are described as follows:

1. Dissolved Oxygen (DO)

In water the most important oxidizing agent is dissolved molecular oxygen (O_2) the concentration of which ranges from 4 - 8 ppm. The organic matter is oxidized with the help of this dissolved oxygen in water.It is a parameter to determine the quality of water. The dissolved oxygen value less than 4 ppm indicates that water is polluted.

2. Biochemical Oxygen Demand (BOD)

It is the capacity of organic matter in natural water to consume oxygen within a period of five days. The value of BOD is the amount of oxygen consumed as a result of biological oxidation of dissolved organic matter in the sample.

The oxidation reaction is catalyzed by microorganisms which are already present in the natural water. It is measuredexperimentally by calculating the concentration of oxygen at the beginning and at the end of five days period, in which a sealed water sample is maintained in the dark at constant temperature either at 20°C or 25°C.

3. Chemical Oxygen Demand (COD)

The organic content of water which consumes oxygen during chemical oxidation is evaluated by its chemical oxygen demand. The oxygen demand of water can be determined directly by treating it with dichromate ions $Cr_2O_7^{2-}$ which is a powerful oxidizing agent.

The organic matter in water is oxidized, while the remaining dichromate is determined titremetrically:

Value of COD is a direct measure of chemically oxidizable matter in water. Higher values of COD will indicate more pollution.

16.3.1 Purification of Water

The surface or ground water is normally used for drinking and other domestic purposes. The quality of untreated surface or ground water varies largely from place to place. Ground water is usually more clean than the surface water.

Depending upon its quality it may or may not need further treatment to make it fit for human consumption. The surface water, however, is invariably contaminated and requires treatment to make it potable i.e., safe for human consumption.

The raw water is treated to remove all the foreign materials and make it useable for drinking and other domestic purposes. The treatment is carried out in various stages i.e., aeration to settle suspended matters, coagulation of small particles and suspended matters, precipitation and removal of solid matters and finally treating the water with chlorine to kill viruses and bacteria.

1. Aeration

The quality of raw water is improved by aeration. In this process air is passed through water to remove the dissolved gases such as foul smelling H_2S, organosulphur compounds and volatile organic compounds. Some of the organic materials in the raw water which could be easily oxidized with air produce CO_2 in the aeration process. The remaining portions of organic material if necessary are removed by passing water over activated carbon. Aeration process also oxidizes water soluble Fe^{2+} to Fe^{3+} which then forms insoluble $Fe(OH)_3$ and can be removed as solid. Aeration also improves the oxygen level of raw water.

2. Coagulation

The materials which are suspended or present in the colloidal form in raw water are removed by coagulation. The coagulant such as aluminium sulphate or alum is added to the raw water, which causes the precipitation of suspended impurities. For example, aluminium hydroxide is precipitated when alum is added to water in alkaline medium i.e.,

$$K_2SO_4.Al_2(SO_4)_3.24H_2O + 3Ca(OH)_2 \rightarrow 3CaSO_4 + 2Al(OH)_3 + K_2SO_4 + 24H_2O$$

Many suspended particles get adsorbed on the surface of gelatinous aluminium hydroxide precipitate. Ferric salts are also commonly used as coagulants but they are difficult to handle because an insoluble ferric oxide is produced in the pH range from 3.0 to 13.0.

The process of coagulation can remove more than 80% of the suspended solids in the raw water. The surface or ground water may also contain calcium and magnesium salts which make the water hard. The hard water is then appropriately treated to remove Ca^{2+} and Mg^{2+}.

3. Water Disinfection by Chlorine

Chlorine is frequently used to disinfect water. Chlorine treatment is very effective in killing the pathogens that may cause serious water-borne diseases such as typhoid and cholera which have killed many thousands of people around the world. The most commonly used disinfecting agent is hypochlorous acid HOCl. This neutral covalent compound kills microorganisms readily by passing through their cell membranes. The hypochlorous acid is not stable thus it cannot be stored, it is therefore generated by either dissolving molecular chlorine gas or sodium and calcium hypochlorites in water.Disinfection by chlorine is inexpensive.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$

Generating HOCl from sodium or calcium hypochlorites avoides the transportation and use of chlorine cylinders.

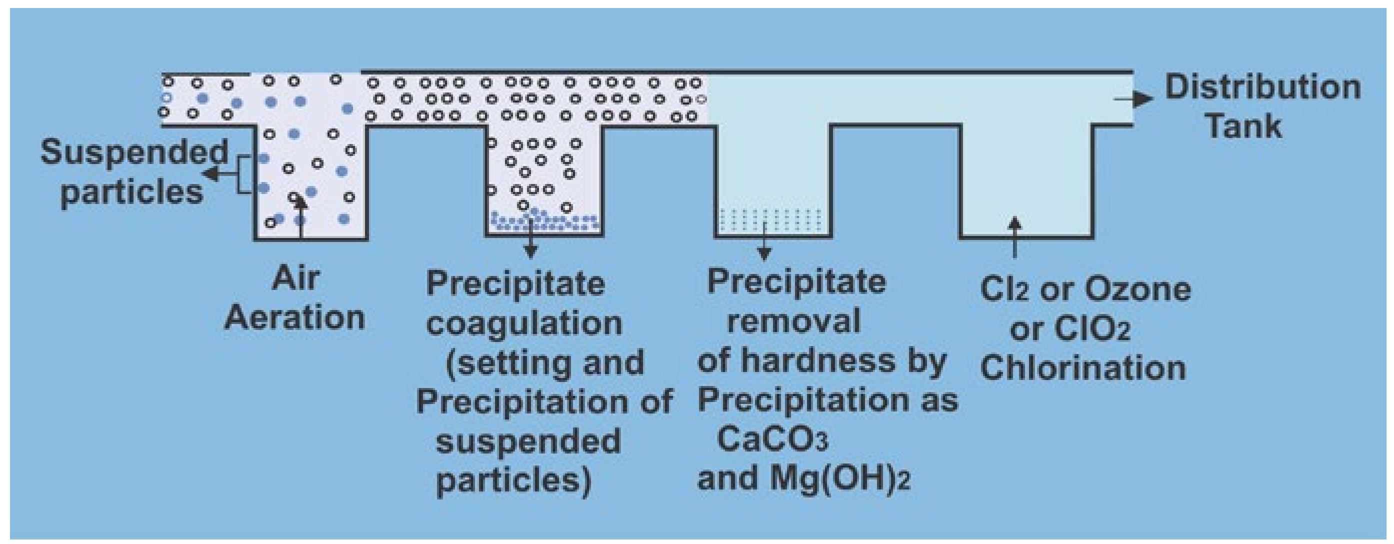


Fig. 16.1 Purification of Water

Harmful effects of chlorination of water are due to its reactions with dissolved ammonia and organic matters present in water. The hypochlorous acid reacts with dissolved ammonia to form chloramines NH_2Cl, $NHCl_2$ and especially nitrogen trichloride NCl_3 which is a powerful eye irritant.

$$NH_3 + 3HOCl \rightarrow NCl_3 + 3H_2O$$

The alkaline pH can prevent the formation of chloramines.
Chlorination of water containing organic materials also forms some organic compounds which are toxic. For example, if phenol is present in water then chlorinated phenols are formed which have offensive odour and taste and are toxic.

Chloroform $CHCl_3$ is formed when hypochlorous acid reacts with organic matter (humic acid) dissolved in water. Chloroform is suspected liver carcinogen and also has negative reproduction and development effects in humans. The risk of bladder and rectal cancer increases by drinking chlorinated water. To avoide the formation of toxic compounds with chlorine, ozone or chlorine dioxide is used for the disinfection of water.

16.4 SOLID WASTE MANAGEMENT

The disposal of domestic refuse, commercial and industrial solid wastes or semisolid materials are studied under the title solid waste management. The domestic municipal solid waste mostly consists of papers, vegetables, plastics, wood, glass, rubber, leather, textile, metals and food wastes.

16.4.1 Effects of Dumping Waste in Sea and Rivers

Water covers more than 70% of the earth and is valuable source for food and minerals. Sea and rivers have long been used for dumping waste of industrial and municipal discharges such as acids, refinery wastes, pesticides waste, construction and demolition debris, explosives, domestic refuse, garbage and radioactive waste, etc. The dumping of waste materials in water has damaged the marine environment and caused health hazards to human beings.

16.4.2 Landfill

The municipal solid waste is mainly disposed off by dumping it in a landfill. The landfill is a large hole in the ground or even a bare piece of land. When the landfill becomes full with waste it is covered by soil or clay. The site of land is selected on a number of factors such as topography, location of the ground, water table, nature of the solid waste, type of soil and rock and location of disposal zone in the surface water and ground water flow system. The ground water which seeps in the landfill and liquid from the waste itself all percholate through the refuse producing leachate. The leachate contains dissolved, suspended and microbial contaminants. The gases which are produced in landfills from the waste are methane, ammonia, hydrogen sulphide and nitrogen. The leachate contains volatile organic acids such as acetic acid and various fatty acids, bacteria, heavy metals and salts of common inorganic ions such as Ca^{2+}. The micropollutants present in municipal solid waste include common volatile organic compounds such as toluene and dichloremethane.

16.4.3 Incineration of the Muncipal Solid Waste

Incineration is a waste treatment process in which solid waste is burned at high temperatures ranging from 900 to 1000 °C. The burning of the solid waste in the incinerator consumes all combustible materials leaving behind the non-combustible materials and the ash residues. The ash residues of the incinerator are disposed off on the land or landfills. The incineration may reduce the volume of the waste by two third. The combustible components of garbage such as paper, plastics and wood provide fuel for the fire. In incineration the heat of combustion may be used in producing steam which runs the turbines to produce electricity.

16.4.4 Treatment of Industrial Waste

The industrial and hazardous wastes are disposed off in landfill or the waste is first incinerated and the residual ash is then disposed off in the landfill. The landfill for the hazardous waste is monitored more regularly for the leakage of the leachate and its design is almost same as that of landfill for the municipal solid waste, except it has more lining of clay and plastic so that the leachate does not contaminate soil and ground water around.

16.4.5 Incineration otlnckistrial and Hazardous Waste

A general process of high temperature incineration system consists of a rotary kiln which accepts all types of wastes including liquid, solid or sludge. The wastes are burned at temperatures between 650° to 1100°C. Ash from the rotating chamber is collected at waste tank and the remaining liquid gaseous materials are passed to the secondary chamber. This chamber is non-rotating and hence the temperature range of 950° to 1300°C is maintained. In this chamber organic molecules are completely destroyed. The gases produced are then cooled to 230°C by evaporating water spray. The cooled gases are then passed through scrubber system which eliminates the surviving particulates and acid forming components like CO_2. Ash residues and waste water produced in the rotating and secondary chambers are disposed off in the land fills, Fig. 16.2.

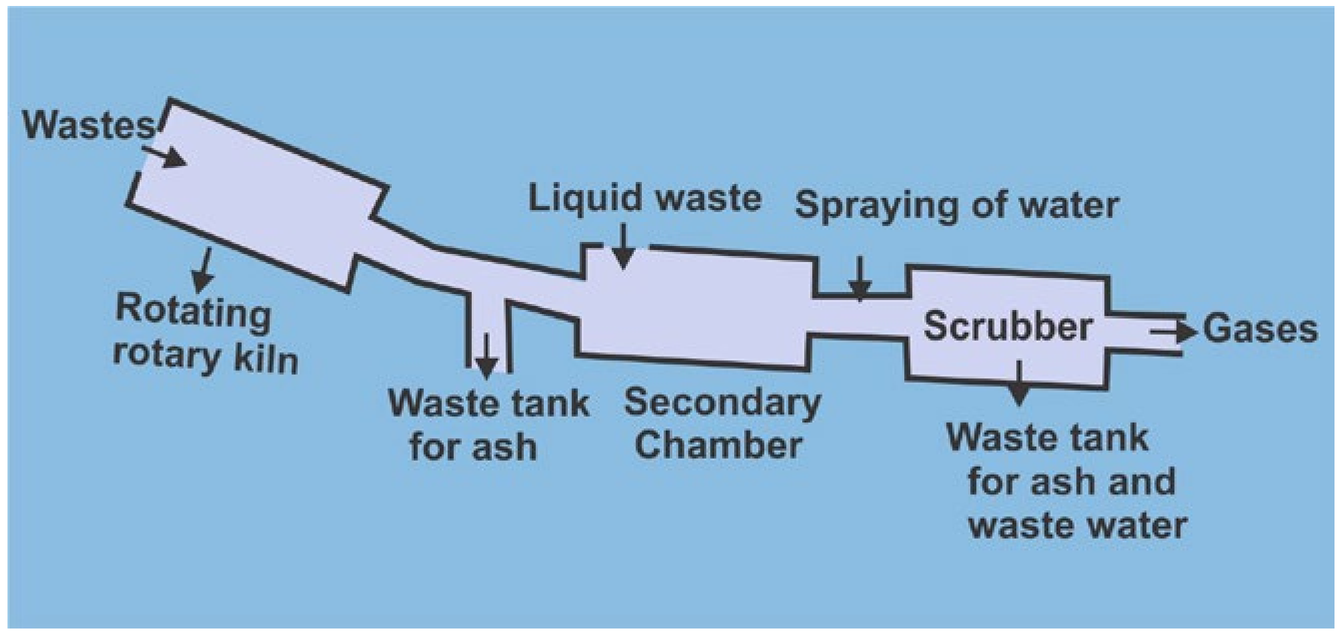


Fig. 16.2 Incineration of industrual waste

Although the volume of solid waste is reduced to a much lesser extent by burning it in the incinerator, it is not a clean process of the disposal of solid wastes, as it produces air pollution and also toxic ash. Incineration of the solid waste is a significant source of dioxins which is a class of carcinogen compounds. Smoke stacks from incineration may emit oxides of nitrogen and sulphur which lead to acid rain. Heavy metals such as lead, cadmium, mercury, etc., may also be present in the leachate of the incinerators.

16.4.6 Recycling of Waste

In recycling some of the used or waste materials are not discarded after their initial use but are processed so that they can be used again. The purpose of recycling is to conserve sources such as raw material and energy. The volume of the waste is also much reduced by recycling of the materials.The most common domestic materials that are recycled are paper, plastic, glass and aluminium.

Animation 16.7 : Recycling
Source and Credit : nasa

The largest item which is recycled is newspaper and in its recycling process the release of chlorine or other bleaching acids and organic solvents is significantly less as compared to formation of these compounds during the processing of virgin newspaper.To improve the whiteness of the recycled newspaper it is blended with the virgin newspaper or sometimes treated with peroxides and hydrosulphites. In recycling process the fibre of the newspaper becomes shorter so it can be recycled again and again for five times.

The recycling of plastics is done by reprocessing, depolymerization or transformation. In reprocessing the used plastics are remelted and styrene which is used for manufacturing of different products e.g., the original use of polystyrene is for the manufacturing of foam, packaging, cutlery, furniture, etc. but after its reprocessing it is used mostly for the manufacturing of toys, trays, etc.

Animation 16.8 : Recycling1
Source and Credit : mansfieldma

Animation 16.9 : Recycling of plastic
Source and Credit : emaze

The depolymerization is a process in which the used plastics are converted back into their original components by a chemical or thermal process so that these can be subsequently polymerized again e.g., polyethylene terephthalate can be thermally depolymeirzed in the presence of a catalyst and heat into its original components. The transformation is a process in which used plastics are converted into low quality substances which are latter used for the production of other materials e.g., cracking of polyethylene at high temperatures gives its monomers which are used for the manufacturing of lubricants.

KEY POINTS

1. Environmental chemistry is the branch of chemistry in which we study the sources, reactions, transportation and effects of the pollutants on the environment. The environment consists of four components.
2. The primary air pollutants are carbon monoxides, sulphur dioxide, sulphur trioxide, nitrogen oxides and hydrocarbons.
3. The acid rain is due to the oxides of sulphur and nitrogen which get mixed with rain water in the presence of pollutants to form sulphuric and nitric acids. The acid rain affects the soil, water and sculptural materials.
4. The main cause of photochemical smog is the presence of oxidants such as nitrogen oxides in the atmospheres. The hydrocarbons also play a key role for smog formation.
5. The ozone is a protective layer in the stratosphere which absorbs harmful ultraviolet radiation of the sun and thus blocks them to reach on the earth.
6. Water which is an essential requirement for all the living beings on the earth is being polluted by livestock waste, oil spillage, detergents, pesticides and industrial wastes. The water pollution results in many infectious diseases such as dysentery, typhoid, hepatitis and in some cases also cancer.
7. The potable water is purified by aeration, coagulation and chlorination. Although chlorination has saved many thousand lives by killing viruses and bacteria, it also forms some chlorinated organic compounds in water which are toxic.
8. The domestic municipal solid waste consists of paper, plastic, vegetables, wood, glass, rubber, leather, textile, metals and food wastes. The waste whether domestic or industrial is managed by disposing it off in the landfills or it is initially incinerated and then the resulting ash is disposed off in the land or in landfills. The dumping of waste in ocean, sea and rivers have damaged the marine environment and caused health hazards for human beings.
9. In the recycling process instead of dumping the waste products i.e., paper, plastic, glass and aluminium, they are processed and made reusable.This process also reduces the volume of the waste.

EXERCISE

Q. 1 Fill in the blanks

1. Only__________ of the total earth's water resources are available as fresh water.
2. __________ is a smaller unit of biosphere which consists of community of organisms and their interaction with environment.
3. Carbon monoxide is highly poisonous gas and causes suffocation if inhaled, it binds blood _____________ more strongly than oxygen thus excluding oxygen from normal respiration.
4. The elevated concentration of_________ is harmful for fish as it clogs the gills thus causing suffocation.
5. The ozone layer in the _________ surrounds the globe and filters most of the harmful UV rays in the sunlight before they could reach the earth.
6. The presence of_____________ in livestock waste can contaminate surface and ground water causing various infectious diseases.
7. The substances which can directly kill the unwanted organisms are called _____________.
8. _____________ is frequently used to disinfect water.
9. Incineration is not a clean process because it produces air pollution and toxic _____________.
10. A process in which some of the used or waste materials are not discarded after their initial use but are processed so that it can be used again is called _____________.

Q. 2 Indicate true or false.

1. Half of the mass of the atmosphere is concentrated in lower 10 km.
2. The oceans cover approximately 71 percent of the earth.
3. The volcanoes produce 55 % of SO_2.
4. The reducing smog is due to the presence of nitric oxide.
5. Ozone is produced in the polar regions by the photochemical reaction of oxygen.
6. The temperature in the troposphere decreases with the increasing altitude from 15 to -56° C.
7. Incineration is a waste treatment process in which solid waste is dumped in a land fill.

8. Acid rain is due to the presence of oxides of sulphur and nitrogen which get mixed with the rain water.
9. The heavy metals have a safe limit where they are not toxic.
10. The reprocessing of the plastics is to convert back to their components by a chemical or thermal process so that these can be used again.

Q. 3 Multiple choice questions. Encircle the correct answer.

(i) The pH range of the acid rain is
(a) 7-6.5 (b)6.5-6 (c) 6-5.6 (d) lessthan 5

(ii) Peroxyacetylnitrate (PAN) is an irritant to human beings and it affects
(a) eyes (b) ears (c) stomach (d) nose

(iii) To avoid the formation of toxic compounds with chiorine which substance is used for disinfecting water.
(a) $KMnO_4$ (b) O_3 (c) Alums (d) Chloramines

(iv) A single chloride free radical can destroy how many ozone molecules
(a) 100 (b) 100000 (c) 10000 (d) 10

(v) Fungicides are the pesticides which
(a) control the growth of fungus (b) kill insects
(c) kill plants (d) kill herbs

(vi) Ecosystem is a smaller unit of
(a) lithosphere (b) hydrosphere (c) atmosphere (d) biosphere

(vii) The main pollutant of leather tanneries in the waste water is due to the salt of:
(a) lead (b) chromium(VI) (c) copper (d) chromium (III)

(viii) In purification of potable water the coagulant used is
(a) nickel sulphate (b) copper sulphate (c) barium sulphate (d) alum

(ix) The temperature in the non-rotating chamber in the incineration of industrial and hazardous waste process has a range

(a) 900 to 1000° C (b) 250 to 500° C
(c) 950 to 1300 °C (d) 500 to 900 °C

(x) Newspaper can be recycled again and again by how many times?
(a) 2 (b) 3 (c) 4 (d) 5

Q. 4 Discuss in detail the components of the environment.

Q. 5 Describe the natural and human sources of carbon monoxide, nitrogen oxides and sulphur oxides.

Q. 6 What is acid rain and how does it affect our environment.

Q. 7 What is smog? Explain the pollutants which are the main cause of photochemical smog.

Q. 8 Why is ozone layer depleting? What will happen when the concentration of ozone will be decreased?

Q. 9 How is oil spillage affecting the marine life?

Q.10 How detergents are threat to aquatic animal life?

Q. 12 Explain how pesticides are dangerous to human beings.

Q. 13 Discuss industrial waste effluents.

Q. 14 How water is purified i.e., made potable. Discuss in detail.

Q. 15 What are leachates?

Q. 16 Explain the process of incineration of industrial waste.